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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

4–8 °C. All samples were analyzed within one month of acquired. Each sample was prepared per duplicate (diluted 1:10) and analyzed trice.

For element quantification, samples were prepared as follow: 1 mL of wine was placed into 15 mL polypropylene flask and then, the volume was completed to 10 mL with HNO_3 (1.0%), and the mixture was shaken vigorously. Rhodium ($^{103}Rh^+$) was added as internal standard (final concentration: 10 μg L^{-1}).

In order to optimize ICPMS operating conditions wine samples prepared as indicate above, were spiked with multielement Perkin–Elmer 3, and Hg monoelement standard solution, to a final concentration of 40 μg L^{-1}. A blank solution was always measured and taken into consideration. The solutions were introduced into the plasma at 0.8 mL min^{-1} applying 1000 W RF power and 0.85 L min^{-1} nebulizer gas flow rate before their optimization. The isotopes measured, in order of mass number, were: ^{7}Li, ^{9}Be, ^{51}V, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{74}Ge, ^{75}As, ^{85}Rb, ^{88}Sr, ^{98}Mo, ^{111}Cd, ^{138}Ba, ^{202}Hg, ^{205}Tl, ^{208}Pb, and ^{209}Bi.

Matrix effects were evaluated through quantification using two alternative calibration approaches; i.e., external calibration against aqueous standards (solutions prepared in 1.0% nitric acid); and matrix matching calibration (prepared in 1.2 %v/v ethanol and 1% nitric acid). The analytes concentrations were 10; 20; 40; 80 and 100 μg L^{-1}. For this study, samples analyzed were spiked to attain a final concentration of 40 μg L^{-1} of the analytes. Addition of rhodium (10 μg L^{-1}) as internal standard was also evaluated.

Samples microwave digestion was performed for comparative purposes. In this case, 500 μL of wine samples were added with 7.0 mL of HNO_3 and 1.0 mL of H_2O_2 in PTFE flasks, then they were submitted to the microwave temperature program (10-min ramp to 200 °C and a step of 10 min at 200 °C, up to 1000 W), and after that, diluted to 50 mL with ultrapure water. Before digest, samples were spiked to reach a final concentration of 40 μg L^{-1} of the analytes. The digested samples were analyzed by ICPMS using the conventional cross-flow nebulizer and a Scott-type spray chamber and external calibration with $^{103}Rh^+$ as internal standard.

2.5. Data analysis

In order to evaluate relationships among element concentrations and type of wine from data sets and assessing those variables that most contribute to the classification of samples, multivariate analysis were performed. Principal component analysis (PCA) as a descriptive tool to visualize the data in two dimensions and linear discriminant analysis (LDA) to evaluate classification models were carried out, both by means of statistical software package Unscrambler X 10.3 software (CAMO-ASA, Trondheim, Norway). A full cross validation test was used to validate the results of the classification (Lavine, 2003).

3. Results and discussion

3.1. Instrument optimization

Is important to note that carbon resultant from complex matrix and solvents could possibly condense on the cones and lens, producing instability of the plasma, leading to a rapid loss of detection power. In spite of that, little amounts of organic compounds can raise the nebulization and aerosol transport efficiencies in the plasma, improving the ionization efficiency of high ionization energy elements by carbon charge transfer reactions (Boorn & Browner, 1982; Hu, Hu, Gao, Liu, & Lin, 2004; dos Santos et al., 2007; Tormen, Chaves, Saint'Pierre, Frescura, & Curtius, 2008). For that reason is mandatory an overall instrument performance optimization, considering mainly sample matrix.

The proposed analytes signals were studied and optimized in ICPMS. Samples were prepared as discussed above (Section 2.4.) and a solution containing only the reagents was compared in order to alleviate carbon-containing polyatomic ions occurring at analyte masses. Sample introduction was carried out using a high-efficiency microconcentric nebulizer coupled to a baffled cyclonic spray chamber, using −5 °C as desolvation temperature. The sample flow rate (Q_l) is a parameter straight correlated to the nebulizer efficiency, making possible the control of the sample input to the ICP and accordingly the amount of carbon. A characteristic Q_l plot could be observed, wherein increasing Q_l, analytes signal started to rise.

The nebulizer gas flow (Q_g), and radiofrequency power (RF power) were also optimized for maximum analyte intensity and minimum background. The effect on analytes signal in terms of Q_g (L min^{-1}), shows that maximum sensitivities of the majority of the analytes become visible at 0.85 L min^{-1}, only As display it at 0.8 L min^{-1}, and Be and Li at 0.9 L min^{-1}. Regarding to the signal to background ratio (SBR) it is suggested that the carbon-containing polyatomic ions did not contribute significantly and evidenced an efficient elimination of the solvent in the spray chamber. A Q_g of 0.85 L min^{-1} was adopted as optimum for further analysis. In the case of the effects of RF Power on analyte signal, it was observed that the increase of RF power resulted in signals rising for every analyte evaluated. The outcome indicates that maximum intensities were achieved at RF Power of 1000 W. The background contribution of carbon-based polyatomic ions (lower SBR) was also evaluated indicating an optimum condition of 1000 W RF power as compromise. Finally, as the addition of small amounts of O_2 to the carrier gas results in the oxidation of the carbon preventing its deposition, the adding was also evaluated. However its use was not necessary since none change in analytes signal intensity was evident.

A simple dilution of white wine samples, along with a fine instrument optimization facilitate diminishing matrix effects and plasma instability; and also assist minimizing related interferences and the possibility of sample contamination. To sum up, the diluted wine solutions were introduced into the plasma at 0.8 mL min^{-1} applying 1000 W RF power and 0.85 L min^{-1} nebulizer gas flow rate before their optimization.

3.2. Calibration strategy: matrix effects

With the intention of assess and alleviate matrix effects and in order to find an appropriate calibration strategy for accurate analysis of wine samples, two approaches were evaluated: i.e. aqueous and matrix matching calibration. Rhodium was also evaluated as internal standard (IS) in each case. Samples were prepared as indicated in Section 2.4. The obtained accuracies (as % recoveries) for each calibration curve were contrasted with those obtained after microwave digestion (reference).

When external calibration against aqueous standard solutions was employed, not all analytes could be properly recovered, while in the case of using matrix matching calibration, with 1.2% of ethanol as matrix "modifier", most analytes reach the best recoveries. Fig. 1 contrast matrix matching calibration with the reference sample digestion, it could be observed that the use of ethanol in the calibration curve, allows the determination of the 18 analytes evaluated, assessing recoveries between 80 and 120 percent. The employment of $^{103}Rh^+$ as IS was recommended.

3.3. Analytical performance

The LOD and LOQ were evaluated according to IUPAC recommendations as 3.3 and 10 times the standard deviation (n = 10) of

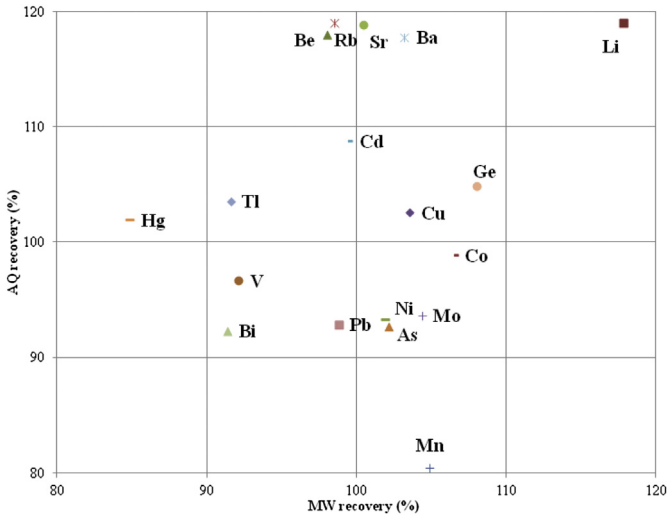

Fig. 1. Correlation recoveries graphs between wine microwave treatments vs. wine sample diluted 1:10, using matrix matching calibration with ethanol.

blank (1.2%v/v of ethanol), respectively. The limits of quantification were between 0.006 (Bi) and 0.24 μg L^{-1} (V). The relative standard deviation (RSD, n = 3) of a standard of 20 μg L^{-1}, used to estimate the precision, was smaller than 8.3% for the analytes evaluated. Table 1 shows the figures of merit for trace elements determination in wine samples.

3.4. Analytical validation and application to real samples

As a certified reference material of wine was not available in our laboratory, recovery studies were carried out with twenty random samples. The samples were spiked to a final concentration of 40 μg L^{-1} of the analytes and prepared as indicated in Section 2.4. In this study, we evaluated the accuracy of the results by comparison (t-test, 95% confidence interval) with an independent sample treatment. In all cases, significant recoveries between 80 and 120 percent were obtained.

The proposed method for wine sample preparation was applied to trace element determination by ICPMS of 57 commercially available wines from Argentine. Table 2 shows the average concentration and standard deviation of the quantified elements in wine. In all cases Hg concentration was lower than the quantification limits.

3.5. Multivariate data analysis

3.5.1. Visualizing group in white wines

Principal component analysis (PCA) is a bilinear modeling method that provides an interpretable overview of the main information contained in a multidimensional table. It is also known as a projection method, because it takes information carried by the original variables and projects them onto a smaller number of latent variables called Principal Components (PC). Each PC explains a certain amount of the total information contained in the original data and the first PC contains the greatest source of information in the data set. It provides a visual representation of the relationships between samples and variables and provides insights into how measured variables cause some samples to be similar to, or how they differ from each other.

Subsequently, PCA was used like exploratory analysis for visualizing groups in Argentinean white wines, element concentration data were used as response matrix. Elements that presented concentration values below the limit of quantification were not statistically evaluated. A matrix with 114 samples and 17 variables (Li, Be, V, Mn, Co, Ni, Cu, Ge, As, Rb, Sr, Mo, Cd, Ba, Tl, Pb and Bi) was constructed, without prior signal pretreatment, and all data were autoscaled for every variable. Two first principal components (PCs) were extracted, explaining 95.95% of the accumulated variance. Score plot in the plane defined by PC1 and PC2, depicted in Fig. 2, shows the separation in four different groups, according to the evaluated regions: Mendoza, Rio Negro, San Juan, and Salta.

Discrimination was possible because of the different concentration of five ultratrace elements (Ba, As, Pb, Mo, and Co) which varies depending on regions. In Fig. 2, the plot of loadings in the plane PC1 versus PC2 shows which variables had more weight in the model. It can be seen that PC1 (84.95% total variance) is mainly associated positively to Ba, plainly separating wines from Salta, and in a lower extent to Pb allowing discriminating between Mendoza and Rio Negro wines. In PC2 (11% total variance) higher loading for As, Mo and Co were achieved; differentiating San Juan white wines.

Contrasting our work with the Argentinean ones, is feasible to highlight that Di Paola-Naranjo et al. (2011) have reported the use of a total of 13 inorganic components for distinguish Argentinean wines from Córdoba, San Juan, and Mendoza; including among them Co, Ba, and Pb. Moreover, Fabani et al. (2010) stated the use of seven descriptor elements for differentiate amongst wines from other three Argentinean regions (Córdoba, La Rioja, and San Juan), of which none of the used element are comparable with the informed in this work.

Some elements, including Ba, are lithophile elements and their origin in wine is mainly related to vineyard soils (Diana, Beni, & Marconi, 2008). Earlier wine studies have demonstrated that contents of Ba have been used for geographical classification purposes in wine (Coetzee et al. 2014; Martin et al., 2012; Rodrigues et al., 2011). Taking this into account is possible to observe that Salta wines have clearly separated by their higher Ba concentration. This would indicate that soils in which grapes grow, from which the wine is made, are mainly rich in this element.

Regarding to Arsenic, several authors have pointed out that along with other ultratrace elements allows the determination of wine origin (Rodrigues et al., 2011; Thiel et al., 2004). The variability of As contents between wines, is not only related with different concentrations of this element in soils (Grillet et al., 2004; Kment et al., 2005) but also with the use of pesticides in grape growing (Inacio, Pereira, & Pinto, 2007). Considering San Juan wines, they are separated through As high concentration, probably according to soil composition, since its contamination is clearly known (O'Reilly, Watts, Shaw, Marcilla, & Ward, 2010). Despite having higher As concentrations in wine than the other provinces, their limits are

Table 1
Figures of merit for trace elements determination in Argentinean white wines.

Analyte	Li	Be	V	Mn	Co	Ni	Cu	Ge	As	Rb	Sr	Mo	Cd	Ba	Hg	Tl	Pb	Bi
(a.m.u.)	7	9	51	55	59	60	63	74	75	85	88	98	111	138	202	205	208	209
LOD (ng L^{-1})	19.1	10.6	72.1	8.8	8.8	34.5	13.1	42.4	6.4	17.0	7.8	25.9	10.2	13.7	19.1	5.2	7.1	1.7
LOQ (ng L^{-1})	63.0	35.0	238	29.1	29.1	114	43.2	140	21.0	56.2	25.6	85.4	33.7	45.3	63.0	17.2	23.4	5.7
RSD (%)	2.5	3.5	3.8	5.5	1.9	7.3	8.0	8.3	4.6	8.3	6.1	2.3	4.3	5.8	5.4	7.2	2.8	5.7

Table 2
Means and standard deviations for the determined analytes in white wine samples from the four studied Argentinean regions.

Analyte [μg L^{-1}]	Sauvignon blanc			Chardonnay		Torrontés		
	Mendoza (n = 12)	Rio Negro (n = 6)	San Juan (n = 3)	Mendoza (n = 15)	San Juan (n = 6)	Mendoza (n = 6)	Rio Negro (n = 3)	Salta (n = 6)
Li	941 ± 855	815 ± 272	1448 ± 2	778 ± 354	1102 ± 370	396 ± 303	146 ± 3	192 ± 175
Be	17 ± 15	11 ± 4	15 ± 1	5 ± 2	19 ± 15	4 ± 3	5 ± 1	7 ± 3
V	358 ± 286	128 ± 11	454 ± 5	192 ± 73	205 ± 65	93 ± 14	73 ± 2	120 ± 28
Mn	1778 ± 454	1370 ± 660	1367 ± 2	1739 ± 762	1689 ± 220	1345 ± 182	1133 ± 1	1544 ± 817
Co	24 ± 6	23 ± 1	28 ± 1	20 ± 4	20 ± 3	14 ± 2	15 ± 1	12 ± 3
Ni	276 ± 42	222 ± 16	343 ± 1	216 ± 46	240 ± 6	154 ± 24	142 ± 1	132 ± 39
Cu	186 ± 164	487 ± 22	243 ± 3	171 ± 32	219 ± 166	82 ± 44	84 ± 1	175 ± 151
Ge	6.3 ± 0.7	6.3 ± 1.0	6.4 ± 0.3	3.2 ± 0.9	2.7 ± 0.6	1.1 ± 0.2	1.7 ± 0.2	1.7 ± 0.2
As	20 ± 5	20 ± 1	36 ± 3	26 ± 10	29 ± 6	18 ± 3	11 ± 1	13 ± 1
Rb	531 ± 253	804 ± 43	800 ± 1	719 ± 95	679 ± 132	592 ± 295	891 ± 1	977 ± 217
Sr	556 ± 217	849 ± 25	923 ± 1	1007 ± 241	1040 ± 46	854 ± 150	855 ± 1	740 ± 107
Mo	10 ± 5	6 ± 2	16 ± 1	9 ± 5	9 ± 1	10 ± 8	3 ± 1	7 ± 3
Cd	(7.0 ± 2.1) × 10^{-1}	(5.4 ± 1.1) × 10^{-1}	(64.0 ± 2.7) × 10^{-2}	(9.1 ± 7.3) × 10^{-1}	(5.4 ± 9.0) × 10^{-2}	(5.5 ± 1.2) × 10^{-1}	(5.7 ± 6.0) × 10^{-2}	2.4 ± 1.3
Ba	29 ± 3	62 ± 1	55 ± 1	44 ± 22	48 ± 7	58 ± 23	56 ± 1	120 ± 9
Tl	(6.5 ± 4.3) × 10^{-1}	(8.8 ± 2.4) × 10^{-1}	1.7 ± 0.1	1.2 ± 0.6	1.1 ± 0.5	2.7 ± 0.8	1.8 ± 0.1	3.0 ± 0.4
Pb	3 ± 2	4 ± 1	7 ± 1	5 ± 3	6 ± 2	13 ± 4	8 ± 1	13 ± 1
Bi	(3.0 ± 2.1) × 10^{-1}	(15.0 ± 2.4) × 10^{-2}	(14.3 ± 4.0) × 10^{-2}	(2.6 ± 2.3) × 10^{-1}	(9.8 ± 4.4) × 10^{-2}	(18.8 ± 9.5) × 10^{-2}	(13.0 ± 1.0) × 10^{-2}	(29.8 ± 6.7) × 10^{-2}

within the maximum established by the Codex Alimentarius Commission (OIV, 2013). With reference to Mo and Co concentrations, they also contribute to San Juan wines differentiation. Both are essential elements for human organism, and their consumption from wines in moderate quantities contributes to the daily requirement.

Concerning to Pb concentration, it has been also considered in white wine geographical origin investigation (Castiñeira Gomez, Feldmann, Jakubowski, & Andersson, 2004). In the case of this work, wines from Mendoza and Rio Negro are differentiated by Pb concentration. These values could be related to anthropogenic origin such as pesticides, fungicides, and fertilizer application during growing seasons of grapes or simply due to nature composition of their soils. From a toxicological point of view, special attention must be paid to the levels of Pb due to health risk and legal requeriments. Concentrations of Pb were contrasted with the limits stated by the Codex Alimentarius Commission, and their limits are within the maximum established (OIV, 2015).

3.5.2. *Classification model for white wines according to geographical origin, grape variety and vintage*

The objective of linear discriminant analysis (LDA) is to determine the best fit parameters for classification of samples by a developed model, in which the categories to which objects are to be classified is known before the model is created. LDA generates all the combinations of variables and selects the combination that reproduces a discriminant function showing the least number of classification errors. The model consists of linear equations involving all or some of the selected variables. Then, model can be used to classify unknown sample (Lavine, 2003).

Consequently, LDA, including the same variables used in PCA, was performed for further evaluation of element concentrations to classifying wine samples according to the geographical origin. Thus, metal contents in wine were taken as chemical descriptors. Data matrix was constructed with five columns (including: Ba, As, Pb, Mo, and Co), using one additional column containing the geographical origin as the dependent categorical variables, namely: Mendoza (M), Rio Negro (RN), San Juan (SJ), and Salta (S); and using all samples. Accordingly, the training and prediction set were randomly shaped by 63 and 51 samples, respectively.

In this study, discriminant functions (DF) were obtained from the training set, to classify samples into four groups; thus, three DF were needed to fully partition the data:

$$DF_1 = -3.48\ 10^{-1}{*}As + 1.13{*}Ba - 1.06448\ 10^{-1}{*}Co + 3.62\ 10^{-1}{*}Mo - 2.75\ 10^{-1}{*}Pb$$

$$DF_2 = -1.04{*}As - 1.18\ 10^{-2}{*}Ba - 1.75\ 10^{-2}{*}Co + 1.09\ 10^{-1}{*}Mo - 1.39\ 10^{-1}{*}Pb$$

$$DF_3 = 8.56\ 10^{-2}{*}As - 3.30\ 10^{-1}{*}Ba - 6.50\ 10^{-1}{*}Co + 5.42\ 10^{-1}{*}Mo + 7.69\ 10^{-1}{*}Pb$$

LDA achieved a high recognition percentage for the classification of the groups, verifying that the attained differences are due to Ba, As, Pb, Mo, and Co concentrations. Table 3 shows that 96.83% and 96.08% of the original grouped cases were correctly classified in the training and prediction sets, respectively, obtaining a low classification error rate in both sets.

A complementary graphical representation of the studied wines was achieved. As a result, Fig. 3 depicted the space defined by the first three discriminant functions, that explained 93.2% of the total variance; in this graph it could be clearly seen the separation

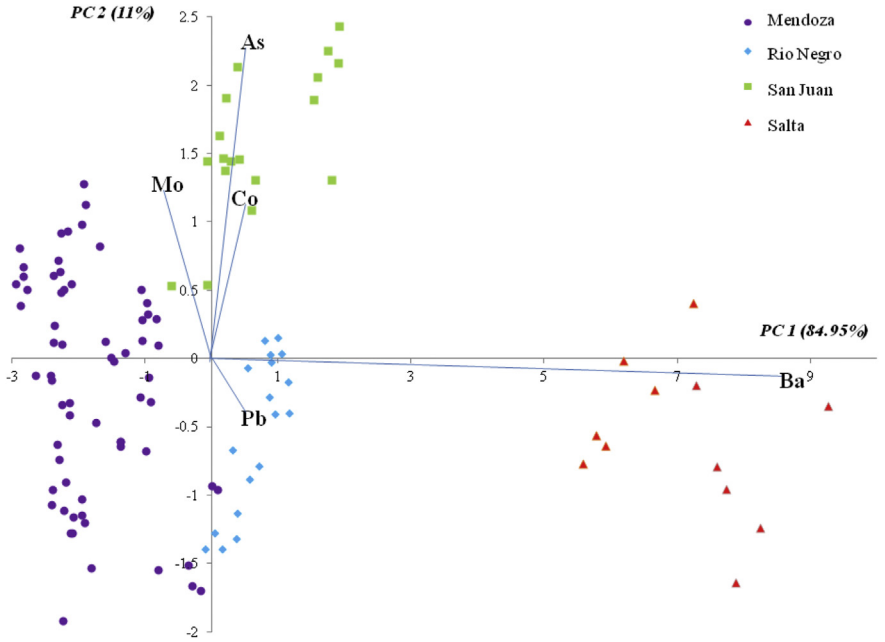

Fig. 2. PCA and loadings plot exhibiting the discrimination of groups through their geographical origin, and verifying variables that had more influence in each group formation for the white wine samples.

amongst wine from Mendoza, Rio Negro, San Juan, and Salta provinces. However, four samples that were not correctly classified in this analysis are highlighted. These samples correspond to Mendoza, Rio Negro and San Juan; perhaps, it is possible that they correspond to a different origin from the stated on the label.

The same multielement and chemometrics studies described above were performed to assess grape variety and vintage discrimination in white wines. Thus, three white wine varieties: Chardonnay, Torrontés, and Sauvignon blanc were evaluated. However, the multielement composition has shown to have little influence on the grape variety and vintage in white wines.

4. Conclusion

The outcomes suggest that the largest contributing factor to the geographical origin discrimination seems to be the element profile of the Argentinean white wines. The easy and rapid method for sample preparation consisting in a simple dilution 1:10, makes the proposed method a striking option for routine analysis, taking into account mainly the multielement determination ability of ICPMS. This, along with multivariate statistical analysis based on a combination of principal component analysis (PCA) and discriminant analysis (DA), allowed differentiation of four Argentinean wine-growing regions: Mendoza, Rio Negro, San Juan, and Salta. Of the overall of elements determined, only Ba, As, Pb, Mo, and Co were identified as suitable indicators for the discrimination.

The developed model indicates a potential application for provenance genuineness purposes, authenticity and quality control of wines. Nevertheless, it would be necessary to perform an assessment of non-correctly classified samples and the possible reasons that contribute to the differences observed. Besides, it

Table 3
Results of the classification ability of the LDA model for different wines according to their geographical origin.

Group	M	RN	S	SJ	Total	Error(%)
Training set						
M	33	1	0	0	34	2.94
RN	0	11	0	0	11	0
S	0	0	7	0	7	0
SJ	1	0	0	10	11	9.09
Total	34	12	7	10	63	3.17
Prediction set						
M	31	1	0	0	32	3.13
RN	1	6	0	0	7	14.28
S	0	0	5	0	5	0
SJ	0	0	0	7	7	0
Total	32	7	5	7	51	3.92

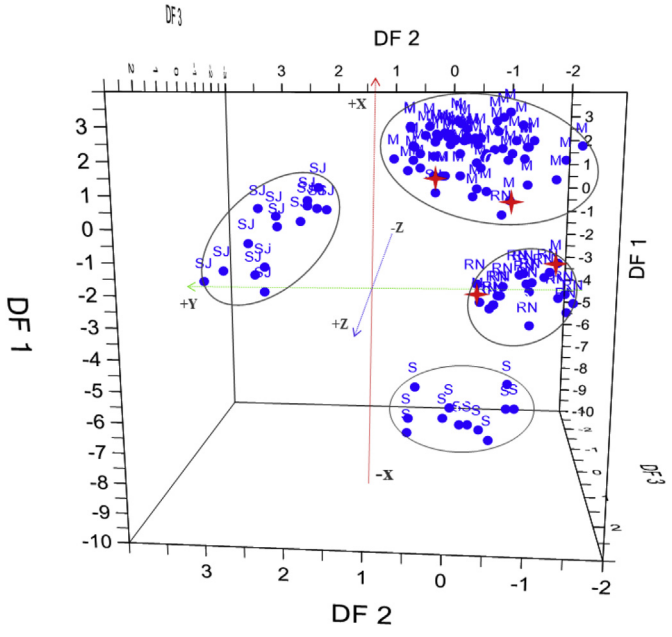

Fig. 3. Distribution of white wine samples in the space defined by LDA first three canonical functions, depicting the classification by their provenance: Mendoza (M), Río Negro (RN), San Juan (SJ), and Salta (S).

might be appropriated to conduct studies involving soil multielement determination to correlate the soil with the respective wine, and thus corroborate and strengthen the research.

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