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Analytical Methods

Evaluation of elemental profile coupled to chemometrics to assess the geographical origin of Argentinean wines

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ABSTRACT

Traceability of wines requires knowledge of their characteristics, which are associated with the geographical origin of grape, soil, water, climate as well as the winery techniques. The aim of this work was to classify wines and soil from three production areas of Argentina according to multielement data. The influence of the provenance soil on the wine element composition was also investigated.

Eleven elements were determined in 31 wine samples and 137 soil samples from regions under study. Stepwise discriminant analysis allows us to correctly classify 100% of the wines analysed from the three regions using only seven parameters (K, Fe, Ca, Cr, Mg, Zn and Mn) and 92% correct classification for soils using seven variables (Ca, Cr, K, Fe, Cu, Zn and, Mg). Canonical analysis between soils and wines datasets affords a correlation coefficient of 0.85 (*P*-value < 0.001). Thus, almost 85% of variability observed amongst wines could be attributed to the soil in which the vines were cultivated.

The analysis of elemental concentrations in the wines and soils, in combination with chemometrics, provides a powerful tool to verify the geographical origin of wines.

1. Introduction

Wine is a widely consumed beverage around the world. It is a complex matrix, which, besides water, sugar and alcohol, contains a great variety of components, inorganic and organic (Álvarez, Moreno, Jos, Cameán, & González, 2007a, 2007b; Sperková & Suchánek, 2005). The huge diversity of viticulture areas generates the need for establishing the provenance of this product. Thus, the wine identifies and is identified with its original territory. The regional name of a product often plays an important role, especially for wines and other alcoholic drinks, as it implies a particular standard of quality which is appreciated by consumers (i.e., Scotch whisky, French champagne, etc.).

Controlled Denomination of Origin (DOC) has been established in Spain, France and other countries (Frías, Conde, Rodríguez-Bencomo, Garcia-Montengolo, & Pérez-Trujillo, 2003; Sperková & Suchánek, 2005). It has been also established in Argentina looking to guarantee the provenance and quality of its wines and also to prevent frauds (Instituto Nacional de Vitivinicultura, 2004). The six major wine-growing regions in Argentina are the provinces of Mendoza, San Juan, La Rioja, Salta, Córdoba, and Río Negro. As far as we know, there is only one report on evaluation of trace element for wine of the province of Mendoza (Lara, Cerutti, Salonia, Olsina, & Martinez, 2005). Thus, information on chemical profile of Argentinean wines is rather scarce.

Each region produces different wines, which composition is influenced by its history, environmental factors, such as climate changes and regional geology as well as by yeast, viticulture practices and by transport, vinification process and storage of the grapes, must, and wine (Almeida & Vasconselos, 2003; Álvarez et al., 2007a, 2007b; Castiñeira Gomez, Brant, Jakubowski, & Andersson, 2004; Frías et al., 2003; Kment et al., 2005; Marengo & Aceto, 2003; Pérez-Magariño, Ortega-Heras, & González-San José, 2002; Rebolo et al., 2000; Sperková & Suchánek, 2005; Taylor, Longerich, & Greenough, 2003). Another factor that may condition that relationship is related with plant uptake, which can vary with the grape variety (Almeida & Vasconselos, 2003).

There are two major sources contributing to the elemental composition of a finished wine. The first, natural source, enter to the wine from the vineyard soil via the roots of the grapevine and the grapes, providing the bigger part of ions present in wine, which is the result of the weathering of parent rocks. The second source of inorganic elements in wine arises from anthropogenic source like fertilisers, inorganic pesticides, pollution of the surrounding environmental industries, which can be introduced during the whole wine process, from grape growth, harvest and wine-production (application of additives, wine-making machinery and other

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operations). This second source can be considered as impurities or contamination (Castiñeira Gomez et al., 2004; Coetzee et al., 2005; Kment et al., 2005).

Differentiation of wine samples can be carried out by using major, trace and ultratrace elements. There are several reports in the literature determining the content of inorganic elements in wines and soil samples, measured by several techniques (FAAS–FAES, ETAAS, ICP-MS, ICP-OES, ICP-AES), with the goal of classifying samples according to their provenance (Iglesias, Besalú, & Anticó, 2007; Sass-Kiss, Kiss, Havadi, & Adányi, 2008; Serapinas et al., 2008). For instance, Moreno et al. (2007) differentiated two Canary DOC wines in according to their elemental content; also Álvarez et al. (2007b) distinguished two Andalusian fine wines by their elemental composition. Therefore, the element profile is becoming popular as a chemical descriptor to classify wines in according to its provenance, giving raise to the concept of "chemical traceability" of wine.

However, there is a need to verify to which extent the element profile of a given wine is related to the soil where grapes were cultivated. Chemical elements selected for identification should not be affected by wine-making, agricultural practices or environmental

Fig. 1. Argentine wine-growing regions studied: Córdoba, La Rioja and San Juan. Boxes indicate sampled regions.

conditions and should correlate with soil composition. As far as we know, only three studies indicate that the element pattern can be used as fingerprint of wines reflecting, at least in part, their provenance due to the direct relationship with growing soil composition (Almeida & Vasconselos, 2003; Kment et al., 2005; Taylor et al., 2003). Taylor et al. (2003) found that Sr was a good indicator of provenance from two wine-growing regions of Canada. Kment et al. (2005) found a statistically significant dependence of Mg content between the vineyard soil and wine. Also Almeida and Vasconselos (2003) found a significant correlation between the multielemental composition of wine and the provenance soil.

Chemometrics provides a useful tool for the characterisation of wine, evaluating several parameters. More specifically, multivariate statistical analysis allows differentiating production areas on the basis of both trace and major element association of wines regions. In contrast to the use of single-element concentrations, multivariate statistical methods allow verifying the contribution of each variable to the model, and its capacity to discriminate one category from another (Coetzee et al., 2005; Díaz, Conde, Estévez, Pérez-Olivero, & Pérez-Trujillo, 2003).

The main goal of this work was to evaluate the correspondence of multielemental composition between wine and soil samples. Thus, we studied 11 elements: K, Na, Ca, Mg, Fe, Cu, Zn, Mn, Ni, Co and Cr, in both wines and soil from three production areas of Argentina: Córdoba, La Rioja and San Juan (Fig. 1), pointing out those elements that enable differentiation amongst wines from these regions by chemometrics, evaluating the correspondence between wines and soil profiles by canonical analysis.

2. Materials and methods

2.1. Reagents and materials

All reagents were of analytical grade or better. Ultra pure water (Millipore, Milli-Q system) was used to prepare standard solutions, dilutions and blanks. AccuStandard® atomic absorption spectrometry standard solutions (1000 mg L^{-1} in 1% nitric acid) were used as stock solutions for calibration and in spike recovery studies. Lanthanum oxide solution, caesium chloride, calcium chloride and hydrogen peroxide (Baker, analytical grade) were used as matrix modifier (molecular suppressor). All glassware used were left with sulfonitric solution overnight and then washed with ultra-pure water.

2.2. Wine samples

Thirty one samples of wine from three major wine-production regions of Argentina (Fig. 1) were analysed: six samples from Córdoba (Cabernet Sauvignon, Malbec, Chardonnay – Frambua, Isabella – Merlot, Pinot Black – Ancellota), 14 samples from La Rioja (Cabernet Sauvignon – Malbec, Bonarda – Syrah, Torrontes Riojano – Alicant) and 11 samples from San Juan (Cabernet Sauvignon, Malbec, Bonarda, Syrah, Chardonnay). Wines were obtained directly from producers having both GMP and traceability systems. Thus, each wine can be traced to a specific vineyard where the grapes were grown to produce the wine. None of studied wines were fermented or aged in wood. All wines were from the same vintage (2005). Samples were collected in 750 mL glass bottles after bottling and stabilisation (at least six months), transported to the laboratory and stored at 4–5 °C until analysis (stabilisation + storage was less than one year). All samples were analysed within one month. The alcoholic content ranged from 12% to 13% vv^{-1} ethanol.

2.2.1. Analytical procedure

For sample preparation, the corks were carefully removed from the bottle and an aliquot was decanted into a 50 mL beaker (Baxter, Crews, Dennis, Goodall, & Anderson, 1997; Castiñeira Gomez et al., 2004). Samples were analysed without preliminary treatment. To overcome possible matrix effects (Coetzee et al., 2005), suitable dilutions were made using 1% nitric acid. The dilution factors of all measured parameters are summarised in Table 1. Each sample was analysed by triplicate. Blank solutions, containing only reagents without wine, were used to subtract element contents arising from reagents and laboratory tools.

2.3. Soil samples

Soil was sampled from the corresponding vineyard plots. Samples were collected using stainless steel shovels and were stored in individual black plastic bags (darkness). Soils were sampled in depths from 10 to 20 cm to avoid surface-soil pollution arising from the surrounding environment and to reduce the effects of fertilisers and variable organic matter content. One-hundred and thirty-seven soil samples were analysed, 71 from the province of Córdoba, 28 samples from the province of La Rioja and 38 samples from the province of San Juan. Each sample was analysed by triplicate. Soils were dried at 30–40 °C, homogenised and sieved through a <2 mm plastic sieve to avoid interferences observed when using metallic sieves (Almeida & Vasconselos, 2003).

2.3.1. Analytical procedure

Bioavailable fraction: the analysis of bioavailable elements in soil was done by extraction with dietilentetraminopentacetic acid (DTPA) as chelating agent (Ramos, 2006), using trietanolamine (TEA – pK_a 7.8) as buffer. This solution simulates the ability of plant roots to uptake nutrients from the soil. *Procedure:* 10 g of dried soil

Table 1
Analytical conditions for the analysis of elements in wine and bioavailable elements in soil samples.

Element	Wavelength (nm)	Wine				Soil		
		Dilution factor[b]	% Recovery[a]	LOD (mg L^{-1})	LOQ (mg L^{-1})	% Recovery[a]	LOD (mg g^{-1})	LOQ (mg g^{-1})
Ca	422.7	1/250	90	0.17	0.51	95	0.034	0.102
Mg	285.2	1/500	112	0.006	0.018	93	0.0012	0.0036
Zn	213.0	1/5	103	0.014	0.042	89	0.0028	0.0084
Cu	324.8	–	105	0.05	0.15	85	0.01	0.03
Cr	357.9	–	115	0.07	0.21	85	0.00078	0.0003
Fe	248.3	–	111	0.16	0.48	115	0.032	0.096
Mn	279.5	1/5	118	0.08	0.24	85	0.00016	0.00048
Ni	232.0	–	107	0.43	1.29	114	0.00056	0.0016
Co	240.7	–	119	0.10	0.30	105	0.0002	0.001
K	766.5	1/500	99	0.31	0.93	103	0.062	0.186
Na	589.0	1/500	108	0.012	0.036	98	0.0024	0.0072

[a] Percentage of recovery, measured by triplicate from two different spiked samples ($n = 6$); SD ⩽ 10%.

[b] Using 1% nitric acid.

was weighed into an Erlenmeyer flask and 20 mL of extraction solution (0.01 M $CaCl_2$ + 0.005 M DTPA + 0.1 M TEA) was added (Ramos, 2006; Ramos & Lopez-Acevedo, 2004). The resulting suspension was shacked for 2 h on a mechanical shaker and filtered through Whatman-42 paper. Blank solutions, containing only reagents without soil, were used to subtract element contents arising from reagents and laboratory tools.

Pseudo total fraction: the method used for the analysis of *pseudo* total elements fraction in soil was using *aqua regia* (HNO_3–HCl, 1:3 vv^{-1}) (Ramos, 2006; Ramos & Lopez-Acevedo, 2004). *Procedure:* 0.5 g of dried soil was weighed into an Erlenmeyer flask adding 7.5 mL of HCl (36.5%) and 2.5 mL of HNO_3 (63%), followed by gently shake overnight at room temperature (23 ± 2 °C). Afterwards, the flask was placed on a hot plate in a ventilated hood and heated until the formation of moist salts, which were allowed to cool and diluted to 100 mL in a volumetric flask. Blanks were prepared using the same protocol without soil.

2.4. Elemental analyses

Elemental analyses were carried out on a Perkin Elmer 3110 flame atomic absorption spectrometer (FAAS). Mono-element hallow cathode lamps were used for measuring eleven minerals by atomic absorption spectrometry: Mg, Ca, Fe, Mn, Zn, Cu, Cr, Co, Ni, K and Na.

Appropriate dilutions and addition of matrix modifiers (CsCl, La_2O_3, $CaCl_2$ and H_2O_2) were performed before measuring individual elements. Repeatability of atomic absorption measurements was usually $\geqslant$97% comparing values obtained from triplicates (three measurements on each sample or spiked sample). The stability of the equipment was verified by measuring the calibration curve before and after samples measurements. The limit of detection (LOD) was established considering three standard deviations (SD) of absorption of the blank, while the limit of quantification (LOQ) was set considering 10SD. Analytical parameters, instrumentation conditions and recovery percentages are summarised in Table 1.

2.5. Statistical

Multivariate statistical methods allowed the contribution of each variable to the model, and its capacity to discriminate one category from another to be verified. Linear discriminant analysis (LDA) is a supervised procedure that maximises the variances between categories and minimises the variances within categories. LDA is a common linear and parametric classification method for classification purposes. We used LDA in the stepwise mode to discriminate amongst categories (wine or soil provenance) in according to *F*-value.

In addition to LDA, we used canonical correlation (CC) to find relationships between levels of elements in soils and wines produced from grapes growing on these soils. Specifically, this analysis allows us to investigate the relationship of two sets of variables, one arising from soil analysis and the second from wine analysis.

The contents (concentrations) of elements in wine and soil samples were taken as chemical descriptors. The data matrix was composed by 11 columns (the analysed elements) and the three regions (Córdoba, La Rioja and San Juan) were defined as the dependent categorical variables. The statistical package, STATISTICA 7 from StatSoft Inc. (2005) was used for chemometrics calculations.

3. Results and discussion

3.1. Content of elements in wine samples

Results for analysed elements in wines from three studied regions are presented in Table 2. We observed some overlap in the range of major elements between three regions. Concentrations of analysed elements in wines are within the order of same elements in plants (Kabata-Pendias & Pendias, 1984). In our case, Co and Ni were not detected in wine samples.

Table 2
Concentration of elements measured in wine samples by FAAS and FAES (mg L^{-1}).

Element	Córdoba (*n* = 18)		La Rioja (*n* = 42)		San Juan (*n* = 33)	
	Median	Range	Median	Range	Median	Range
K	488	460–876	236	152–957	1637	1274–1962
Na	36	6–66	138	6–1050	58	18–142
Mg	70	65–102	111	73–141	107	53–154
Ca	50	19–97	31	12–109	286	151–681
Fe	3.7	2.7–5.4	2.6	1.0–4.5	2.8	2.1–4.3
Zn	0.3	0.2–1.0	0.6	0.3–1.3	1.0	0.5–1.6
Mn	0.8	0.5–1.1	1.1	0.5–2.5	1.1	0.1–1.6
Cu	<LOQ	<LOQ–0.4	<LOQ	<LOQ–0.5	<LOQ	<LOQ–0.5
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	0.8	<LOD–1.7	<LOD	<LOD	0.4	<LOD–1.0
Co	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

The median content of the major elements (K, Ca, Mg and Na) in the three regions was consistent with values reported for European viticulture areas (Kment et al., 2005; Marengo & Aceto, 2003). The minor elements (Fe, Mn and Zn) showed similar levels with those reported by Álvarez et al. (2007a), Moreno et al. (2007) and Díaz et al. (2003). Our present results are not in good agreement with those reported by Lara et al. (2005) for Argentinean wines, although this last report refers to wines from the province of Mendoza.

K and Ca are natural component of grape (Álvarez et al., 2007a), with K being the predominant element in the juice produced by *Vitis vinifera* (Frías, Trujillo, Peña, & Conde, 2001; Marengo & Aceto, 2003), but its concentration, together with Ca, is affected by precipitation of wine during stabilisation and ageing by the formation of potassium bitartrate and calcium tartrate crystals (Lara et al., 2005; Taylor et al., 2003). K content was higher in wines from San Juan. The median concentration of Ca was similar for wines from Córdoba and La Rioja but increased in wines from San Juan.

The presence of Mg in wines is dependent on the natural content in grape (Álvarez et al., 2007a). Mg content in the samples studied was similar for the three regions, while Na concentration was higher in wines from La Rioja. Sodium content in wines comes naturally from soil or from illicit addition (Marengo & Aceto, 2003) and so depends of the distance from the sea (Álvarez et al., 2007a) or from soil composition.

The iron content in wines depends on several factors, like the ground where the grapes are produced, fertilisers and equipments used during wine-making (Kment et al., 2005; Lara et al., 2005). Evaluation of iron content in wines is of major importance due to changes in wine-stability that it may cause as well as its effects on the oxidation and wine ageing (Frías et al., 2001). The iron contents in wines from three studied regions were below 7 mg L^{-1} (range 0.1–5.4 mg L^{-1}), which is considered the minimum concentration required to form ferric cases (Kment et al., 2005).

The median contents of Cu in analysed wines were below LOQ. The presence of Cu in wines comes naturally from the soil (Marengo & Aceto, 2003), being usually associated to the addition of pesticides and the production process (Álvarez et al., 2007a; Kment et al., 2005).

The amount of Mn in wine depends on the uptake capacity of grape as well as on the contribution of the soil (Álvarez et al., 2007a; Kment et al., 2005; Marengo & Aceto, 2003). The concentration of Mn in wines may also be influenced by agricultural practices and equipment of the cellar (Álvarez et al., 2007a). Our current results show similar Mn contents for three studied regions.

Plants absorb Zn from the ground in small quantities. The content of Zn in wine increases when it is stored in zinc containers. The amount of Zn in wines can be also a consequence of anti-fungal treatments (Álvarez et al., 2007a; Lara et al., 2005; Marengo &

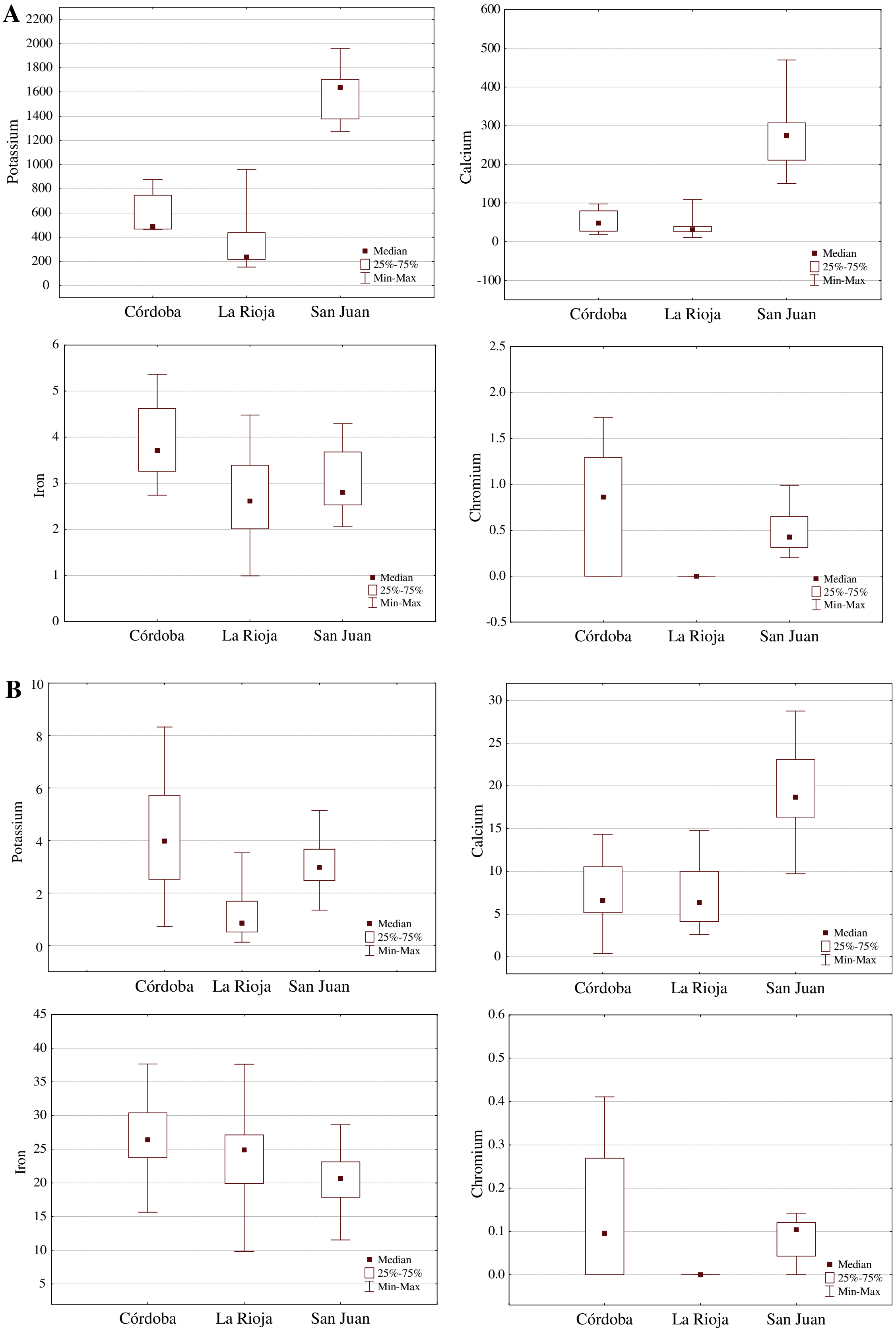

Fig. 2. Multiple Box-and-Whisker plots showing median and range of elements in (A) wine samples (mg L^{-1}) and (B) *pseudo* total in soils (mg g^{-1}), according to the province of origin.

Aceto, 2003). There was some overlap in the range of Zn between three regions, but increased levels in wines from San Juan.

Generally, Cr, Co and Ni are present in wines at very low concentrations. It is generally assumed that these elements come from the contact of must and wine with pumps, pipelines and metallic containers (Almeida & Vasconselos, 2003; Kment et al., 2005). Our results show variable amounts of Cr in wines from Córdoba and San Juan, while this element was below LOD in wines from La Rioja.

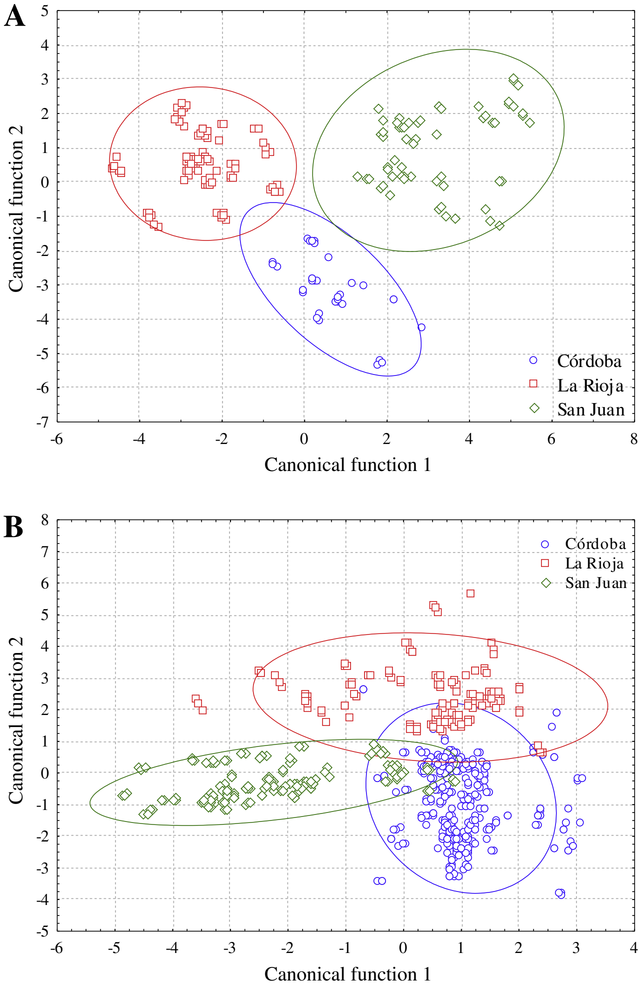

Fig. 3. Distribution of wines (A) and (B) *pseudo* total elements in soil from Córdoba, La Rioja and San Juan in the plane defined by the first two canonical functions of LDA.

The application of backward stepwise LDA allows 100% discrimination amongst wines from three studied areas (data not shown), affording seven descriptors: K, Fe, Cr, Ca, Zn, Mg and Mn for distinguishing between wines from these regions. K, Fe, Ca and Cr showed the highest *F*-value, so they are assumed as the most important variables to differentiate amongst wines from the three studied regions. Fig. 2A shows medians and ranges for some selected elements pointed out by LDA. As we can see from Fig. 2A, K and Ca allow differentiating wines produced in San Juan from other two regions. Also from Fig. 2A we can see that Fe allows discriminating wines from Córdoba, while the amount of Cr is particularly low in wines from La Rioja, differentiating these wines from the rest.

Our current results are in good agreement with Rebolo et al. (2000), who reported the use of iron as one of five key features that allow classification of wines according to their provenance. Our results also agree with a previous report showing that Ca is the main variable allowing to differentiate rosé wines from different Spanish areas (Pérez-Magariño et al., 2002). Furthermore, Latorre, Garcia-Jares, Medina, and Herrero (1994) reported that levels of K, Ca and Fe in wines can be influenced by regional variations in fertilising practice and wine-making; so these parameters could be used to characterise wines according to geographical origin. Additionally, Álvarez et al. (2007b) considered that K and Fe were the key elements to discriminate between two Andalusian DO fine wines. Also Díaz et al. (2003) used K, Fe and Ca out of eight variables allowing to classify wines from Canary Islands.

A graphical representation of studied wines in the plane defined by the first two canonical functions is shown in Fig. 3A, where we can see a good separation amongst wines from three different provinces. Thus, wines from these three regions of Argentina can be clearly differentiated considering their content of K, Fe, Ca, Cr, Mg, Zn and Mn.

3.2. Content of elements in soil samples

The median for the bioavailable and *pseudo* total elements analysed are presented in Tables 3 and 4, respectively. The concentration of studied elements observed in soils fell within typical contents of unpolluted soils (Almeida & Vasconselos, 2003).

3.2.1. Bioavailable elements in soil

Percentages of extracted metals relative to the pseudo total elemental contents varied between 0.01 and 0.06 for Fe, 1.2 and 1.7 for Mg, 1.4 and 5.5 for Zn, 1.2 and 6.1 for Mn, 5.6 and 11.3 for Ca, 6.7 and 18.7 for Cu, 3 and 24 for Na and 2 and 31 for K along soils from three studied areas. These results indicate that the bio-

Table 3
Concentration of bioavailable metals measured in soil samples by FAAS and FAES (mg g^{-1}).

Element	Córdoba (n = 71)		La Rioja (n = 28)		San Juan (n = 38)	
	Median	Range	Median	Range	Median	Range
K	0.10	0.03–2.71	1.61	0.012–0.98	0.12	0.02–0.41
Na	0.16	0.005–1086	0.03	0.13–7.91	0.07	0.02–0.17
Mg	0.11	0.04–0.22	0.07	0.01–0.58	0.09	0.04–0.20
Ca	0.42	0.001–1.46	0.97	0.11–10.04	1.18	0.30–2.49
Fe	0.017	0.003–0.62	0.006	0.002–0.029	0.003	0.001–0.01
Zn	0.005	0.0008–1.00	0.003	0.0003–0.011	0.001	<LOD–0.003
Mn	0.03	0.008–0.49	0.01	0.001–0.13	0.006	<LOD–0.013
Cu	0.015	0.001–0.16	0.005	<LOD–0.048	0.002	0.001–0.009
Ni	<LOQ	<LOD–0.92	<LOD	<LOD	<LOD	<LOD
Cr	<LOD	<LOD–1.00	<LOD	<LOD	<LOD	<LOD < LOQ
Co	<LOD	<LOD–1.00	<LOD	<LOD	<LOD	<LOD

Table 4
Concentration of pseudo total metals measured in soil samples by FAAS and FAES (mg g^{-1}).

Element	Córdoba ($n = 71$)		La Rioja ($n = 28$)		San Juan ($n = 38$)	
	Median	Range	Median	Range	Median	Range
K	3.98	0.73–8.32	1.01	0.05–14.50	2.98	1.35–5.14
Na	0.66	0.18–5.56	5.05	0.38–11.74	2.21	0.90–3.40
Mg	6.48	2.43–15.61	5.42	0.62–11.84	7.48	3.20–14.26
Ca	7.50	0.41–14.37	8.04	1.83–14.79	18.66	9.72–28.75
Fe	26.42	15.65–37.66	24.89	9.80–37.59	20.65	11.55–28.62
Zn	0.09	0.05–1.16	0.22	0.04–1.00	0.07	0.05–0.11
Mn	0.49	0.006–1.70	0.32	0.11–1.02	0.49	0.19–0.77
Cu	0.08	<LOD–0.37	0.06	<LOD–0.86	0.03	<LOD–0.05
Ni	0.013	<LOD–0.036	<LOD	<LOD	<LOD	<LOD
Cr	0.10	<LOD–0.41	<LOD	<LOD	0.11	<LOD–0.16
Co	<LOD	<LOD–0.57	<LOD	<LOD	<LOD	<LOD–0.03

Pseudo total: LOD (mg g^{-1}): Co (0.02); Zn (0.002); Mn (0.02); Ni (0.006); Cr (0.003). LOQ (mg g^{-1}): Co (0.10); Zn (0.006); Mn (0.05); Ni (0.16); Cr (0.08).

available concentration of metals change for different elements in according to the nature of the soil, since bioavailability is conditioned by both the chemical form of metal and the binding strength of soil.

The median content of K was higher in La Rioja and similar in soils from Córdoba and San Juan. The content of sodium was quite different amongst three provinces. The concentration of Ca was similar in soils from La Rioja and San Juan. Median concentration of available Mg was comparable between the three wine-regions.

The amount of bioavailable Mn was higher than 1 mg kg^{-1}, which is the limit to indicate its deficit in soils. Mn is readily uptaken from soil and transported by the plant from the roots to the shoots (Marcet, Andrade, Amoedo, & Fernández, 2003).

Zn is an essential element for grapevine growth, although grape varieties and rootstocks vary widely in susceptibility to Zn deficiency (Ramos & Lopez-Acevedo, 2004). Our current results show that median values of available Zn in soils of Córdoba, La Rioja and San Juan are greater than the concentration necessary for vineyards (>0.8 mg kg^{-1}) (Ramos & Lopez-Acevedo, 2004).

The bioavailable fraction of Fe, Cu, Cr, Ni and Co is higher in vineyards of Córdoba than those corresponding to La Rioja and San Juan.

LDA afforded eight descriptors (Ca, Ni, Mn, Mg, K, Cu, Cr and Zn) for distinguishing between three studied regions with 90% accuracy. Despite of this last result, we did not observe good correlation between descriptors allowing discrimination of wines with those pointed out to discriminate bioavailable fractions of vineyard soils. So far, we disregarded the use of bioavailable fraction in soil to look for correlation between wine and provenance soil.

3.2.2. Pseudo total element in soil

Medians observed in our present work are similar to that reported by Buckman and Brady (1977).

Although Fe is considered a trace element with respect to feeding needs of the vine, it is a major constituent of the soil (Olson & Roscoe Ellis, 1982, chap. 17). Soils from Córdoba and La Rioja showed higher concentration of Fe than those from San Juan.

The contents of Ca and Mg in soils are strongly influenced by the composition of parent rocks (Kment et al., 2005). In our case, San Juan soil presented the highest level of Ca and Mg.

We found similar values of Na in soils from Córdoba, La Rioja and San Juan, while soils from La Rioja show the highest values of K.

The median concentration of Mn in the vine-growing soils was 400 mg kg^{-1}, showing less variation within the three regions studied. The level of Mn found during this study is similar to that reported by Ramos (2006) in vineyard soils of the Penedés area (NE Spain).

Soil from San Juan have lower level of Zn (70 mg kg^{-1}) than soils from Córdoba (90 mg kg^{-1}) and La Rioja (220 mg kg^{-1}), while Ramos (2006) reported concentrations ranging from 44 to 90 mg kg^{-1} in vineyard soils of Penedés area (NE Spain).

The content of Cu in soils of Córdoba is higher than 60 mg kg^{-1}, which is the value proposed by Kabata-Pendias and Pendias (1984) as having toxic effects on plants.

The concentration of Ni was below LOD in soil from La Rioja and San Juan. The levels of Cr and Co in soils from Córdoba were higher than the corresponding to La Rioja and San Juan.

Fig. 2B shows medians and ranges of *pseudo* total elements in soils for selected elements. As we can see from Fig. 2B, Ca allows differentiating soil of San Juan from those of Córdoba and La Rioja. There is some overlap in the range of iron and potassium for the three studied regions. Chromium distinguishes the soil of La Rioja from the rest.

LDA allowed distinguishing with 92% certainty amongst soils from three studied areas, pointing out to seven *pseudo* total elements: Ca, Cr, K, Fe, Cu, Zn and Mg. Fig. 3B shows a graphical representation of differentiation amongst studied soils considering *pseudo* total contents.

So far from soil data discussed above, we conclude that soils from three studied areas can be distinguished using bioavailable as well as *pseudo* total elements, or both. However, the elements to be considered are different from one method to the other.

3.3. Correspondence between soil and wine

The uptake of elements from the vine depends on the accumulation, transport and solubility of these elements that strongly depends on soil characteristics like pH and content of organic matter (Almeida & Vasconselos, 2003).

Our present results show good correspondence in the levels of Ca, Fe and Cr between wines (Fig. 2A) and the *pseudo* total fraction of soils (Fig. 2B).

Although K is the most significant variable to discriminate wines from different regions, its content in wine is not correlated with the *pseudo* total fraction of vineyard soil.

Kment et al. (2005) and Frías et al. (2001) found that the Mg content in wine is dependent on its concentration in the vineyard soil, being one useful element to evaluate wine provenance. Although Ca and Mg have similar chemical properties, the dependence between Ca content in soil and wine has not been demonstrated. Our present results show that Ca has the best correspondence between its content in wines and vineyard soil. Nevertheless, Sauvage, Frank, Stearne, and Millikan (2002) noted that the calcium content appears to be similar, regardless of the country of origin.

Cr and Fe have been reported as possible markers of origin in studies of wine provenance from European countries (Kment et al., 2005; Rebolo et al., 2000). The amount of Fe in wine is affected by both soil composition and technological processes involved in wine-making (Díaz et al., 2003; Rebolo et al., 2000). Although we observed some degree of overlap in the level of Fe in wine samples (Fig. 2A), the trend observed in wine is similar to that observed in soils (Fig. 2B). Besides, Cr shows the same trend in both wines and vineyard soils (Fig. 2A and B).

To elucidate how important Ca, Fe and Cr are to distinguish amongst wines from three studied areas, we carried out LDA using only these three variables as descriptors, obtaining 87% correct classification (data not shown). Lithophile elements Ca and Cr are components of rocks and corresponding soils therefore can be assumed that their origin in wines is mostly derived from the vineyard soils (Frías et al., 2003). Thus, we suggest the use of these elements as chemical descriptors allowing a good association between wine and soils for the three regions studied. Further studies are necessary to evidence if this is also applicable to wines and soils from other regions.

Despite of above-mentioned results, which were obtained by analysis of results from single elements analysed in both wine and soil, we were interested in evaluate if both matrix (elements in wine and *pseudo* total elements in soils) show good statistical correlation considering all the studied variables. Thus, we carried out canonical correlation. To do that, we defined two datasets: the set 1 includes variables of the LDA model for *pseudo* total elements in soil (Ca, Ni, K, Na, Cr, Fe, Cu and Mg), while set 2 includes variables of the LDA model for wine (Ni, Cr, Mg, Fe, K, Ca, Zn, Cu and Na), plus a new variable that accounts for geographical origin.

Significant correlation (r: 0.86; P 0.0000) was observed between the multielemental composition of wine and soil. This indicates that the metal content in vineyard soil is reflected in wine with an overall correlation of 86%. It is worthy to remark that the correlation calculated from canonical analysis is coincident with the 87% correct classification obtained by LDA using Ca, Fe and Cr to distinguish the provenance of wines. Thus, two independent multivariate statistical methods afford the same prediction.

So far, we conclude that 86% of metal contents in wines could be explained by the composition of vineyard soil. The remainder 14% could be attributed to other factors, like climate, agricultural practices, pollution, grape maturity at harvesting, wine-making techniques, etc. This last result reinforces the importance of studying both soil and wine composition to obtain reliable markers of wine provenance. The same approach could be valid for other foodstuffs, opening a new era in the evaluation of food provenance, namely chemical traceability.

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