

Elemental Analysis of Wines from South America and their Classification According to Country

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Elementos majoritários, minoritários e traço em vinhos provenientes de países produtores na América do Sul (Argentina, Brasil, Chile e Uruguai) foram determinados. A espectrometria de emissão óptica com plasma indutivamente acoplado (ICP OES) e a espectrometria de massa com plasma indutivamente acoplado (ICP-MS) em conjunto com nebulização pneumática e/ou nebulização ultra-sônica foram utilizadas. Foram determinados 45 elementos (Al, Ag, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, Sb, Sn, Se, Sm, Sr, Tb, Ti, Tl, Tm, U, V, Yb e Zn) em 53 vinhos tintos. Mediante análise multivariada, os vinhos puderam ser discriminados de acordo com o país de origem, independentemente do tipo da uva. Os elementos discriminantes foram Tl, U, Li, Rb e Mg.

Major, minor and trace elements in wines from wine-producing countries in South America (Argentina, Brazil, Chile, and Uruguay) were determined. Inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) combined with pneumatic and/or ultrasonic nebulization were used. The concentrations of 45 elements (Al, Ag, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, Sb, Sn, Se, Sm, Sr, Tb, Ti, Tl, Tm, U, V, Yb, and Zn) in 53 red wines were determined. By means of multivariate analysis, the wines could be discriminated according to the country of origin, regardless of the type of grape. The discriminant elements were Tl, U, Li, Rb, and Mg.

Keywords: red wine provenance, multivariate analysis, element concentration, ICP OES, ICP-MS

Introduction

Wine has a long history dating back to biblical times. With the evolution of the viticulture, a wide sort of wines became available to consumers due to the varieties of grape grown and different methods of wine producing.

Several elements (especially Cd, Cu, Fe, Mn, Sn and Zn) when present in excessively high concentration in wines, adversely affect the organoleptic quality and the stability of the wine. They may cause a metallic taste, undesired color change or give rise to obstinate hazing and cloudiness.¹The concentration of some elements can be a sort of fingerprint of the wine. The element profile does not depend exclusively on the geochemistry of the provenance soil but is affected by the winemaking process and the grape variety. Identifying the origin of wine is of great interest to producers and consumers, as it provides criteria for deciding about the quality of wine. Therefore, a method for verifying authenticity is an essential requirement to control the product origin claims.

Studies have shown that the concentration profile of elements can be used to identify the provenance of a wine as well as its authenticity.²⁻⁶ Lanthanides have been suggested as a fingerprint for the provenance of wines.^{2,4} However, caution must be taken because contamination may occur at the production step, transport and storage, as well as by inadequate winemaking practices.^{7,8}

Currently, ICP-MS, due to high sensitivity, ability to measure isotopes and multielement feature is one of the

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most appropriate techniques for the determination of trace elements in wine.9 However, the formation of molecular species in the plasma, such as Ar2+, ArO+, ArN+, ArH+, MAr⁺, ArX⁺ (M is a metal and X a non-metal) and other polyatomic species (MO⁺, MOH⁺, XO⁺, XO₂⁺, XOH⁺) that cause isobaric interferences may worsen precision and accuracy.¹⁰⁻¹² Additionally, the formation of oxides can also deteriorate the sensitivity for elements such as U, Ba and lanthanides.^{13,14} It is worth citing that the conditions of operation of the instrument, the instrument type and quality of aerosol introduced into the plasma influence the formation of molecular species. The use of nebulizers in conjunction with desolvation systems is a simple and effective way to decrease the formation of O and H interfering species, since most of the water is removed before the introduction of the sample solution into the plasma. Thus, the formation of oxide and hydroxides ions is drastically reduced.^{12,15} In addition, the limits of detection (LODs) are better (typically in one order of magnitude) because more sample is transported to the plasma.¹⁴ With the introduction of dry aerosol, the plasma is also more stable and consequently precision is improved. Molecular species of Ar and N interfere in the determination of Al, As, Se, Fe, K, Ca and Mg.¹⁴⁻¹⁶These elements can be better determined by using a double focusing sector field mass spectrometer¹⁷ or ICP OES (in the case of Al, Fe, K, Ca and Mg). Another way to minimize interferences by polyatomic ions in ICP-MS is the use of electrothermal vaporization (ETV) for introducing the sample into the plasma.^{18,19} However, elements such as B, Mo,²⁰ lanthanides and actinides produce thermally stable carbides in the graphite tube, increasing the LODs.

Due to the high content of organic compounds in wine, pretreatment of the sample is preferable for element determination by ICP OES and ICP-MS. The most common sample preparation procedure used is wet acid digestion or simple dilution of the sample. Although simple dilution is faster, not all investigated elements in the wine sample can be correctly determined in this way.

Studies to identify the origin of wines have already been published,^{2-6, 21,22} but none of them compared wines from different countries of South America. Therefore, the main goal of this study was to develop a method for identifying the origin of red wines produced in Argentina, Brazil, Chile and Uruguay (the wine-producing countries in South America) by the concentration of major, minor and trace elements. The data was statistically processed by multivariate analysis in an attempt to identify the country of origin of the analyzed wines. A set of 45 elements was investigated in order to find those that would better discriminate the wines. Different procedures of sample treatment are evaluated in order to achieve good precision and accuracy of the results.

Experimental

Instrumentation

Major and minor elements (Al, Ba, Ca, Fe, K, Mg, Mn, Na, P. Rb, Sr, Ti, and Zn) were determined by using an Optima 2000 DV ICP OES spectrometer (Perkin-Elmer, Shelton, CT, USA). The following spectral lines (wavelength in nm) were monitored: Al (396.153), Ba (233.527), Ca (317.933), Fe (238.204), K (766.490), Mg (285.213), Mn (257.610), Na (589.592), P (213.617), Rb (780.023), Sr (407.771), Ti (334.940) and Zn (206.200). A pneumatic nebulizer fitted to a cyclonic spray chamber was used for introducing the sample solution into the plasma. An ELAN DRC II instrument (from PerkinElmer/ SCIEX, Thornhill, Canada) was employed for minor and trace elements determination. Instrumental parameters (using the ICP-MS instrument in standard mode) such as the nebulizer gas flow rate, RF power and lens voltage were optimized in order to obtain the maximum intensity of ¹¹⁵In⁺ and minimum intensity of Ba⁺⁺/Ba⁺ and LaO⁺/La⁺. The following isotopes were monitored: 7Li, 9Be, 51V, 53Cr, ⁵⁸Ni, ⁵⁹Co, ⁶⁵Cu, ⁷⁵As, ⁸²Se, ⁹⁸Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹²⁰Sn, ¹²¹Sb, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi, ²³⁸U, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷²Yb, and ¹⁷⁵Lu. An ultrasonic nebulizer was used for the determination of Be, Ag, Cd, Sn, Sb, Tl, Bi, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The heating and cooling temperatures of the ultrasonic nebulizer were set at 140 °C and – 4 °C, respectively. A concentric nebulizer (Meinhard®, Golden, CO, USA) fitted to a cyclonic spray chamber was used for the determination of Li, V, Cr, Ni, Co, Cu, As, Mo, Se, and Pb.

The spray chambers and MicroMist nebulizer used were from Glass Expansion (Melbourne, Australia), the ultrasonic nebulizer was from CETAC (Omaha, NE, USA), whereas the Meinhard nebulizer was from Meinhard Associates. The conditions established for the elements determination in the wine samples are summarized in Table 1. The SPSS 18.0 software was used for statistical analysis. Factorial, cluster and discriminant analysis were used.

Reagents and solutions

Nitric acid (from Merck, Darmstadt, Germany), purified by distillation in sub-boiling quartz apparatus was used. High-purity water (resistivity of 18.2 M Ω cm) obtained from a Milli-Q system (Millipore Corp., Billerica, MA,

		ICP-MS		
Parameter	ICP OES	Pneumatic Nebulization	Ultrasonic Nebulization	
RF Power / W	1500	1200	1100	
Plasma gas flow rate / (L min ⁻¹)	15	15	15	
Auxiliary gas flow rate / (L min-1)	0.20	1.20	1.20	
Nebulizer carrier gas flow rate / (L min ⁻¹)	0.75	1.03	1.00	
Sample uptake rate / (mL min ⁻¹)	0.75	1.2	-	
Nebulizer	MicroMist MCN-600	Meinhard® type A	US-5000 AT+	
Background correction	2 points/peak	-	-	
Spray chamber	Cinnabar cyclonic unbaffled	Cinnabar cyclonic-baffled	-	
Injector tube	alumina 2-mm id	quartz 2-mm id		

USA) was used for the preparation of all samples and solutions. Calibration solutions were prepared (in 5% v/v HNO₃) from serial dilutions of 10 mg L⁻¹ multielemental stock solutions (Plasma Cal SCP33MS from SCP Science-Canada and CLMS-1 from SPEX, Metuchen, NJ, USA). The calibration solutions of P were prepared from a 1000 mg L⁻¹ P stock solution (Titrisol/Merck). The calibration solutions concentration and techniques used for each group of elements are summarized in Table 2. The elements quantification was assessed using external calibration.

Samples and sample preparation

Samples of red wine from different regions of the four wine-producing countries in South America (Argentina, Brazil, Chile and Uruguay) were purchased in local markets. The geographical origin and cultivars were given on the label of the wine bottle. The identification of the analyzed samples is given in Table 3. Excepting Bordeaux and Isabella, the wines were produced from grapes of *Vitis vinifera* species (specific for wine production). Assemblage is a type of wine produced by a blend of different grapes, unlike a varietal wine, which is made from only one grape and carrying the name of that grape. The blend of different grapes aims to add new flavors and aromas to the wine, leaving it more complex, or soft, depending on the goal. For instance, wine-tasting tannins such as Tannat can be softened by addition of Merlot grape. Another example of combination of aromas and flavors is the blend of the grapes Shiraz (also named Syrah) and Cabernet Sauvignon. According to Table 3, the number of samples was not the same for each country because not all cultivars are produced in the four wine-producing countries in South America or not easily found in the market.

The wine samples were decomposed according to the following procedure: 1 mL of wine was transferred to polytetrafluoroethylene (PTFE) flasks, to which 3 mL of HNO₃ were added and the mixture let to stand for 15 h. Subsequently, the vessels were closed and heated in a metal block, in three steps: 50 °C for 1 h, 100 °C for 1 h and 150 °C for 3 h. After cooling, the obtained solution was transferred to graduated-polypropylene vial and the volume was made up to 25 mL with water. This solution was tenfold diluted with 5% v/v HNO₃ for determinations by ICP OES, twofold diluted with 5% v/v HNO₃ for determinations by ICP-MS or directly analyzed by ICP-MS. All samples were analyzed in triplicate.

Analyte recovery tests and comparison of results obtained by ICP-MS and ICP OES were used to evaluate possible interferences and check precision and accuracy. For evaluation of the sample preparation procedure, a red

Table 2. Stock solutions, concentrations range of calibration curves and nebulizers used for the elements determination by ICP-MS and ICP OES

Stock Solution	Element	Concentration range of calibration curve / (µg L ⁻¹)	Technique/nebulizer
CLMS-1	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.01-1.0	ICP-MS/ultrasonic
SCP 33MS	Be, Se, Ag, Cd, Sn, Sb, Tl, Bi, U	0.01-1.0	ICP-MS/ultrasonic
SCP 33MS	Li, V, Cr, Ni, Co, Cu, As, Mo and Pb	0.05-10	ICP-MS/Meinhard
SCP 33MS	Al, Ba, Ca, Fe, K, Mg, Mn, Na, Rb, Sr, Ti and Zn	50-500	ICP OES/MicroMist ICP-MS/Meinhard
Titrisol	Р	100-1000	ICP OES/MicroMist

Country	Grape	Region	Year	Country	Grape	Region	Year
Argentina	Cabernet Sauvignon	Salta	2006	Chile	Cabernet Sauvignon	Maipo	2007
		Mendoza	2006			Colchagua	2003
		Mendoza	2005			Curicó	2006
	Malbec	Mendoza	2008			Requinoa	2005
		Mendoza	2007			Requinoa	2008
		Mendoza	2007		Malbec	Curicó	2005
		Mendoza	2006			Aconcagua	2006
		Mendoza	2005		Merlot	Requinoa	2002
	Merlot	Mendoza	2008			Maipo	2007
		Mendoza	2006			Racangua	2007
	Shiraz	Mendoza	2007		Carmenere	Colchagua	2008
	Pinot Noir	Patagonia	2009		Shiraz	Racangua	2007
	Assemblage	Mendoza	2002		Pinot Noir	Requinoa	2008
Brazil	Cabernet Sauvignon	Bento Gonçalves/RS	2005	Uruguay	Cabernet Sauvignon	Montevideo	2006
		Santana do Livramento/RS	2007			San José	2006
		Farroupilha/RS	2009			Colonia	2007
		Santa Maria/RS	2006			Canelones	2004
		Santa Maria/RS	1999		Malbec	Florida	2007
	Malbec	Bento Gonçalve/RS	2005		Merlot	Colonia	2007
		Bento Gonçalves/RS	2006			Florida	2007
	Merlot	Santana do Livramento/RS	2008		Tannat	Canelones	2007
		Bento Gonçalves/RS	2006			Montevideo	2007
		Bento Gonçalves/RS	2009			Canelones	2007
	Pinot Noir	Santana do Livramento/RS	2007		Shiraz	Artigas	2008
	Shiraz	Casa Nova/BA	2007		Pinot Noir	Canelones	2008
	Tannat	Santana do Livramento/RS	2007				
	Isabella	Cotiporã/RS	2006				
	Bordeaux	Antônio Prado/RS	2007				

Table 3. Wine samples identification

wine sample was simply diluted with nitric acid solution (to obtain 5% v/v HNO₃) or left in contact with HNO₃ (1 mL of wine + 3 mL of HNO₃) or decomposed as above described.

Results and Discussion

Chemical analysis

Wine is a complex matrix, producing spectral and nonspectral interferences in the plasma. Investigations were firstly carried out with respect to wine sample preparation, with the aim to analyze the wine samples directly (without decomposition), which would simplify the work. The results obtained for some elements are presented in Table 4. It shows that the concentrations of the elements tend to be higher when the wine is decomposed with acid. With respect to major elements, there is no significant statistic difference (at 95% of confidence level, according to the *t*-student test) between the procedures of sample preparation, except for diluting the sample with nitric acid. However, the concentrations of La and Ce (trace elements) are different. Change of plasma characteristics due to the organic matrix loading can be one of the reasons for the lower results observed, and/or the residence time

in the plasma is not sufficient for all processes (matrix decomposition and analyte ionization). Some wine samples that were simply diluted were also analyzed by ICP-MS. In this case, the main problem observed was the enhancement of the signals of As and Se, probably due to the presence of carbon.²³ On the other hand, progressive signal suppression of other elements was observed, caused mainly by carbon deposits on the interface (cones, photon stop and lens) of the ICP-MS instrument. Therefore, according to the results obtained in this step of the work and keeping in mind the large number of elements to be determined by ICP-MS or ICP OES, the wine samples were acid digested.

Since there was no certified wine available, the matrix influence was investigated by means of recovery tests and/ or analyte determination by both ICP OES and ICP-MS. For the recovery tests, the solution of a digested sample (1 mL of wine was digested and the obtained solution diluted to 25 mL) was spiked with the elements of interest. As shown in Table 5, either analyte recovery was close to 100% or the results obtained by ICP-MS and ICP OES were in agreement (similar at 95% level, according to the *t*-student test).

As expected, the LODs improved and oxide formation rate reduced for a group of elements (Be, Ag, Cd, Sn, Sb, Tl, Bi, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) by using ultrasonic nebulization (a dessolvated aerosol is produced) for sample introduction into the plasma.¹¹ However, Se could not be determined by using ultrasonic nebulization due to signal instability (the relative standard deviation was higher than 30%). The instability of the signal is possibly due to heating and volatilization of Se in the ultrasonic nebulizer. Then, pneumatic nebulization was used for Se determination in all samples. With respect to major elements measured by ICP OES (K, P, Mg, Ca, and Na) no interferences were observed. In this case, the digested sample solution was diluted at least 100 fold.

The concentrations of the investigated elements in the wine samples are summarized in Table 6 and Table S1 (Supplementary Information, SI). According to the results shown in these tables, the concentrations of most elements are heterogeneous within the samples. This may be caused not only by the soil type where the vines are grown, but also by the chemicals used as pesticides, winemaking processes and storage. It can be observed that the highest concentrations of V, Mo, As, Cd, Ag and Bi were found in wines from Chile; Rb, Tl, Mn, Be and Ba in wines from Brazil; Li and U in wines from Argentina; and Cu, Pb and Ni in wines from Uruguay. The concentrations of some elements in several samples are lower than the LODs. The LOD is the concentration equivalent to (B + 3s)fd, where B is the average concentration of ten consecutive measurements of the sample blank, s is the standard deviation of ten consecutive measurements of the same blank, and fd is the dilution factor of the wine sample (1 mL of wine diluted to 25 mL). Values lower than the LODs were treated by assuming the LOD values in the calculations of the means and standard deviations shown in Tables 6 and S1.

Statistical analysis

An exploratory analysis of the data was initially carried out. A Merlot wine from Chile was considered an extreme value and for that reason it was excluded. With respect to the other analyzed wines, only those obtained from grapes of *Vitis vinifera* strains were considered for multivariate analysis. Therefore, four wine samples were excluded from the multivariate analysis: one Merlot (from Chile) and the assemblage, Isabella and Bordeaux (see Table 3). Of the

Table 4. Elements determined (mg L^{-1}) in red wine, as a function of different sample preparation procedures. Results are the average and standard deviation of triplicates

Element	Acid deco	mposition	Left in contact with	Dilution with	
	Closed Vessel	Open Vessel	HNO ₃ overnight	5% v/v HNO ₃	
Mn	0.83 ± 0.05	0.84 ± 0.08	0.78 ± 0.09	0.77 ± 0.05	
Fe	3.58 ± 0.27	3.23 ± 0.42	2.85 ± 0.53	3.04 ± 0.32	
Ca	61.1 ± 4.2	62.5 ± 1.7	59.0 ± 2.1	58.2 ± 0.7	
Mg	116 ± 2.0	114 ± 4.2	110 ± 1.6	104 ± 1.6	
Zn	0.25 ± 0.05	0.28 ± 0.05	0.24 ± 0.02	0.15 ± 0.05	
K	1229 ± 97	1233 ± 83	1229 ± 73	1204 ± 29	
La ^a	505 ± 31	510 ± 14	190 ± 21	191 ± 16	
Ce ^a	542 ± 12	510 ± 46	339 ± 51	336 ± 27	

^ain (ng L⁻¹).

Table 5. Recovery of the elements in a digested Cabernet Sauvignon wine determined by ICP-MS or by two different techniques for Sr, Fe, Al, Ba, Mn, Rb, Sn, and Ti. Uncertainties are the standard deviations of triplicates

Element	Concentration found in the sample / ($\mu g L^{-1}$)	Added / Found / (μg L ⁻¹) (μg L ⁻¹)		Recovery / %
Cu	52.8 ± 0.6	2.50	98	
V	6.44 ± 0.30	2.50	2.50 8.68 ± 0.25	
Li	13.1 ± 2.9	2.50	15.5 ± 2.1	99
Мо	3.30 ± 0.41	2.50	5.69 ± 0.45	98
Cr	2.84 ± 015	2.50	5.51 ± 0.20	103
Ni	18.7 ± 1.3	2.50	20.8 ± 15	98
As	3.11 ± 0.36	2.50	5.50 ± 0.28	98
Pb	8.40 ± 0.34	2.50	11.1 ± 0.38	102
Co	2.50 ± 0.04	2.50	5.00 ± 0.06	100
Se	< 0.25 ^a	2.50	2.48 ± 0.10	99
Sn	15.2 ± 1.4	2.50	17.0 ± 1.2	96
Sb	0.249 ± 0.041	2.50	2.64 ± 0.03	96
Cd	< 0.10 ^a	2.50	2.48 ± 0.12	99
Ag	< 0.05	2.50	2.45 ± 0.01	98
Tl	4.12 ± 0.11	2.50	6.62 ± 0.14	100
Bi	< 0.025ª	2.50	2.48 ± 0.05	99
Be	0.930 ± 0.08	2.50	3.40 ± 0.08	99
U	< 0.025	2.50	2.50 2.48 ± 0.02	
La	0.610 ± 0.090	0.250	0.869 ± 0.070	101
Ce	0.800 ± 0.090	0.250	1.08 ± 0.027	103
Pr	0.201 ± 0.012	0.250	0.455 ± 0.040	101
Nd	< 0.025 ^a	0.250	0.247 ± 0.030	99
Sm	0.147 ± 0.013	0.250	0.389 ± 0.018	98
Eu	0.063 ± 0.034	0.250	0.307 ± 0.040	98
Gd	0.152 ± 0.034	0.250	0.410 ± 0.038	102
Tb	0.020 ± 0.004	0.250	0.267 ± 0.005	99
Dy	0.153 ± 0.031	0.250	0.399 ± 0.030	99
Но	0.043 ± 0.008	0.250	0.293 ± 0.007	100
Er	0.139 ± 0.013	0.250	0.363 ± 0.016	101
Tm	0.022 ± 0.003	0.250	0.272 ± 0.005	100
Yb	0.153 ± 0.019	$0.250 0.399 \pm 0.023$		99
Lu	0.024 ± 0.004	0.250	0.269 ± 0.005	99
	ICP OES / (µg L ⁻¹)		ICP-MS / (µg L ⁻¹)	
Sr	570 ± 90		576 ± 121	
Fe	1918 ± 75		1841 ± 53	
Al	296 ± 27		302 ± 33	
Ba	250 ± 10		240 ± 15	
Mn	3232 ± 43		3167 ± 78	
Rb	7644 ± 154		7338 ± 191	
Zn	343 ± 22		333 ± 34	
Ti	1145 ± 31		1123 ± 26	

alimits of detection.

total of 45 variables (elements) five of them (Mg, Li, Rb, U and Tl) were actually used after exploratory analysis of the data. Figure 1 shows the box-plot graphs related to these elements, showing the differences observed between the countries, which were significant according to the F test with sampling descriptive level of p < 0.001. According to Figure 1, three values of Rb are outliers, which were kept for the subsequent multivariate analysis. In this work, the outliers and extreme values were defined as those values whose distances from the nearest quartile were 1.5 and 3.0 times greater than the interquartile range, respectively.



Figure 1. Box plots showing the median and concentration range of Mg, Li, Tl, U and Rb in red wines according to the country. The horizontal lines in each box plot represent from bottom to top the minimum value, the first quartile, the median, the third quartile and the maximum value, respectively. Outlier values are indicated as individual points (o) outside the box. Values in the y axis refer to ln + 1; ln is the logarithm of the element concentration.

Two approaches were used for multivariate analysis. Firstly, the principal component and cluster analysis were used by considering only the chemical elements (variables) measured in the wines. Secondly, the classification of the samples according to their origin was used to fit a classification model by considering the chemical elements as discriminatory variables. With respect to the first approach, two components were obtained that explained 80.26% of the total variability of the original data: 51.75% was assigned to the first component and 28.5% to the second component. Figure 2 shows the dispersion between the components 1 and 2 and the loading for each variable (chemical element).

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Table 6. Concentrations range (μ g L⁻¹), means (in bold) and standard deviations (values in parenthesis) of minor and trace elements found in red wines. Number of samples: 13 from Argentina, 15 from Brazil, 13 from Chile, and 12 from Uruguay

	Argentina	Brazil	Chile	Uruguay		Argentina	Brazil	Chile	Uruguay
Rb	523-1247	2004-7644	1110-5935	2344-3965	Eu	< 0.008-0.002	< 0.008-0.06	< 0.008-0.6	< 0.008-0.05
	799 (260)	4679 (1482)	3476 (1404)	3155 (451)		0.012 (0.004)	0.02 (0.02)	0.07 (0.17)	0.02 (0.01)
Zn	155-1239	184-891	140-1359	174-1359	Gd	< 0.01-0.2	< 0.01-0.2	< 0.01-0.14	< 0.01-0.12
	648 (263)	486 (211)	525 (247)	674 (382)		0.07 (0.03)	0.10 (0.05)	0.07 (0.05)	0.07 (0.02)
Ti	111-168	36-286	70-186	75-84	Tb	< 0.002-0.01	< 0.002-0.02	< 0.002-0.14	< 0.002-0.12
	137 (37)	126 (60)	143 (32)	143 (32)		0.003 (0.004)	0.006 (0.008)	0.003 (0.005)	0.003 (0.004)
Cu	20-249	28-222	73-346	21-1290	Dy	< 0.01-0.08	< 0.01-0.2	< 0.01-0.2	< 0.01-0.08
	103 (74)	90 (55)	137 (86)	320 (439)	5	0.05 (0.02)	0.09 (0.07)	0.03 (0.04)	0.04 (0.02)
V	1.4-80	2-76	21-281	19-99	Ho	< 0.002-0.02	< 0.002-0.04	< 0.002	< 0.002-0.013
	37 (30)	29 (28)	74 (72)	58 (26)		0.007 (0.007)	0.01 (0.01)		0.002 (0.005)
Li	71-354	2-27	3-14	18-42	Er	< 0.002-0.05	< 0.002-0.14	< 0.002-0.08	< 0.002-0.05
	189 (91)	8 (6)	9 (4)	28 (10)		0.03 (0.01)	0.06 (0.04)	0.03 (0.02)	0.02 (0.01)
Mo	1.3-20	1.2-21	2.2-38	3.1-8	Tm	< 0.002-0.01	< 0.002-0.02	< 0.002-0.01	< 0.002-0.02
	7 (5)	7 (6)	18 (25)	5 (1)		0.004 (0.003)	0.008 (0.008)	0.003 (0.004)	0.002 (0.003)
Cr	6-68	5-50	3-61	5-57	Yh	< 0.005-0.06	< 0.005-0.2	< 0.005-0.02	< 0.005-0.04
01	29 (16)	24 (15)	23 (18)	21 (12)	10	0.02 (0.02)	0.02 (0.04)	0.008 (0.01)	0.02 (0.01)
Ni	12-42	5-42	3-28	25-59	Lu	< 0.002-0.02	< 0.002-0.03	< 0.002-0.02	< 0.002-0.01
1.11	27 (9)	25 (12)	18 (9)	38 (10)	24	0.007 (0.004)	0.01 (0.01)	0.006 (0.004)	0.003 (0.004)
As	4-28	0.5-17	4-79	3-17	Ce	0 33-1 0	04-30	0 3-3 3	0.2-0.8
110	14 (7)	7 (6)	17 (19)	12 (5)	00	0.7 (0.2)	1.2 (0.7)	0.9 (0.9)	0.5 (0.2)
Ph	2-53	0.6-26	2 5-28	8-82	Pr	0.04-0.35	0.04-0.6	< 0.02-1.5	< 0.02-0.4
10	20 (14)	11 (8)	11 (9)	26 (27)		0.1 (0.1)	0.2 (0.1)	0.2 (0.3)	0.06 (0.02)
Mn	641-1125	1052-3295	430-3270	706-1867	Sm	< 0.02-0.09	< 0.02 - 0.23	$< 0.02 \cdot 1.1$	< 0.02-0.1
	932 (140)	2195 (628)	1397 (807)	1250 (369)	om	0.1 (0.03)	0.1 (0.07)	0.1 (0.3)	0.05 (0.04)
Co	2-7	2-8	2-12	2-7	Nd	< 0.02-0.5	$< 0.02 \cdot 1.4$	$< 0.02 \cdot 1.0$	< 0.02 - 0.4
0	$\frac{2}{3}(1)$	5 (2)	4 (3)	4 (2)	itu	0.2 (0.2)	0.3 (0.4)	0.2 (0.3)	0.1 (0.1)
Se	< 0.25-6	< 0.25-6	< 0.25-2	<0.25-2	La	03-16	< 0.02-1.8	< 0.02-3.0	< 0.02-0.9
50	1.3 (1.8)	1.6 (1.8)	0.5 (0.8)	0.4 (0.6)	Du	0.6 (0.4)	0.7 (0.5)	0.6 (0.9)	0.3 (0.3)
Sn	< 0.07-3	< 0.07-19	< 0.07-1	< 0.07-24	A1	486-1208	296-1130	177-1676	230-1062
511	1 (1)	4 (7)	0.4 (0.4)	4 (8)	7 11	690 (193)	660 (274)	800 (440)	725 (303)
Sh	0 2-2 5	0.2-3	0.2-4	0.2-1	Fe	908-2285	454-2151	625-4879	398-2827
50	0.7 (0.6)	0.7 (0.8)	0.7 (1.0)	0.5 (0.4)	10	1793 (423)	1355 (576)	2657 (1207)	1791 (1036)
Cđ	< 0.01-0.6	< 0.01-0.6	< 0.01-6	< 0.01-0.5	Sr	697-1400	365-1178	425-1008	520-1228
cu	0.3 (0.2)	0.2 (0.2)	0.6 (1.7)	0.1 (0.2)	51	909 (200)	723 (282)	697 (183)	901 (201)
Aσ	< 0.05-0.38	< 0.05-0.2	< 0.05-1	< 0.05-0.1	T1	0.1-0.2	0.6-5	0.1-0.6	0.4-1.3
	0.05 (0.11)	0.02 (0.04)	0.3 (0.4)	0.02 (0.03)		0.1 (0.03)	2.3 (1.3)	0.3 (0.1)	0.7 (0.3)
Bi	< 0.02-0.6	< 0.02-0.9	< 0.02 - 1.9	< 0.02-1.0	Be	< 0.01-0.7	< 0.01-2.7	< 0.01-0.7	< 0.01-0.5
DI	0.2 (0.3)	0.1 (0.2)	0.8 (0.6)	0.3 (0.3)	De	0.2 (0.2)	0.9 (0.7)	0.2 (0.2)	0.2 (0.2)
II	< 0.02-2.5	< 0.02-0.5	$< 0.02 \cdot 1.2$	0.2-1.3	Ba	52-410	91-675	42-513	98-525
U	1.2 (0.8)	0.1 (0.2)	0.4 (0.3)	0.2 (0.4)	Du	175 (107)	300 (164)	172 (145)	192 (109)
Caa	39-98	51-98	28-73	40-107	Naa	7 2-63	1 6-69	3 3-49	14-67
Cu	66 (15)	71 (17)	58 (13)	71 (21)	144	29 (17)	27 (22)	13 (12)	34 (19)
Moa	92,116	84-106	99_12/	79_88	Da	329-000	350-634	503-1358	525-612
1718	104 (7)	93 (7)	112 (6)	83 (3)	1	643 (157)	488 (82)	664 (301)	579 (27)
Ka	826-1703	890-1636	899-1395	195-1856					
iX.	1172 (240)	1189 (206)	1094 (161)	951 (465)					
	< - J	< /	< - /	×/					

^aconcentration in (mg L⁻¹).



Figure 2. Scatter plot of components 1 and 2 and respective loadings of Mg, Rb, Tl, U, and Li.

The result of cluster analysis is depicted in Figure 3, which highlights the similarity of the composition of the wines with respect to the elements shown in Figure 2. The similarity matrix was obtained using squared Euclidean, while distance and clustering were produced using the Ward's method. Figure 3 shows strong evidence that the similarity observed is closely associated with the country of origin, since the resulting groups are primarily structured according to the origin. Excepting a Chilean wine (sample 34), classified within the group dominated by Brazilian wines, all other observations (samples) follow a pattern of very high similarity within a country and extremely high dissimilarity between countries.

Figure 4 shows the dispersion of the scores of principal component analysis associated with each wine, with an indication of each group resulting from cluster analysis presented in Figure 3. By analyzing Figures 2 and 4 together it is observed that Li and U are higher in Argentinean wines in comparison to Brazilian and Chilean wines; Rb and Tl are higher in Brazilian and Chilean wines when compared with Argentinean wines; Mg is higher in Chilean and some Argentinean wines at the same time as it is lower in Uruguayan and some Brazilian wines.

In the second approach the discriminant model was employed, which considered the origin of the wines as the dependent variable and the five elements previously identified (Li, Mg, Rb, Tl and U) as the independent variable. The non-standardized coefficients for each canonical discriminant function (used to discriminate the five countries as a function of the five chemical elements) and the correlation between discriminating variables and standardized discriminant function are presented in Table 7. The discriminant variables (B) show that Li and Rb are more correlated with function 1, Mg with functions 2 and 3, and Tl and U with function 3.



Figure 3. Dendrogram of cluster analysis of Li, Mg, Rb, Tl, and U in red wines (49 samples) from wine-producing countries in South America.

As a result, the centroids for each country were obtained; the dispersion among the scores from the discriminant functions 1 and 2 are shown in Figure 5. According to this figure, function 1 discriminates the samples from Argentina in a group and samples from Brazil and Chile in another group; function 2 discriminates the samples from Chile of those from Brazil and Uruguay; and function 3 discriminates the samples from Brazil of those from Uruguay.

Additionally, a cross validation text was performed. The results of classification of cases revealed that the proposed model of classification was successful in 100% of the cases and the results were 100% accurate.



Figure 4. Scatter plot of the scores of the two principal component analysis of red wines (49 samples) from South America showing similarity within the country and dissimilarity between countries.



Figure 5. Scatter plot of the unstandardized canonical discriminant functions 1 and 2 describing the countries of red wines (49) origin.

Table 7. Non-standardized coefficients of the canonical discriminant functions (A) and correlation between the discriminant function and the measured chemical element (B)

	Function							
Variable	1	2	3	1	2	3		
		А			В			
Mg	-6.476	17.94	5.676	-0.041	0.639ª	0.639ª		
Li	1.786	-0.492	-0.246	0.720ª	0.111	0.019		
Tl	0.148	-3.714	3.532	-0.255	0.450	0.651ª		
U	0.636	1.356	-0.613	0.235	0.035	-0.256ª		
Rb	-1.913	0.413	-1.858	0.543ª	0.253	-0.391		
(Constant)	83.40	-206.3	-51.49	-	-	-		

^aLargest absolute correlation between each variable and the discriminant function.

Conclusions

By multivariate analysis based on the concentration of chemical elements it was possible to discriminate red wines from the four wine-producing countries in South America according to country. Lithium, Mg, Rb, Tl, and U allowed discrimination of varietal red wines obtained from grapes of *Vitis vinifera* species. The type of yeast used, the way the vines are cultivated, knowledge of the winemaker that influences the way of making wine, storage form, fertilizers and fungicides used may have contributed for the differences among the wines.

Although some authors have recommended that the lanthanides alone can distinguish wines,^{2,4} this strategy was not feasible in the present work. The concentrations of these elements are very low in most wines from South America and not all of them were detected in several samples, despite using a highly sensitive technique (ICP-MS and ultrasonic nebulization for sample introduction into the plasma).

It was observed that the concentrations of some elements measured in red wine may be lower than the actual concentrations if the sample is simply diluted instead of being digested.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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