

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

Fabrina R. S. Bentlin,^a Fernando H. Pulgati,^b Valderi L. Dressler^c and Dirce Pozebon^{*,a}

^aInstituto de Química and ^bInstituto de Matemática, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre-RS, Brazil

^cDepartamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria-RS, Brazil

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.¹ The 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

*e-mail: dircepoz@iq.ufrgs.br

most appropriate techniques for the determination of trace elements in wine.⁹ However, the formation of molecular species in the plasma, such as Ar_2^+ , ArO^+ , ArN^+ , ArH^+ , MAr^+ , ArX^+ (M is a metal and X a non-metal) and other polyatomic species (MO^+ , MOH^+ , XO^+ , XO_2^+ , 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.¹⁴⁻¹⁶ These 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 $^{115}\text{In}^+$ and minimum intensity of $\text{Ba}^{++}/\text{Ba}^+$ and LaO^+/La^+ . The following isotopes were monitored: ^7Li , ^9Be , ^{51}V , ^{53}Cr , ^{58}Ni , ^{59}Co , ^{65}Cu , ^{75}As , ^{82}Se , ^{98}Mo , ^{107}Ag , ^{111}Cd , ^{120}Sn , ^{121}Sb , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{238}U , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{172}Yb , and ^{175}Lu . 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 MΩ cm) obtained from a Milli-Q system (Millipore Corp., Billerica, MA,

Table 1. Instrumental and optimized operating conditions

Parameter	ICP OES	ICP-MS	
		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	P	100-1000	ICP OES/MicroMist

Table 3. Wine samples identification

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	
	Merlot	Mendoza	2005		Merlot	Requinoa	2002
		Mendoza	2008			Maipo	2007
	Shiraz	Mendoza	2006			Racangua	2007
		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
	Malbec	Bento Gonçalves/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
	Tannat	Santana do Livramento/RS	2007				
	Isabella	Cotiporã/RS	2006				
	Bordeaux	Antônio Prado/RS	2007				

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 non-spectral 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 desolvated 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 $(B + 3s)/d$, 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 *d* 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 decomposition		Left in contact with HNO ₃ overnight	Dilution with 5% v/v HNO ₃
	Closed Vessel	Open Vessel		
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 / ($\mu\text{g L}^{-1}$)	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	Recovery / %
Cu	52.8 ± 0.6	2.50	54.2 ± 0.4	98
V	6.44 ± 0.30	2.50	8.68 ± 0.25	97
Li	13.1 ± 2.9	2.50	15.5 ± 2.1	99
Mo	3.30 ± 0.41	2.50	5.69 ± 0.45	98
Cr	2.84 ± 0.15	2.50	5.51 ± 0.20	103
Ni	18.7 ± 1.3	2.50	20.8 ± 1.5	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	< 0.025 ^a	2.50	2.48 ± 0.05	99
Be	0.930 ± 0.08	2.50	3.40 ± 0.08	99
U	< 0.025	2.50	2.48 ± 0.02	99
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
Ho	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 ± 0.023	99
Lu	0.024 ± 0.004	0.250	0.269 ± 0.005	99
	ICP OES / ($\mu\text{g L}^{-1}$)		ICP-MS / ($\mu\text{g L}^{-1}$)	
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.

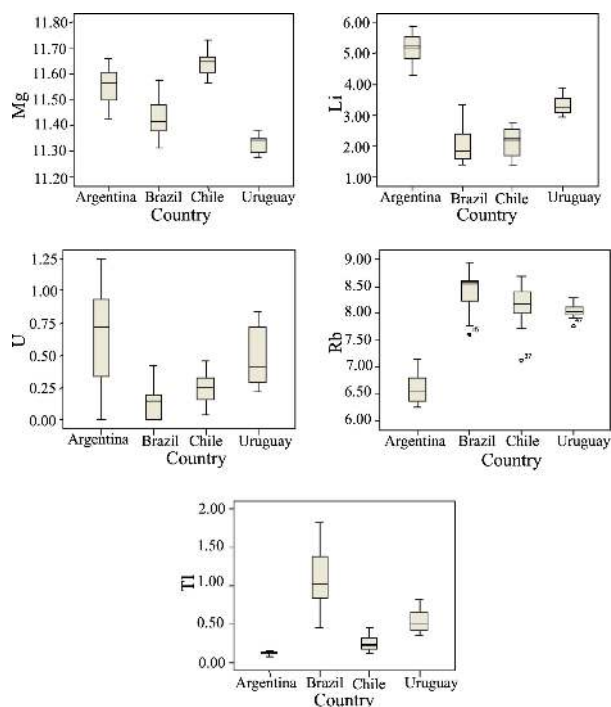


Figure 1. Box plots showing the median and concentration range of Mg, Li, Tl, U and Rb in red wines according to the country. The horizontal lines in each box plot represent from bottom to top the minimum value, the first quartile, the median, the third quartile and the maximum value, respectively. Outlier 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).

Table 6. Concentrations range ($\mu\text{g L}^{-1}$), 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 799 (260)	2004-7644 4679 (1482)	1110-5935 3476 (1404)	2344-3965 3155 (451)	Eu	< 0.008-0.002 0.012 (0.004)	< 0.008-0.06 0.02 (0.02)	< 0.008-0.6 0.07 (0.17)	< 0.008-0.05 0.02 (0.01)
Zn	155-1239 648 (263)	184-891 486 (211)	140-1359 525 (247)	174-1359 674 (382)	Gd	< 0.01-0.2 0.07 (0.03)	< 0.01-0.2 0.10 (0.05)	< 0.01-0.14 0.07 (0.05)	< 0.01-0.12 0.07 (0.02)
Ti	111-168 137 (37)	36-286 126 (60)	70-186 143 (32)	75-84 143 (32)	Tb	< 0.002-0.01 0.003 (0.004)	< 0.002-0.02 0.006 (0.008)	< 0.002-0.14 0.003 (0.005)	< 0.002-0.12 0.003 (0.004)
Cu	20-249 103 (74)	28-222 90 (55)	73-346 137 (86)	21-1290 320 (439)	Dy	< 0.01-0.08 0.05 (0.02)	< 0.01-0.2 0.09 (0.07)	< 0.01-0.2 0.03 (0.04)	< 0.01-0.08 0.04 (0.02)
V	1.4-80 37 (30)	2-76 29 (28)	21-281 74 (72)	19-99 58 (26)	Ho	< 0.002-0.02 0.007 (0.007)	< 0.002-0.04 0.01 (0.01)	< 0.002 0.002 (0.002)	< 0.002-0.013 0.002 (0.005)
Li	71-354 189 (91)	2-27 8 (6)	3-14 9 (4)	18-42 28 (10)	Er	< 0.002-0.05 0.03 (0.01)	< 0.002-0.14 0.06 (0.04)	< 0.002-0.08 0.03 (0.02)	< 0.002-0.05 0.02 (0.01)
Mo	1.3-20 7 (5)	1.2-21 7 (6)	2.2-38 18 (25)	3.1-8 5 (1)	Tm	< 0.002-0.01 0.004 (0.003)	< 0.002-0.02 0.008 (0.008)	< 0.002-0.01 0.003 (0.004)	< 0.002-0.02 0.002 (0.003)
Cr	6-68 29 (16)	5-50 24 (15)	3-61 23 (18)	5-57 21 (12)	Yb	< 0.005-0.06 0.02 (0.02)	< 0.005-0.2 0.02 (0.04)	< 0.005-0.02 0.008 (0.01)	< 0.005-0.04 0.02 (0.01)
Ni	12-42 27 (9)	5-42 25 (12)	3-28 18 (9)	25-59 38 (10)	Lu	< 0.002-0.02 0.007 (0.004)	< 0.002-0.03 0.01 (0.01)	< 0.002-0.02 0.006 (0.004)	< 0.002-0.01 0.003 (0.004)
As	4-28 14 (7)	0.5-17 7 (6)	4-79 17 (19)	3-17 12 (5)	Ce	0.33-1.0 0.7 (0.2)	0.4-3.0 1.2 (0.7)	0.3-3.3 0.9 (0.9)	0.2-0.8 0.5 (0.2)
Pb	2-53 20 (14)	0.6-26 11 (8)	2.5-28 11 (9)	8-82 26 (27)	Pr	0.04-0.35 0.1 (0.1)	0.04-0.6 0.2 (0.1)	< 0.02-1.5 0.2 (0.3)	< 0.02-0.4 0.06 (0.02)
Mn	641-1125 932 (140)	1052-3295 2195 (628)	430-3270 1397 (807)	706-1867 1250 (369)	Sm	< 0.02-0.09 0.1 (0.03)	< 0.02-0.23 0.1 (0.07)	< 0.02-1.1 0.1 (0.3)	< 0.02-0.1 0.05 (0.04)
Co	2-7 3 (1)	2-8 5 (2)	2-12 4 (3)	2-7 4 (2)	Nd	< 0.02-0.5 0.2 (0.2)	< 0.02-1.4 0.3 (0.4)	< 0.02-1.0 0.2 (0.3)	< 0.02-0.4 0.1 (0.1)
Se	< 0.25-6 1.3 (1.8)	< 0.25-6 1.6 (1.8)	< 0.25-2 0.5 (0.8)	< 0.25-2 0.4 (0.6)	La	0.3-1.6 0.6 (0.4)	< 0.02-1.8 0.7 (0.5)	< 0.02-3.0 0.6 (0.9)	< 0.02-0.9 0.3 (0.3)
Sn	< 0.07-3 1 (1)	< 0.07-19 4 (7)	< 0.07-1 0.4 (0.4)	< 0.07-24 4 (8)	Al	486-1208 690 (193)	296-1130 660 (274)	177-1676 800 (440)	230-1062 725 (303)
Sb	0.2-2.5 0.7 (0.6)	0.2-3 0.7 (0.8)	0.2-4 0.7 (1.0)	0.2-1 0.5 (0.4)	Fe	908-2285 1793 (423)	454-2151 1355 (576)	625-4879 2657 (1207)	398-2827 1791 (1036)
Cd	< 0.01-0.6 0.3 (0.2)	< 0.01-0.6 0.2 (0.2)	< 0.01-6 0.6 (1.7)	< 0.01-0.5 0.1 (0.2)	Sr	697-1400 909 (200)	365-1178 723 (282)	425-1008 697 (183)	520-1228 901 (201)
Ag	< 0.05-0.38 0.05 (0.11)	< 0.05-0.2 0.02 (0.04)	< 0.05-1 0.3 (0.4)	< 0.05-0.1 0.02 (0.03)	Tl	0.1-0.2 0.1 (0.03)	0.6-5 2.3 (1.3)	0.1-0.6 0.3 (0.1)	0.4-1.3 0.7 (0.3)
Bi	< 0.02-0.6 0.2 (0.3)	< 0.02-0.9 0.1 (0.2)	< 0.02-1.9 0.8 (0.6)	< 0.02-1.0 0.3 (0.3)	Be	< 0.01-0.7 0.2 (0.2)	< 0.01-2.7 0.9 (0.7)	< 0.01-0.7 0.2 (0.2)	< 0.01-0.5 0.2 (0.2)
U	< 0.02-2.5 1.2 (0.8)	< 0.02-0.5 0.1 (0.2)	< 0.02-1.2 0.4 (0.3)	0.2-1.3 0.7 (0.4)	Ba	52-410 175 (107)	91-675 300 (164)	42-513 172 (145)	98-525 192 (109)
Ca ^a	39-98 66 (15)	51-98 71 (17)	28-73 58 (13)	40-107 71 (21)	Na ^a	7.2-63 29 (17)	1.6-69 27 (22)	3.3-49 13 (12)	14-67 34 (19)
Mg ^a	92-116 104 (7)	84-106 93 (7)	99-124 112 (6)	79-88 83 (3)	P ^a	329-900 643 (157)	350-634 488 (82)	503-1358 664 (301)	525-612 579 (27)
K ^a	826-1703 1172 (240)	890-1636 1189 (206)	899-1395 1094 (161)	195-1856 951 (465)					

^aconcentration in (mg L^{-1}).

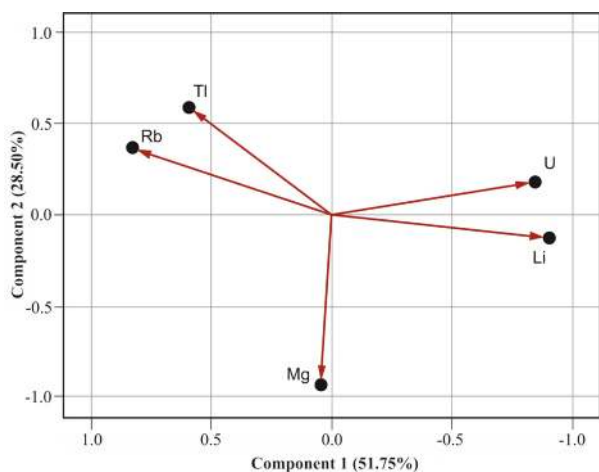


Figure 2. Scatter plot of components 1 and 2 and respective loadings of Mg, Rb, Tl, U, and Li.

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.

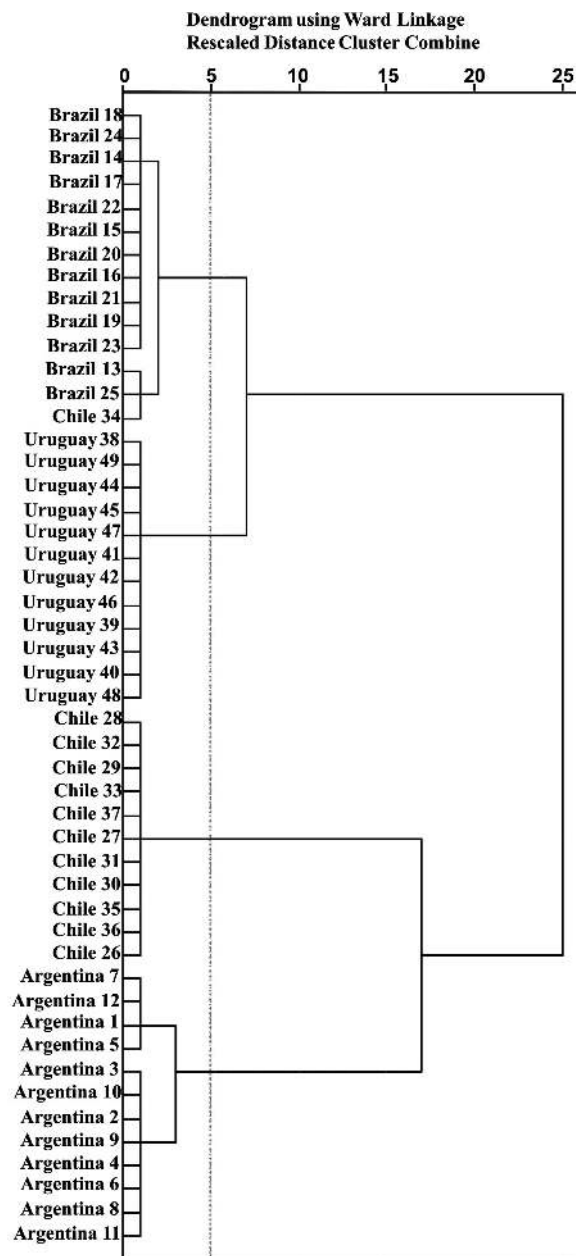


Figure 3. Dendrogram of cluster analysis of Li, Mg, Rb, Tl, and U in red wines (49 samples) from wine-producing countries in South America.

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 test 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.

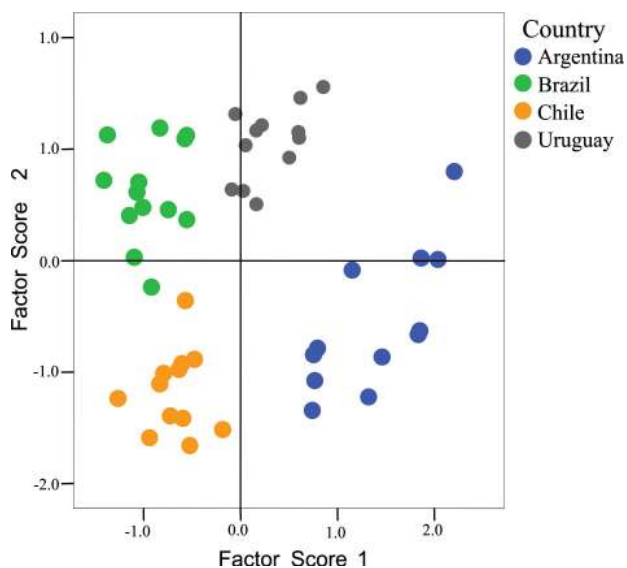


Figure 4. Scatter plot of the scores of the two principal component analysis of red wines (49 samples) from South America showing similarity within the country and dissimilarity between countries.

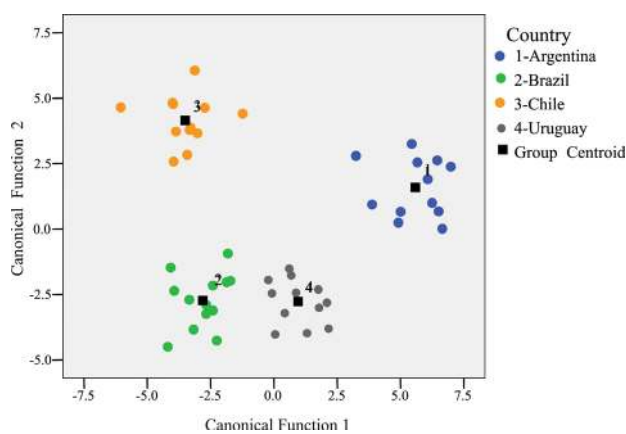


Figure 5. Scatter plot of the unstandardized canonical discriminant functions 1 and 2 describing the countries of red wines (49) origin.

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

Variable	Function					
	A			B		
	1	2	3	1	2	3
Mg	-6.476	17.94	5.676	-0.041	0.639 ^a	0.639 ^a
Li	1.786	-0.492	-0.246	0.720 ^a	0.111	0.019
Tl	0.148	-3.714	3.532	-0.255	0.450	0.651 ^a
U	0.636	1.356	-0.613	0.235	0.035	-0.256 ^a
Rb	-1.913	0.413	-1.858	0.543 ^a	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://jbcbs.sbgq.org.br>, as PDF file.

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Supplementary Information

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

Fabrina R. S. Bentlin,^a Fernando H. Pulgati,^b Valderi L. Dressler^c and Dirce Pozebon^{,a}*

^a*Instituto de Química and ^bInstituto de Matemática, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre-RS, Brazil*

^c*Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria-RS, Brazil*

Table S1. Concentrations (in $\mu\text{g L}^{-1}$) range, means (in bold) and standard deviations (in parenthesis) of minor and trace elements found in the wines. Concentrations of K, P, Mg, Ca and Na are in mg L^{-1} . Those wines marked with * only one sample was analysed

Wine	K	P	Mg	Ca	Na	Sr	Fe	Al	Mn	Rb
Chile/Cabernet	898-1230 1054 (161)	542-849 642 (133)	111-124 116 (53)	50-80 61 (12)	3-13 8 (4)	551-995 669 (185)	1770-4849 3373 (1547)	388-1676 1118 (468)	832-3270 1601 (979)	3377-4973 3969 (698)
Uruguay/Cabernet	502-852 618 (159)	525-597 578 (35)	79-85 83 (3)	40-67 51 (13)	17-40 24 (11)	520-847 724 (149)	907-1629 1261 (394)	230-394 327 (72)	1251-1867 1455 (282)	3108-3574 3246 (219)
Argentina/Cabernet	1184-1316 1244 (67)	534-895 665 (200)	92-108 101 (8)	48-71 60 (11)	20-55 39 (18)	697-991 844 (147)	1938-2271 2068 (178)	694-805 744 (56)	873-982 911 (62)	557-1247 905 (345)
Brazil/Cabernet	1068-1487 1222 (160)	350-552 476 (81)	84-98 90 (5)	62-84 74 (11)	14-69 34 (24)	365 -1382 771 (392)	454-1918 1254 (736)	296 -1130 572 (347)	1217-3232 2155 (747)	2348-7644 4804 (1977)
Argentina/Malbec	827 -1087 1013 (108)	627-900 713 (107)	100-116 107 (7)	57-79 66 (9)	10-63 32 (22)	705-1070 902 (151)	1387-2099 1824 (323)	486 -1208 703 (319)	798 -1125 1015 (133)	523-865 669 (139)
Uruguay/Malbec	908	554	85	62	55	842	3177	946	706	3072
Brazil/Malbec	938 -1187 1062 (176)	407 -572 489 (117)	87 -95 91 (4)	49 -51 50 (1)	56-62 59 (3)	593-1178 886 (414)	857-1015 936 (112)	530 -850 690 (226)	1761-1957 1859 (139)	5332-5391 5362 (42)
Chile/Malbec	1078-1117 1097 (27)	503-1358 930 (604)	105-113 109 (6)	28-49 38 (14)	3-16 10 (8)	760-846 803 (61)	2033-2078 2056 (32)	443 -653 548 (148)	2273-2545 2509 (192)	4264-4387 4326 (87)
Brazil/Merlot	1094-1300 1203 (104)	449-634 535 (93)	82-103 94 (11)	58-83 72 (13)	13-23 19 (5)	478-829 640 (177)	516-2098 1318 (791)	548 -1014 818 (242)	1784 -2407 2194 (355)	3253-6343 4970 (1573)
Argentina/Merlot	987 -1237 1112 (177)	329-661 495 (235)	97-110 104 (9)	65 -67 66 (1)	22-38 33 (6)	887-983 935 (68)	1227-1567 1397 (240)	555-695 625 (99)	641 -766 704 (88)	585-658 622 (52)
Chile/Merlot	955-1395 1094 (260)	559-997 718 (242)	99-117 108 (9)	51 -56 53 (2)	8-49 23 (22)	425-885 638 (232)	2231-2828 2524 (299)	765 -921 861 (84)	892 -975 938 (42)	1110- 3613 1986 (1410)
Uruguay/Merlot	895-1439 1167 (272)	545-595 567 (35)	84 -88 86 (2)	62 -75 68 (6)	19 -55 37 (18)	830-857 844 (14)	2400-2728 2564 (232)	801 -882 842 (41)	723 -1193 958 (235)	2729-3070 2900 (170)
Chile/Carmenere	1085	886	116	65	23	606	625	780	1096	5935
Chile/Shiraz	1340	302	116	73	10	1008	2327	182	840	2568
Chile/Pinot Noir	1048	217	106	68	9	580	3038	177	590	2237
Uruguay/Tannat	1126-1856 1417 (387)	564-612 582 (26)	79-81 80 (1)	73-107 88 (17)	17-67 40 (25)	897-1194 1070 (154)	398-3267 1511 (1539)	897-981 945 (43)	1043-1894 1351 (472)	2344-3813 3069 (735)

*e-mail: dircepoz@iq.ufrgs.br

Tabela S1. Continued

Wine	K	P	Mg	Ca	Na	Sr	Fe	Al	Mn	Rb
Uruguay/Shiraz*	195	595	87	102	14	1228	2827	871	1382	3965
Uruguay/Pinot Noir*	1255	597	80	78	46	948	785	1062	1119	2828
Argentina/Assemblage*	976	773	105	39	7	615	2285	613	984	1138
Argentina/Pinot Noir*	1541	538	98	98	23	892	908	673	1004	1235
Argentina/Shiraz*	1703	505	107	79	8	1400	2003	682	919	709
Brazil/Tannat*	1636	543	106	81	33	1014	1511	439	3295	5114
Brazil/Pinot Noir*	1222	544	901	59	12	585	1318	1030	1649	5215
Brazil/Bahia/Shiraz*	1350	509	89	71	8	637	2151	758	1052	2004
Brazil/Isabel*	893	368	90	75	2	559	1633	602	2434	4646
Brazil/Bordô*	890	390	100	978	4	507	1618	367	2273	3557
Wine	Zn	Ba	Cu	Ti	V	Li	Mo	Cr	Ni	As
Chile/Cabernet	214-926 592 (324)	133-195 155 (24)	64-177 113 (45)	101-171 136 (26)	21-137 65 (55)	7-14 11 (4)	2-91 31 (36)	2-22 13 (9)	3-16 12 (5)	4-23 12 (7)
Uruguay/Cabernet	337-818 526 (209)	142-184 168 (18)	124-247 170 (54)	75-182 141 (47)	19-88 54 (35)	19-30 25 (6)	3-5 4 (1)	17-25 20 (4)	27-43 34 (7)	3-21 11 (8)
Argentina/Cabernet	591 -685 630 (49)	122-410 229 (158)	20-249 149 (117)	132-158 149 (15)	21-67 43 (23)	175-283 226 (54)	5-19 12 (7)	15-31 25 (9)	15-42 28 (13)	11-15 13 (2)
Brazil/Cabernet	184-681 412 (189)	117-303 244 (73)	38-56 49 (7)	36-161 93 (50)	2-52 16 (21)	3-13 6 (4)	1-12 5 (4)	9-37 17 (12)	19-44 28 (10)	< 0.5-8 4 (3)
Argentina/Malbec	460-1239 800 (299)	100-158 134 (26)	23-133 107 (73)	111-168 145 (25)	< 0.9-80 34 (41)	71-354 173 (112)	1-10 6 (4)	6-37 23 (12)	20-38 29 (8)	4-28 14 (10)
Uruguay/Malbec	737	525	1290	179	42	21	5.5	17	33	8.5
Brazil/Malbec	308-530 419 (157)	432-481 457 (35)	28-161 95 (94)	79-112 96 (23)	3-5 4 (1)	3-5 4 (1)	1-4 3 (2)	20-43 31 (16)	11-18 15 (4)	1.7-2.0 1.8 (0.3)
Chile/Malbec	544-1181 863 (450)	452-513 483 (43)	73-77 75 (3)	124-179 152 (39)	29-83 56 (38)	5-11 8 (4)	3-23 13 (14)	24-32 28 (6)	3-28 16 (18)	5-16 11 (8)
Brazil/Merlot	232-891 619 (344)	279-675 425 (218)	39 -115 80 (38)	80-180 127 (57)	15-31 21 (9)	5-14 9 (5)	3-9 5 (3)	5-13 10 (4)	19-39 29 (10)	5-10 8 (3)
Argentina/Merlot	561-823 692 (185)	305-341 323 (25)	54-76 65 (15)	131-157 144 (18)	1-50 26 (51)	169-184 177 (11)	3-8 5 (3)	28-31 29 (1)	22-38 30 (11)	7-20 14 (7)
Chile/Merlot	670-1359 933 (372)	42-53 47 (5)	95-346 186 (130)	145-186 161 (22)	40-281 139 (126)	9-14 11 (3)	4-32 14 (16)	14-61 34 (24)	26-28 27 (1)	13 -79 35 (38)
Uruguay/Merlot	231-737 484 (253)	98-115 107 (8)	86-1210 648 (562)	121-144 133 (12)	64-70 68 (2)	21-49 35 (14)	4-6 5 (1)	5 -12 9 (4)	25-59 42 (17)	13 -14 13 (1)
Chile/Carmenere	923	105	290	165	35.1	3.19	5.41	55.1	23.9	10.1
Chile/Shiraz	174	108	123	153	42.5	4.31	4.67	12.4	24.3	11.2
Chile/Pinot Noir	186	121	98	70.2	44.3	3.92	6.84	10.6	14.7	13.9
Uruguay/Tannat	390-890 665 (254)	176-212 191 (19)	20.8-196 101 (88)	116-184 140 (38)	37-99 61 (33)	18-42 32 (10)	4-8 6 (2)	15-57 31 (23)	29-47 40 (8)	10-14 12 (2)
Uruguay/Shiraz*	358	162	182	157	34.8	20.9	4.20	21.2	48.4	13.8
Uruguay/Pinot Noir*	140	159	89	136	82.6	29.4	6.03	23.6	38.1	17.3
Argentina/Assemblage*	618	52.7	30.3	119	11.5	127	1.43	68.4	26.6	10.5
Argentina/Pinot Noir*	155	132	64	168	66.9	90.3	7.47	15.2	12.3	18.5
Argentina/Shiraz*	381	96	132	33	42.8	345	11.5	44.9	18.7	17.3
Brazil/Tannat*	444	293	76	144	62.9	27.3	13.8	37.1	40.9	15.1
Brazil/Pinot Noir*	499	91.1	124	156	76.5	9.85	11.4	50.2	42.0	15.8
Brazil/Bahia/Shiraz*	278	100	134	145	62.8	4.04	21.0	48.1	22.5	17.2
Brazil/Isabel*	767	479	118	118	74.0	3.75	9.53	26.5	11.5	15.6
Brazil/Bordô*	552	122	222	286	7.06	2.23	2.50	28.9	5.42	2.24

Tabela S1. Continued

Wine	Pb	Co	Se	Sn	Sb	Cd	Ag	Tl	Bi	Be
Chile/Cabernet	2-28 13 (11)	2-12 5 (4)	< 0.25-2 0.8 (1)	0.3-0.9 0.5 (0.2)	0.3-4 1.2 (1.6)	< 0.01-1 0.2 (0.5)	< 0.05-1 0.4 (0.5)	0.1-0.3 0.2 (0.1)	1-2 1 (1)	< 0.01-0.5 0.2 (0.2)
Uruguay/Cabernet	9-11 10 (1)	3-7 5 (2)	< 0.25-2 1 (1)	< 0.07	0.2-1.1 0.5 (0.4)	< 0.01-0.3 0.1 (0.2)	< 0.05-0.1 0.03 (0.05)	0.5-1 0.7 (0.3)	0.1-0.3 0.2 (0.1)	< 0.01-0.5 0.2 (0.3)
Argentina/Cabernet	2-30 19 (15)	3-7 5 (2)	< 0.25-2 1 (1)	1.6-2.0 1.8 (0.2)	0.2-1.4 0.8 (0.5)	0.4-0.4 0.4 (0)	< 0.05-0.4 0.2 (0.2)	0.1-0.2 0.1 (0.1)	< 0.02-0.1 0.04 (0.05)	0.1-0.3 0.2 (0.1)
Brazil/Cabernet	4-22 13 (8)	2-5 4 (1)	< 0.25-2 1 (1)	< 0.07-19 10 (9)	0.04-0.6 0.3 (0.2)	< 0.01-0.6 0.2 (0.3)	< 0.05	0.6-4 2 (1)	< 0.02	< 0.01-1 0.8 (0.4)
Argentina/Malbec	2-20 15 (11)	2-4 3 (1)	< 0.25-3 1 (1)	0.3 – 2 1 (1)	0.2-0.8 0.4 (0.3)	0.2-0.6 0.4 (0.2)	< 0.05	0.1-0.2 0.1 (0.1)	< 0.02-0.6 0.3 (0.3)	< 0.01-0.6 0.3 (0.2)
Uruguay/Malbec	82	3.1	< 0.25	19	1.18	0.45	0.07	0.55	< 0.02	0.7
Brazil/Malbec	< 0.06-10 5 (6)	3-4 3.5 (0.5)	< 0.25-2 1 (2)	< 0.07	0.6-0.7 0.6 (0.1)	< 0.01-0.4 0.2 (0.2)	< 0.05-0.2 0.1 (0.1)	1-5 3 (2)	< 0.02	0.5-0.9 0.7 (0.2)
Chile/Malbec	4-9 7 (3)	3-4 3 (1)	< 0.25	< 0.07	0.2-0.4 0.3 (0.1)	< 0.01-0.2 0.1 (0.1)	< 0.05-0.1 0.1 (0.1)	0.4-0.6 0.5 (0.1)	< 0.02-0.1 0.1 (0.1)	0.2-0.7 0.5 (0.2)
Brazil/Merlot	5-25 17 (11)	3-8 5 (3)	< 0.25-6 3 (3)	< 0.07-5 3 (2)	0.3-3 1 (2)	< 0.01 -0.4 0.2 (0.2)	< 0.05	1.0-1.9 1.5 (0.4)	< 0.02	0.6-2.0 1.2 (0.8)
Argentina/Merlot	21-27 24 (3)	3.1-2.9 3 (0.1)	< 0.25-6 3 (4)	3-3 3 (0)	0.330 0.350	0.1 -0.6 0.4 (0.3)	< 0.05	0.1 -0.1 0.1 (0)	< 0.02-0.4 0.2 (0.2)	0.3-0.5 0.4 (0.1)
Chile/Merlot	3-23 14 (9)	2.9-3.0 3 (0.1)	< 0.25-2 0.7 (1)	< 0.07-1 0.7 (0.6)	0.3-0.5 0.4 (0.1)	< 0.01 -6 2 (4)	< 0.05 -1 0.5 (0.5)	0.2-0.2 0.2 (0)	< 0.02-1.4 0.7 (0.7)	< 0.01-0.2 0.1 (0.1)
Uruguay/Merlot	35-80 57 (23)	2-3 2 (1)	< 0.25-1 0.4 (0.5)	< 0.07-24 12 (12)	0.9-1.3 1.1 (0.3)	< 0.01-0.5 0.1 (0.3)	< 0.05	0.6 -0.6 0.6 (0)	< 0.02	< 0.01-0.5 0.2 (0.3)
Chile/Carmenere	7.03	3.12	< 0.25	< 0.07	0.30	0.17	0.29	0.41	0.76	< 0.01
Chile/Shiraz	3.17	3.41	< 0.25	< 0.07	0.23	< 0.01	< 0.05	0.25	0.68	< 0.01
Chile/Pinot Noir	5.97	3.53	< 0.25	< 0.07	0.29	< 0.01	< 0.05	0.29	0.58	< 0.01
Uruguay/Tannat	9-28 19 (10)	3-6 4 (2)	< 0.25-1 0.4 (0.6)	< 0.07	0.3-0.3 0.3 (0)	< 0.01-0.5 0.2 (0.3)	< 0.05	0.4-1.1 0.8 (0.4)	< 0.02-1 0.6 (0.4)	< 0.01-0.2 0.1 (0.1)
Uruguay/Shiraz*	13.2	5.30	< 0.25	< 0.07	0.22	< 0.01	< 0.05	1.27	0.63	< 0.01
Uruguay/Pinot Noir*	7.95	2.72	< 0.25	< 0.07	0.23	< 0.01	< 0.05	0.68	0.57	< 0.01
Argentina/Assemblage*	52.9	3.47	2.05	< 0.07	0.35	0.18	< 0.05	0.14	0.80	0.180
Argentina/Pinot Noir*	9.23	2.62	< 0.25	< 0.07	0.24	0.43	< 0.05	0.17	< 0.02	< 0.01
Argentina/Shiraz*	15.3	2.28	< 0.25	< 0.07	2.48	< 0.01	< 0.05	0.10	< 0.02	< 0.01
Brazil/Tannat*	4.49	5.39	4.92	< 0.07	0.02	< 0.01	< 0.05	2.99	< 0.02	2.667
Brazil/Pinot Noir*	5.39	4.59	< 0.25	< 0.07	1.37	0.47	< 0.05	3.36	0.92	0.900
Brazil/Bahia/Shiraz*	4.43	4.78	1.06	< 0.07	1.05	0.42	< 0.05	1.09	0.27	0.391
Brazil/Isabel*	5.20	7.23	< 0.25	< 0.07	1.44	0.17	< 0.05	1.80	0.23	0.452
Brazil/Bordô*	20.4	5.58	1.83	1.82	0.27	< 0.01	< 0.05	3.46	0.23	0.550

Tabela S1. Continued

Wine	U	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Chile/Cabernet	< 0.02-0.4 0.2 (0.1)	0.2-3 1 (1)	0.5-2.5 1 (1)	< 0.02-0.2 0.1 (0.1)	< 0.02-1 0.3 (0.4)	< 0.02-0.09 0.05 (0.04)	< 0.01-0.1 0.03 (0.04)	< 0.01-0.1 0.08 (0.04)	< 0.002-0.01 0.01 (0.01)
Uruguay/Cabernet	0.2-0.5 0.3 (0.1)	< 0.02-0.5 0.1 (0.2)	0.3-0.7 0.5 (0.2)	< 0.02 -0.1 0.08 (0.02)	< 0.02 0.3 (0.2)	< 0.02-0.1 0.03 (0.06)	< 0.01-0.05 0.02 (0.03)	0.06-0.1 0.07 (0.03)	< 0.002-0.01 0.04 (0.07)
Argentina/Cabernet	0.2-2 1.4 (1.1)	0.4-1 0.7 (0.3)	0.8-1 0.9 (0.1)	0.1-0.3 0.2 (0.1)	0.1-0.5 0.3 (0.2)	0.05-0.09 0.07 (0.02)	< 0.008 0.1 (0.1)	0.07-0.2 0.1 (0.1)	< 0.002
Brazil/Cabernet	< 0.02-0.5 0.1 (0.2)	< 0.02 -1 0.6 (0.5)	0.5-2 1 (0.5)	< 0.02-0.2 0.1 (0.1)	< 0.02 0.1 (0.1)	< 0.02-0.2 0.1 (0.1)	< 0.01-0.06 0.03 (0.03)	0.06-0.2 0.15 (0.05)	< 0.002-0.02 0.01 (0.01)
Argentina/Malbec	0.2-2.2 1.1 (0.7)	0.4-1.6 0.9 (0.5)	0.4-1 0.6 (0.3)	< 0.02-0.1 0.07 (0.02)	< 0.02-0.3 0.1 (0.1)	0.05-0.09 0.07 (0.02)	< 0.01 0.06 (0.02)	< 0.01-0.08 0.06 (0.02)	< 0.002
Uruguay/Malbec	1.2	0.3	0.5	0.06	< 0.02	0.050	< 0.01	0.05	< 0.002
Brazil/Malbec	< 0.02-0.2 0.1 (0.1)	0.4-1.7 1.0 (0.7)	0.4-0.4 0.4 (0)	< 0.02-0.06 0.05 (0.01)	< 0.02	< 0.02-0.04 0.02 (0.02)	< 0.01	< 0.01 -0.04 0.02 (0.02)	< 0.002
Chile/Malbec	0.4-0.6 0.5 (0.1)	0.2-0.6 0.4 (0.2)	0.3-0.9 0.6 (0.3)	< 0.02-0.1 0.1 (0.1)	< 0.02	< 0.02-0.07 0.04 (0.03)	< 0.01	< 0.01-0.07 0.04 (0.03)	< 0.002 0.012
Brazil/Merlot	< 0.02-0.3 0.2 (0.1)	0.5-0.7 0.6 (0.1)	0.9-1.4 1.1 (0.3)	< 0.02-0.2 0.1 (0.1)	< 0.02-0.6 0.3 (0.3)	< 0.02-0.1 0.1 (0.01)	< 0.01	0.06-0.1 0.1 (0.04)	< 0.002-0.02 0.01 (0.01)
Argentina/Merlot	1.0-1.5 1.3 (0.3)	0.3-0.4 0.3 (0.1)	0.5-0.6 0.5 (0.1)	< 0.02	0.2-0.2 0.2 (0)	0.03-0.04 0.03 (0.01)	< 0.01	0.04-0.05 0.04 (0.01)	< 0.002
Chile/Merlot	0.3-1.2 0.6 (0.5)	0.3-2.8 1.2 (1.4)	0.3-3.3 1.4 (1.6)	< 0.02-1.5 0.6 (0.8)	< 0.02-1 0.4 (0.5)	< 0.02 -1 0.4 (0.6)	< 0.01 -0.6 0.2 (0.4)	0.05 -0.2 0.1 (0.1)	< 0.002
Uruguay/Merlot	0.3 -1.1 0.7 (0.6)	0.3-0.3 0.3 (0)	0.4-0.5 0.4 (0.1)	< 0.02-0.07 0.3 (0.4)	< 0.02-0.2 0.1 (0.1)	< 0.02-0.05 0.02 (0.03)	< 0.01	0.06-0.06 0.06 (0)	< 0.002
Chile/Carmenere	0.15	<0.02	0.30	< 0.02	< 0.001	< 0.02	< 0.008	< 0.01	< 0.002
Chile/Shiraz	0.27	0.30	0.32	< 0.02	< 0.02	0.07	0.01	0.06	< 0.002
Chile/Pinot Noir	< 0.02	0.83	0.62	< 0.02	< 0.02	0.07	0.02	0.06	< 0.002
Uruguay/Tannat	0.4-0.8 0.6 (0.2)	0.2-0.4 0.3 (0.1)	0.2-0.8 0.5 (0.3)	< 0.02-0.1 0.05 (0.03)	< 0.02-0.4 0.2 (0.2)	0.07-0.09 0.08 (0.01)	< 0.01	0.06-0.08 0.07 (0.01)	< 0.002
Uruguay/Shiraz*	0.97	0.88	0.35	< 0.02	< 0.02	0.07	0.02	0.06	< 0.002
Uruguay/Pinot Noir*	1.31	0.80	0.67	< 0.02	< 0.02	0.07	0.02	0.06	< 0.002
Argentina/Assemblage*	2.09	0.26	0.33	0.05	0.22	0.07	< 0.01	< 0.01	< 0.002
Argentina/Pinot Noir*	1.04	0.23	0.56	< 0.02	< 0.02	0.17	0.02	0.16	< 0.002
Argentina/Shiraz*	< 0.02	0.63	0.87	0.10	0.37	0.07	0.02	0.06	< 0.002
Brazil/Tannat*	< 0.02	1.61	1.91	0.61	< 0.02	0.07	0.02	0.06	< 0.002
Brazil/Pinot Noir*	0.33	0.80	1.68	0.22	< 0.02	0.17	0.05	0.16	< 0.002
Brazil/Bahia/Shiraz*	0.18	1.47	3.02	0.39	1.44	0.23	0.06	0.19	< 0.002
Brazil/Isabel*	0.18	0.64	0.950	0.11	0.34	0.09	0.05	0.07	0.01
Brazil/Bordô*	< 0.02	0.48	1.15	0.13	0.55	0.16	0.04	0.14	0.02

Tabela S1. Continued

Wine	Dy	Ho	Er	Tm	Yb	Lu
Chile/Cabernet	< 0.01-0.03 0.01 (0.02)	< 0.002	< 0.002-0.06 0.02 (0.04)	< 0.002	< 0.005	< 0.002-0.02 0.01 (0.01)
Uruguay/Cabernet	< 0.01-0.08 0.04 (0.03)	< 0.002	< 0.002-0.02 0.01 (0.01)	< 0.002	< 0.005	< 0.002
Argentina/Cabernet	0.06-0.08 0.07 (0.01)	< 0.002-0.02 0.01 (0.01)	0.04-0.05 0.04 (0.01)	< 0.002	< 0.005-0.04 0.01 (0.03)	< 0.002
Brazil/Cabernet	< 0.01-0.1 0.09 (0.06)	< 0.002-0.05 0.02 (0.02)	< 0.002-0.1 0.07 (0.05)	< 0.002-0.02 0.01 (0.01)	< 0.005-0.1 0.05 (0.06)	< 0.002-0.02 0.01 (0.01)
Argentina/Malbec	0.03-0.08 0.06 (0.02)	< 0.002-0.01 0.01 (0.01)	< 0.002-0.05 0.03 (0.02)	< 0.002-0.01 0.01 (0.01)	< 0.005	< 0.002-0.01 0.01 (0.01)
Uruguay/Malbec	0.05	0.01	0.04	< 0.002	< 0.005	< 0.002
Brazil/Malbec	< 0.01-0.03 0.01 (0.02)	< 0.002	< 0.002-0.03 0.01 (0.02)	< 0.002	< 0.005	< 0.002
Chile/Malbec	< 0.01-0.07 0.04 (0.03)	< 0.002	0.01-0.05 0.03 (0.02)	< 0.002	< 0.005	< 0.002-0.01 0.01 (0.01)
Brazil/Merlot	< 0.01-0.1 0.08 (0.02)	< 0.002-0.03 0.01 (0.02)	< 0.002-0.07 0.05 (0.03)	< 0.002-0.01 0.01 (0.01)	< 0.005-0.08 0.03 (0.04)	< 0.002-0.01 0.01 (0.01)
Argentina/Merlot	0.04-0.04 0.04 (0)	< 0.002-0.01 0.01 (0.01)	0.03 -0.03 0.03 (0)	< 0.002	0.03-0.04 0.03 (0.01)	< 0.002-0.01 0.01 (0.01)
Chile/Merlot	< 0.01-0.2 0.1 (0.1)	< 0.002	< 0.002-0.1 0.05 (0.05)	< 0.002-0.01 0.01 (0.01)	< 0.005	< 0.002-0.02 0.01 (0.01)
Uruguay/Merlot	< 0.01-0.06 0.04 (0.02)	< 0.002-0.01 0.01 (0.01)	0.02-0.04 0.03 (0.01)	< 0.002	< 0.005-0.04 0.02 (0.02)	< 0.002
Chile/Carmenere	0.026	< 0.002	0.02	0.01	< 0.005	< 0.002
Chile/Shiraz	< 0.01	< 0.002	< 0.002	< 0.002	< 0.005	< 0.002
Chile/Pinot Noir	< 0.01	< 0.002	< 0.002	< 0.002	< 0.005	< 0.002
Uruguay/Tannat	< 0.01-0.1 0.04 (0.06)	< 0.002	< 0.002	0.010	< 0.005	< 0.002-0.01 0.01 (0.01)
Uruguay/Shiraz*	< 0.01	< 0.002	< 0.002	< 0.002	< 0.005	< 0.002
Uruguay/Pinot Noir*	< 0.01	< 0.002	< 0.002	< 0.002	< 0.005	< 0.002
Argentina/Assemblage*	0.04	< 0.002	< 0.002	< 0.002	< 0.005	0.01
Argentina/Pinot Noir*	0.13	0.03	0.06	0.01	< 0.005	0.0182
Argentina/Shiraz*	< 0.01	< 0.002	< 0.002	< 0.002	< 0.005	< 0.002
Brazil/Tannat*	< 0.01	< 0.002	< 0.002	< 0.002	< 0.005	< 0.002
Brazil/Pinot Noir*	0.13	0.03	0.06	0.01	< 0.005	0.02
Brazil/Bahia/Shiraz*	0.20	< 0.002	0.12	0.02	< 0.005	0.03
Brazil/Isabel*	0.17	< 0.002	0.04	0.01	< 0.005	0.01
Brazil/Bordô*	< 0.01	0.02	0.09	0.01	< 0.005	0.01