

Analysis of major metallic elements in Chilean wines by atomic absorption spectroscopy

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Abstract

V. F. Laurie, E. Villagra, J. Tapia, J. E. S. Sarkis, and Marcos A. Hortellani. 2010. Analysis of major metallic elements in Chilean wines by atomic absorption spectroscopy. Cien. Inv. Agr. 37(2): 77-85. A set of 75 wine samples from seven of the major wine producing regions in Chile were analyzed with flame atomic absorption spectroscopy (AAS) to determine their content of major metallic elements (K, Mg, Ca, Na, Fe and Zn). The results obtained were further analyzed with principal component analysis (PCA) in an attempt to loosely discriminate these wines according to grape type and geographical origin. The metal concentrations measured were within normal ranges, according to previously published data from other wine producing countries. Multivariate statistics allowed the possibility to reasonably discriminate between red and white wines, and to show a distinctive pattern of Na concentration, with higher total contents for the wines produced in the northern parts of the country.

Key words: Wine, metal, AAS, multivariate analysis.

Introduction

Chile is a wine producing country with a wide variety of geological and climatic regions, with most vineyards falling approximately between the latitudes of 29 and 38° south. Empirical information suggests that certain Chilean sub-regions can produce distinctive wines which attributes have been linked mainly to soil type and weather conditions.

The main variables that determine the composition and concentration of minerals in wines are: (a) the mineral content of the soil and the plant's capacity to uptake and accumulate these elements in the grape berry, (b) viticulture and winemaking treatments with metal-containing products (e.g. copper based fungicides and bentonite respectively), and (c) contamination with external sources such as non-stainless steel winery equipment, irrigation water, and air pollution (Ough and Amerine, 1988; Angelova *et al.*, 1999; Jakubowski *et al.*, 1999; Orescanin *et al.*, 2003; Pyrzynska, 2004; Catarino *et al.*, 2006; Mihucz *et al.*, 2006; La Pera *et al.*, 2008; Serapinas *et al.*, 2008).

The most widely used techniques for the determination of major and trace elements in wine are AAS and inductively coupled plasma mass-spectrometry (ICP-MS) respectively (Ough and Amerine, 1988; Aceto *et al.*, 2002; Thiel *et al.*, 2004; Coetzee *et al.*, 2005). So far, several published studies of mineral identification in wines from different world regions have had the purpose of surveying the content of certain metals and testing the wines provenance, or region of origin, including South Africa (Coetzee *et al.*, 2005), Canada (Taylor *et al.*, 2002; Taylor *et al.*, 2003; Greenough *et al.*, 2005), New Zealand (Angus *et al.*, 2006), and Germany (Gomez *et al.*, 2004), among others, mostly European areas (Muranyi and Kovacs, 2000; Barbaste *et al.*, 2003; Marenngo and Aceto, 2003; Kment *et al.*, 2005; Korenovska and Suhaj, 2005; La Pera *et al.*, 2008).

The normal content of Fe and Zn in the grape berry is quite low, but their concentration can be greatly increased by effect of dust, pesticides residues, and other forms of contamination (Ough and Amerine, 1988). On the contrary, cations such as K, Ca, Na, and Mg have a much higher natural concentrations, especially in the grape skins (Storey, 1987; Iland and Coombe, 1988; Cabanne and Doneche, 2003). A series of published studies have reported concentration ranges for some of the major cations in wine, none of which has included a significant amount of Chilean wine samples (Ough *et al.*, 1982; Ough and Amerine, 1988; Lazos and Alexakis, 2007).

The significance of metallic elements determination in wines has to do mainly with their influence on wine stability and oxidation reactions (Boulton *et al.*, 1996; Ribéreau-Gayon

et al., 2006). Metals have an important role as catalysts in biological systems, they participate of important redox processes, and some are essential for the metabolism of wine yeast and bacteria (Pereira, 1988; Aceto *et al.*, 2002). Alternatively, the content of metallic elements has been evaluated with nutritional and toxicological purposes (Puig-Deu *et al.*, 1994; Boulton *et al.*, 1996; Suhaj and Korenovska, 2005; Ribéreau-Gayon *et al.*, 2006).

Considering that metal ions have a determining role in important wine processes, and given that, to our knowledge, compositional information of this kind for Chilean wines is scarce, is that this research was undertaken.

Materials and methods

Wine samples

Samples of commercial wines were obtained directly from wineries located between the Elqui and Itata Valleys, or purchased from local supermarkets or wine stores. A set of 75 wine samples elaborated from six grape varieties, both reds and whites were used. The white varieties Chardonnay ($n = 9$) and Sauvignon blanc ($n = 18$), and the red varieties Cabernet Sauvignon ($n = 19$), Carménère ($n = 19$), Pinot noir ($n = 5$), and Syrah ($n = 5$) were chosen to represent the following wine producing areas: Elqui, Limarí, Casablanca, Maipo, Colchagua, Maule and Itata regions (located approximately between the 29 and 38° latitude south) (Table 1).

Table 1. Wine samples utilized for the analysis of abundant metallic elements (K, Mg, Ca, Na, Fe and Zn) by Chilean wine area.

Wine area	No of samples	Grape varieties	Years
Elqui	6	Sauv. blanc ^a , Carménère, Syrah	2005 - 2008
Limari	5	Chardonnay, Sauv. blanc ^a , Carménère, Syrah	2006 - 2007
Casablanca	12	Chardonnay, Sauv. blanc ^a , Pinot noir	2006 - 2008
Maipo	12	Chardonnay, Sauv. blanc ^a , Cab. Sauv. ^b	2006 - 2007
Colchagua	14	Cab. Sauv. ^b , Carménère	2005 - 2007
Maule	21	Chardonnay, Sauv. blanc ^a , Cab. Sauv. ^b , Carménère, Syrah	2006 - 2008
Itata	5	Cab. Sauv. ^b , Carménère, Pinot noir, Syrah	2003 - 2006

Where: ^a: Sauvignon blanc and ^b: Cabernet Sauvignon.

Reagents and solutions

All solutions were prepared using ultra pure, type I water obtained from a Millipore system (Bedford, MA, USA), and supra pure quality chemicals (Merck, Darmstadt, Germany). The standard solutions developed for the calibration curves of each of the ions analyzed were prepared daily by rigorous dilution of 1000 mg L⁻¹ certified chemicals standard solutions (Spex Industries Inc., Edison, NJ, USA). All intermediate solutions were stored in polyethylene bottles. Glassware was cleaned by soaking in 10% v/v HNO₃ for 24 hours and rinsing at least three times with ultra pure water. Then, the material was dried and stored in a class 100 laminar flow hood.

Wine sample preparation

Before the measuring procedure is applied, samples have to be carefully prepared in order to avoid chemical and physical interferences (Lima and Rangel, 1990). In this case, samples were taken from freshly opened bottles of wine and prepared according to the following procedure of organic matter digestion: 2 mL of wine were precisely weighted and evaporated in an ultrasonic bath at 70 °C, followed by the addition of 0.5 mL of 30% H₂O₂, with 4 hours resting time. After that, 1 mL of 21% v/v HNO₃ was added and evaporated for 1 hour in an ultrasonic bath at 70 °C (performed under a hood). Lastly, the sample's volume was adjusted to 10 mL with type I ultra pure water, at room temperature (20 °C) and accurately weighted for further calculations.

In order to ensure that the sample concentrations were within the linear ranges for each calibration curve, the following dilutions, by weight, with ultra pure water were applied: 1:1 for Na, 1:20 for Ca and Mg, 1:400 for K, whilst Fe and Zn were analyzed directly, without further dilution. Digested samples were stored in 15 mL polyethylene centrifuge tubes prior to analysis.

Spectral analysis

AAS analyses of K, Mg, Ca, Na, Fe y Zn were performed on a flame atomic absorption spectrometer Varian Spectra AA 220 FS (Lake Forest, CA, USA) equipped with deuterium background corrector, according to the conditions detailed in Table 2. Highly concentrated elements (K, Mg, Ca, and Na) were measured using a hollow cathode lamp. The combination of air-acetylene flame was used for K, Na, Fe and Zn, whilst Mg and Ca were measured using a nitrous oxide-acetylene flame. Factors with the potential to cause interferences were eliminated, and the final method was found to be highly precise. Precision values for K, Mg, Na, Fe and Zn were below 1%, whilst Ca variability was equal to 5.56%. Even though AAS does not have a good sensitivity for other cations, it is well suited for determining the ions selected here (Aceto *et al.*, 2002).

Data analysis

Descriptive statistics (mean, standard deviation, range, and median) and principal compo-

Table 2. Analytical conditions used for the analysis of abundant metallic elements in Chilean wines by flame atomic absorption spectrometry.

Instrument conditions	Element					
	K	Mg	Ca	Na	Fe	Zn
Mode	Emission	Emission	Emission	Emission	Absorbance	Absorbance
Wavelength (nm)	766.5	285.2	422.7	589.0	248.3	213.9
Slit width (nm)	0.2	0.2	0.2	0.2	0.2	1.0
Calibration interval (µg g ⁻¹)	0.2 - 2.0	0.2 - 2.0	0.5 - 5.0	0.2 - 2.0	0.1 - 2.0	0.2 - 2.0

ment analysis (PCA) were performed using the commercial software package, Statgraphics centurion XV, version 15.01.03 (Statpoint technologies, Warrenton, VA, USA). PCA was used as a method of data reduction to allow the construction of new uncorrelated variables known as principal components (PC) (Kaufmann, 1997). Graphical representations of results were performed using the software package Sigma-Plot version 11 (Systat software Inc., Chicago, IL, USA) and Statgraphics centurion XV for the PCA analysis.

Results

AAS analysis

The average content of the most abundant metallic elements in a set of 75 Chilean wines samples (48 reds and 27 whites), including central tendency measures, are summarized in Table 3. As expected, K was the cation with the highest average concentration (832.9 mg L⁻¹ for all wines, 1110.9 mg L⁻¹ for reds, and 344.6 mg L⁻¹ for whites samples) (Iland and Coombe, 1988), whilst Zn was the least concentrated (0.7 mg L⁻¹ for all wines, 0.72 mg L⁻¹ for reds, and 0.67 mg

L⁻¹ for white samples). The results of Table 3 indicate also that red wines have higher absolute concentrations for most cations analyzed, with the exception of Na.

The content of metals across wine varieties

When a comparison of the concentration of metals was performed grouping the wines by grape varieties, a large concentration variation for most of the ion analyzed was observed (Figure 1). Overlapping concentration ranges were seen for most of the elements analyzed, except for K, where white varieties (Sauvignon blanc and Chardonnay) showed a significantly lower content than most red varieties (Cabernet Sauvignon, Carménère, and Syrah).

The content of metals across wine areas

The concentration ranges of most elements overlapped when a comparison of mean values across valleys was performed (Figure 2). Conversely, Na was the only element exhibiting a distinctive concentration pattern across wine regions (Figure 2). The higher average concen-

Table 3. Summary of the concentration of abundant metallic elements (K, Mg, Ca, Na, Fe and Zn) in Chilean wine samples.

	Ion concentration (mg L ⁻¹)					
	K	Mg	Ca	Na	Fe	Zn
All wines (n = 75)						
Mean	832.9	121.5	84.9	22.6	3.13	0.7
SD	414.5	26.1	19.4	11.3	1.15	0.28
Range	115.29 - 1732.94	68.17 - 196.02	51.54 - 160.89	5.90 - 68.1	0.036 - 8.12	0.21 - 1.63
Median	967.3	125.7	84.4	20.8	1.43	0.69
Red wines (n = 48)						
Mean	1110.9	135.8	90.3	18.2	3.98	0.72
SD	206.3	18.2	20.6	6.9	2.3	0.3
Range	650.65 - 1732.94	94.27 - 196.02	53.06 - 160.89	5.9 - 34.95	0.98 - 8.12	0.21 - 1.63
Median	1095.9	133.4	89.5	18.7	3.46	0.71
White wines (n = 27)						
Mean	344.6	96.4	75.2	30.3	1.64	0.67
SD	154.3	17.4	12.2	13.3	1.36	0.26
Range	115.29 - 612.16	68.17 - 131.01	51.54 - 108.81	10.49 - 68.1	0.036 - 6.76	0.28 - 1.49
Median	307.4	94	76.8	27.6	1.27	0.62

Were SD: Standard deviation.

trations of Na, for both reds and white wines, were encountered in the wines produced in the northern regions (Elqui and Limari) and the lower average contents in the wines produced in the southern areas analyzed (Maule and Itata).

Principal component analysis

Even though several combinations of the elements under study were tested, poor discrimination possibilities were found when wine

varieties or region of origin were compared. PCA only showed a reasonable degree of discrimination when white and red wines were compared, influenced mainly by the Na concentration of wine samples. A graphical representation of the prior is given in Figure 3. From this plot, it is clear that red and white wines can be separated in two clusters. The analysis showed that the distribution of the variability was mainly explained by two principal components (which eigenvalues were greater than or equal to 1) that accounted for approximately 62.7% of the variability in the original data.

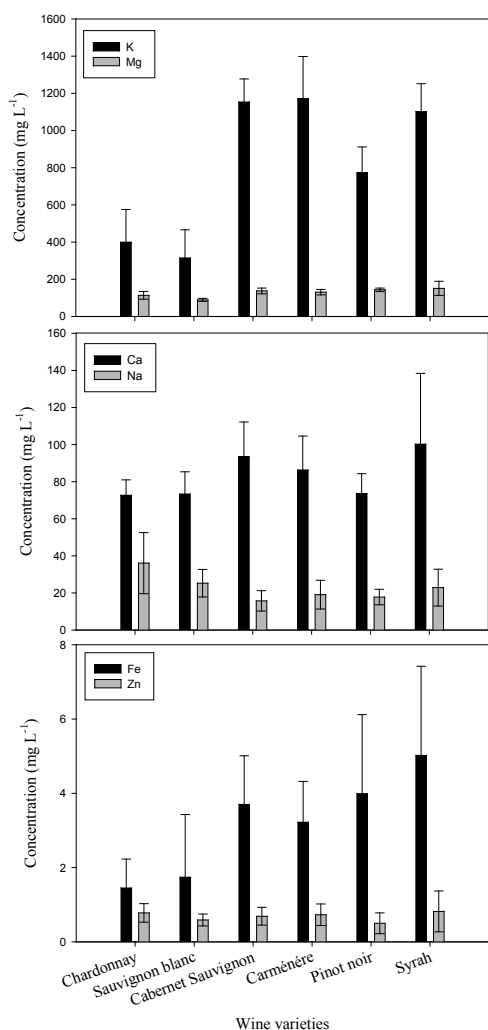


Figure 1. Concentration of major metallic elements across wine varieties in 75 Chilean wines samples (error bars represent the standard deviation of the mean).

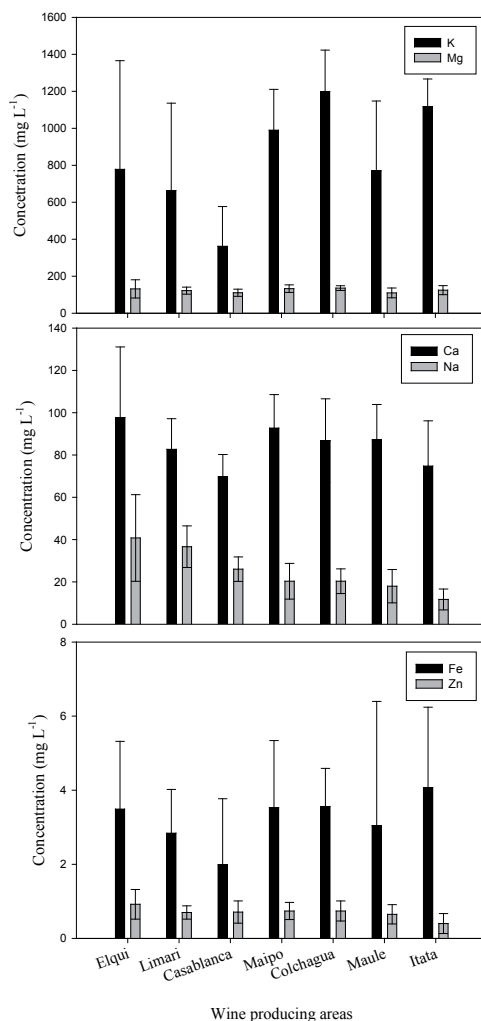


Figure 2. Concentration of major metallic elements across wine producing areas in 75 Chilean wines samples (error bars represent the standard deviation of the mean).

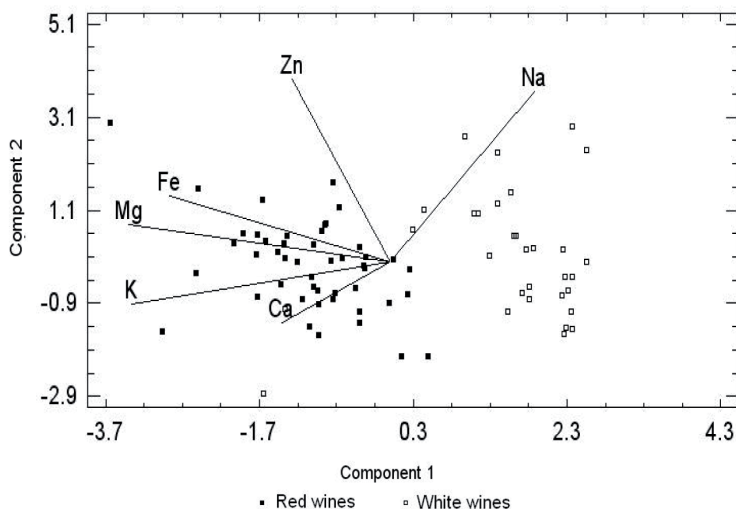


Figure 3. Score plot of the first two principal components of the atomic absorption spectroscopy analysis of major metallic elements in 75 Chilean wine samples.

Discussion

AAS analysis

The concentrations measured for all cations were within normal ranges according to previously published data for wines from other world regions. Some of the concentration ranges reported in these studies are: K, 0.28 – 2.04 g L⁻¹; Mg, 0.021 – 0.245 g L⁻¹; Ca, 0.006 – 0.31 g L⁻¹; Na, 0.003 – 0.32 g L⁻¹; Fe, trace – 35 g L⁻¹; and Zn, trace – 0.0117 g L⁻¹ (Ough *et al.*, 1982; Ough and Amerine, 1988; Lazos and Alexakis, 2007).

As opposed to white wines, red winemaking includes grape skins and seeds as part of the fermenting material. The fact that some metals, particularly K and Ca are highly concentrated in the grape skins (Storey, 1987; Iland and Coombe, 1988) could help explaining the observation that red wines have higher absolute average concentrations for most of the ions analyzed. In other words, white and red wines which grapes have originated in the same place can differ in their element composition due to variable skin contact time and element leach out during the winemaking process. This type of trend variation has been observed in the past for other wine elements (Serapinas *et al.*, 2008).

The content of metals across wine varieties

The results of this study are consistent with previous observations indicating that red wines may have higher concentration of metals than white wines (Coetzee *et al.*, 2005). These results are also a clear indication of the need to consider the effect of wine variety when presenting cation compositional information.

Moreover, it is worth noticing that 10 of the samples analyzed (8 reds and 2 whites) presented Fe concentrations above 5 mg L⁻¹, the borderline content of iron over which there might be a risk of Fe casse (Zoecklein *et al.*, 1999). Contamination during wine storage has also been cited as a possible cause of high contents of Fe and Zn (Orescanin *et al.*, 2003).

The content of metals across wine areas

Chile's geological and climatic diversity seems to be determining in the concentration of major wine elements. Results indicating that the content of Na is higher in wines from Elqui and Limarí valleys are consistent with reports showing that the soils from the northern parts of the country have a considerable concentra-

tion of this element (Sierra, 2000; Sierra *et al.*, 2001; Sierra *et al.*, 2007). The high content of Na in soils from desertic and semidesertic areas, such as the northern parts of Chile, has been explained as a result of cation accumulation due to the lack of rainfall (White, 2003). The content of Na observed in wines produced in the Elqui and Limarí areas could help support the empirical observation that the Chilean wines produced in these valleys have a distinctive feel, normally described as ‘minerality’; a term that is vaguely defined, non-objective, and not well understood.

In addition, the reasons for the large variation observed in some of the valleys studied are multiple. For instance, large regions such as Maule valley have several soil types and even weather variations that could be broadening the observed variability (Serapinas *et al.*, 2008).

Principal component analysis

If multivariate analyses are performed with the intention of determining wine provenance in a higher number of geographical regions (e.g. within a country), the potential for finding unequivocal discrimination are more complicated, and require to consider an investigation of the content of other elements, at trace concentrations, and the influences of production and storage practices (Jakubowski *et al.*, 1999; Almeida *et al.*, 2002; Almeida and Vasconcelos, 2003; Perez-Magarino *et al.*, 2004). Moreover, an increase in the number of samples

analyzed could be useful to improve the quality of the discrimination.

Like in this report, other studies have also been able to discriminate between red and white wines using PCA (Coetzee *et al.*, 2005).

Conclusions

For the first time, the content of six of the most abundant metallic elements of a large number of Chilean wines samples was accurately measured. All metal concentrations were within normal ranges as compared to previously reported data from other world wine areas. The concentration of Na was higher in the wines produced in the northern parts of the country, a situation that could help to explain part of the organoleptic peculiarities of these wines, normally referred to as ‘minerality’. Analysis of the content of minor elements and further studies aimed to elucidate the relationship between cation concentration, wine oxidation reactions, and wine sensory perception should be performed.

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Resumen

V.F. Laurie, E. Villagra, J. Tapia, J. E. S. Sarkis y Marcos A. Hortellani. 2010. Análisis de metales mayoritarios en vinos chilenos por espectrometría de absorción atómica. Cien. Inv. Agr. 37(2): 77-85. Setenta y cinco muestras de vinos provenientes de siete de las principales zonas vitivinícolas de Chile fueron analizadas por espectrometría de absorción atómica de llama (AAS) para determinar su contenido de elementos mayoritarios (K, Mg, Ca, Na, Fe y Zn). Los resultados obtenidos fueron analizados mediante la metodología de análisis de componentes principales (PCA) en un intento por discriminar los vinos de acuerdo a su variedad u origen geográfico. Las determinaciones de concentración de metales encontradas resultaron dentro de los rangos normales previamente descritos para vinos producidos en otras regiones del mundo. La técnica de estadística multivariada utilizada permitió discriminar

adecuadamente entre vinos blancos y tintos, y evidenció un importante patrón de distribución de Na, con mayores concertaciones de dicho elemento para los vinos producidos en la zona norte de Chile.

Palabras clave: Vino, metal, espectroscopía de absorción atómica, análisis multivariados.

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