

Trace element determination of Argentine wines using ETAAS and USN-ICP-OES

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Abstract

The objective of this work was to develop a method to determine the metal content in wine samples from the province of Mendoza in Argentina. Ten samples of white wine and 10 samples of red wine available in the supermarket were analyzed for the metals aluminium, cadmium, calcium, chromium, copper, iron, nickel, lead and zinc by electrothermal atomic spectrometry (ETAAS) and ultrasonic nebulization was coupled to inductively coupled plasma optical emission spectrometry (USN-ICP-OES).

The aluminium, cadmium, calcium, copper, iron, lead, zinc, chromium concentrations were between 17.0–18.0 $\mu\text{g l}^{-1}$, 1.0–4.7 $\mu\text{g l}^{-1}$, 10.0–15.0 mg l^{-1} , 23.0–28.0 $\mu\text{g l}^{-1}$, 480–790 $\mu\text{g l}^{-1}$, 50–90 $\mu\text{g l}^{-1}$, 24–130 $\mu\text{g l}^{-1}$, and <0.2–6.25 $\mu\text{g l}^{-1}$, respectively. The levels compare well with those reported for similar wines from some other parts of the world. A significant aspect in this paper is the samples mineralization step, which allowed the direct determination of the metals. Concerning to the Cd determination, a refluxing digestion system was used for the pretreatment of the samples.

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1. Introduction

Wine is a widely consumed beverage with thousands of years of tradition. Wine composition strongly determines its quality besides having a great relevance on wine characterization, typification and frauds detection. The composition of wine is influenced by many factors related to the specific production area: grape varieties, soil and climate, and viticultural practices (Baluja-San-

tos and Gonzalez-Portal, 1992; Augagneur et al., 1996; Frank and Kowalski, 1984; Pérez-Jordán et al., 1998).

Numerous studies (Doll et al., 1994; Gronbaek et al., 1995; Klatsky et al., 1992) have shown that a moderate consumption of wine, especially red, improves good health and longevity when it is combined with a balanced diet.

Daily consumption of wine in moderate quantities contributes significantly to the requirements of the human organism for essential elements such as K, Ca, Mg, Cr, Co, Fe, F, I, Cu, Mn, Mo, Ni, Se, Zn (Eschauer and Neeb, 1988). On the other hand, several metals, such as Pb, Cd and As, are known to be potentially toxic. At the same time, the analysis for certain elements in wines is of special interest due to their toxicity in case of excessive intake, and also the effect they seem to have on the organoleptic properties of wine.

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Modern societies appear to consume large amounts of wine, beer and other alcoholic products (Mena et al., 1996; Galani-Nikolakaki et al., 2002), sometimes increasing the daily intake of heavy metals above the maximum permissible levels. When wine or wine products are consumed in large quantities the toxic effects of their pollutants may have an additive effect to induction of alcoholism. A typical example is the presence of lead in wines (Roses et al., 1997; Lopes et al., 1997).

The content of some metals in wine has been determined by several techniques, among them, flame atomic absorption spectrometry (FAAS) (Ortega et al., 1999; Onianwa et al., 1999), electrothermal atomic absorption spectrometry (ETAAS) (Karadjova et al., 2002; Freschi et al., 2001), inductively coupled plasma mass spectrometry (ICP-MS) (Dean et al., 1990; Rodushkin et al., 1999; Marengo and Aceto, 2003), inductively coupled plasma optical emission spectrometry (ICP-OES) (Wuilloud et al., 2001a,b; Aceto et al., 2002).

ETAAS and ICP-OES are effective techniques for trace element analysis. On the other hand, the use of an ultrasonic nebulizer can provide a 5–50 fold improvement in detection limits of ICP-OES (Wuilloud et al., 2001a,b, 2000). The direct determination of Cd by ETAAS is a relative rapid method for monitoring the amount of this toxic metal in wine. In this work, the addition of chemical modifier is not required. Cadmium was determined by ETAAS due to the insufficient detection capacity of USN-ICP-OES. Other elements presented in the wine samples such as Zn, Fe, Ni, Cr, Al, Ca, Cu, Pb, were determined using ultrasonic nebulization (USN) coupled to ICP-OES.

The present work is aimed at establishing the metal content in wines from the province of Mendoza (Argentina) due to which we have not found from the literature information about the metal content of Argentine wines. The proposed methodology was validated by recovery studies on doped artificial samples.

2. Experimental

2.1. Reagents

Standard solution for each metal was prepared by appropriate dilutions of a 1000 mg l⁻¹ stock solution (Merck, Darmstadt, Germany) immediately before use.

Ultrapure water (18 M Ω cm) was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA).

All solvents and reagents were of analytical-reagent grade or better.

2.2. Instrumentation

The measurements for cadmium determination were performed with a Shimadzu Model AA-6800 atomic

absorption spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, a 6500-electrothermal atomizer and an ASC-6100 autosampler. Wall atomization with standard high-density graphite tubes (Shimadzu, Tokyo, Japan) was used. Cadmium hollow-cathode lamp (Hamamatsu Photonics K.K., Japan) was employed as radiation source. The instrument settings and furnace program for Cd are detailed in Table 1.

The measurements for aluminum, calcium, chromium, copper, iron, lead, nickel and zinc were performed with a sequential inductively coupled plasma spectrometer [BAIRD (Bedford, MA, USA) ICP 2070]. The 1m-Czerny Turner monochromator had a holographic grating with 1800 grooves mm⁻¹. An ultrasonic nebulizer, U 5000 AT [CETAC Technologies (Omaha, NE, USA)], with desolvation system was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table 2.

2.3. Sample

We analyzed commercial samples of red and white wines (10 samples for each one). All samples were obtained from products that are widely consumed in Argentina.

2.4. Sample pretreatment

To 5 ml of wine sample, 1 ml of concentrated perchloric acid and 2 ml of concentrated nitric acid were added and the sample was digested by heating the mixture until dryness. The residues were dissolved in 0.2 ml of nitric acid concentrated; the solution was diluted with water to 10 ml.

Table 1
Main instrument parameters and furnace temperature program for Cd determination

Parameters				
Wavelength, nm				228.8
Spectral bandpass, nm				1.0
Lamp current, mA				8.0
Background correction				Deuterium lamp
Furnace program				
Stage	Temperature (°C)	Time (s)		Argon gas flow (l min ⁻¹)
		Ramp	Hold	
Drying	150	20.0	–	0.10
	250	10.0	–	0.10
Pyrolysis	500	10.0	–	1.0
	500	–	10.0	1.0
	500	–	3.0	0.0
Atomization	2200	–	2.0	0.0 (read)
Cleaning	2400	–	2.0	1.0

Table 2
ICP and ultrasonic nebulizer instrumental parameters

ICP conditions	
RF generator power	1.0kW
Frequency of RF generator	40.68 MHz
Outer gas flow rate	8.51min ⁻¹
Auxiliary gas flow rate	1.01min ⁻¹
Observation Height	15.0mm
Al wavelength	308.114nm
Ca wavelength	422.593nm
Cr wavelength	267.653nm
Cu wavelength	324.653nm
Fe wavelength	238.204nm
Ni wavelength	232.0nm
Pb wavelength	220.373nm
Zn wavelength	213.8nm
Ultrasonic nebulizer conditions	
Heater temperature	140°C
Condenser temperature	4°C
Carrier gas flow rate	1.01min ⁻¹

The sample pretreatment takes approximately 40 min. However, it must be taken into account that it is possible to simultaneously treat as many samples as can be placed in the water bath. In comparison, our method is faster than the procedures reported by other authors (Galani-Nikolakaki et al., 2002; Onianwa et al., 1999).

Concerning cadmium, the first step of the sample pretreatment was carried out using a refluxing digestion system. A clear solution was obtained. Then, the samples were dried in the conventional way. Following that procedure, losses of cadmium, which can reach 20% in a system of digestion without reflux, were avoided.

3. Results and discussion

There are various sources contributing to the metal composition of the finished wine (Scollary, 1997). The sample pretreatment procedure must take into account the analyte of interest, the matrix characteristics and the time requirements of the analytical technique considered.

In this work, all the elements were analyzed by USN coupled to ICP-OES. Except cadmium, it was determined by ETAAS due to the insufficient detection capacity of USN-ICP-OES. The results of the analyses are summarized in Table 3.

3.1. Aluminium

During recent years, interest concerning aluminium has considerably increased due to the knowledge about potential toxic effects of this element. Aluminium is widespread throughout nature, air, water, plants, and consequently in all the food chain (López et al., 2000). The concentration of aluminium in wines may be elevated due to the use of bentonite for filtration and,

Table 3
Concentration of metals measured in white and red wines by ETAAS and USN-ICP-OES

Metal	DL (µg l ⁻¹)	Range (µg l ⁻¹)	White wine (n = 10) Mean (µg l ⁻¹)	Red wine (n = 10) Mean (µg l ⁻¹)
Al	0.3	17.0–18.0	17.2	17.5
Cd	0.008	1.0–4.7	1.2	3.6
Ca	0.02	10000–15000	11000	14100
Cr	0.2	ND–7.0	ND	6.25
Cu	0.04	23–28	26.5	27.0
Fe	0.2	480–790	650	600
Ni	5.0	ND	ND	ND
Pb	0.28	50–90	60.0	85.0
Zn	0.1	24–130	95.0	110.0

ND = not detected; DL = detection limit.

a lesser extent, from contact with aluminium surfaces (Scollary, 1997). In this study, aluminium concentrations were between 17.0 and 18.0 µg l⁻¹.

3.2. Cadmium

The Cd levels in wines can be of anthropogenic origin due to residues of agrochemical products used as insecticides and fungicides, which contain cadmium; it can also be due to other reasons, environmental contamination in those places where industrial complexes exist close to vineyards. In addition, a significant amount of Cd, which is present in wine, is due to contact with the apparatus used in wine production and packaging process, and to enological products used in wine-making. Generally, the cadmium content in wine has been found to be quite low; however, when the consumption of large quantities of wine causes the dietary intake of Cd to reach the maximum allowable levels, it may be physiologically significant. The presence of cadmium has been detected in all the samples we analyzed. The values of cadmium content determined in white and red wines were in the range 1.0–4.7 µg l⁻¹. These results are in good agreement with those reported by Mena et al. for Spain wines (1996) and by Lara et al. for Argentine wines (2001).

3.3. Calcium

Calcium is a natural component of grape, although the concentration of calcium in wine can be affected by the traditional practices of de-acidification (CaCO₃ addition) or plastering (CaSO₄ addition) (Scollary, 1997). The values obtained ranged from 10.0 to 15.0 mg l⁻¹.

3.4. Chromium

The chromium content of wines may increase during the ageing process through long contact with stainless steel or glass utensils and bottles (Eschnauer, 1982). In

this work, the chromium concentration in white wines was $<0.2 \mu\text{g l}^{-1}$, while the chromium content in red wines was $6.25 \mu\text{g l}^{-1}$.

3.5. Copper

Copper may be carried over into wine from the use of copper-based vineyard sprays, although the concentration in freshly fermented wine is generally low owing to the ability of dead yeast cells to take up copper (Scolary, 1997). The levels of Cu found in the studied wines are ranged between 23.0 and $28.0 \mu\text{g l}^{-1}$. The results obtained are in good agreement with those reported by Sauvage et al. for wines from vineyards outside the metropolitan region of Melbourne, Australia (2002).

3.6. Iron

Iron is found in substantial quantities in all grape and wine varieties. The iron concentration of grapes and wines depends upon several factors, the most important being the ground where the grapes are produced. Evaluation of Fe content in wines is of major importance either due to the changes in stability it may cause and to its effects on the oxidation and wine aging. In the present study, iron concentrations from 480 to $790 \mu\text{g l}^{-1}$ were detected. The results obtained are in good agreement with those reported by Sauvage et al. for wines from Australia (2002).

3.7. Nickel

The nickel concentrations of the wines were independent of the type of the wine container and they did not change as a function of the wine storage time inside the container. The samples analyzed had concentrations below the method detection limit ($5 \mu\text{g l}^{-1}$).

3.8. Lead

All analyzed wine samples contained lead to levels lower than the upper established by the Office International de la Vigne et du Vin (OIV), which is at present $200 \mu\text{g l}^{-1}$ (Lemos et al., 2002). In the present study, lead concentrations from 50 to $90 \mu\text{g l}^{-1}$ were detected. The results obtained are in good agreement with those reported by Roses et al. for wines from Argentina (1997).

3.9. Zinc

The plants absorb zinc from the ground in small quantities (Carvalho et al., 1996). The zinc content in wines increases when zinc containers are used during the processing and ageing stages and also when zinc-containing pesticides are used. The amounts of zinc found in this study were in the range of $24\text{--}130 \mu\text{g l}^{-1}$.

Table 4

The analysis results for 5, 50, $40 \mu\text{g l}^{-1}$ concentration of cadmium, lead, and copper, respectively

Element	Sample	Quantity Added ($\mu\text{g l}^{-1}$)	Quantity Found ($\mu\text{g l}^{-1}$)	Technique
Cd	1	5	4.8	ETAAS
	2	5	4.8	ETAAS
	3	5	4.9	ETAAS
Pb	1	50	47	ICP-OES
	2	50	51	ICP-OES
	3	50	49	ICP-OES
Cu	1	40	39	ICP-OES
	2	40	41	ICP-OES
	3	40	38	ICP-OES

These concentrations were added to in doped artificial samples (matrix: water with 12% (v/v) ethanol).

3.10. Validation study

In order to demonstrate the validity of this method and digestion recovery, we have used the procedure proposed by Galani-Nikolakaki et al. (2002). Three quality control samples were prepared. We added absolute ethanol to ultrapure water in order to achieve a final alcohol concentration similar to that of a typical wine sample (12% v/v). Cadmium, lead, and copper were added to 5, 50, $40 \mu\text{g l}^{-1}$ concentration, respectively. These samples were mineralized under the same conditions used for wines. The samples were analyzed by ETAAS and USN-ICP-OES. The obtained results are presented in Table 4.

4. Conclusions

The present investigation indicates that ETAAS and ICP-OES with ultrasonic nebulization techniques are suitable for determination of aluminium, cadmium, calcium, chromium, copper, iron, nickel, lead and zinc in red and white wines from province of Mendoza in Argentina. The analytical values obtained for the analyzed metals were in good agreement with those reported by others researchers.

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