Monitoring of Cd, Cr, Cu, Fe, Mn, Pb and Zn in Fine Uruguayan Wines by Atomic Absorption Spectroscopy

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INTRODUCTION

Wine quality is affected by several factors. Historically, the expertise of the sage winemaster was used to gauge the quality of the product. Nowadays, many environmental concerns, health factors, and governmental rules prompt the producers of fine wines to monitor several important components in the grape must, the fermentation vats, and in the final wine.

One of them is the content of metallic ions. The knowledge of metal content in wine is used to identify the geographic region in which the grapes were grown and the type of pesticide applied as well. It also enables to assure some of the organoleptic characteristics of wine and to carry on close control of the toxic metals content in the final product (1–14).

As a way to control the metal ions in wine, some countries have imposed rules restricting metal content in wines. These rules must be followed by the producers to gain the right to export to the markets. For instance, the Office International de la Vigne et du Vin (OIV) has legislated the concentrations to 0.2 mg/L As, 0.01 mg/L Cd, 1 mg/L Cu, 0.2 mg/L Pb, 60 mg/L Na, and 5 mg/L Zn (15).

It is well-known that several elements in the finished wine influence both its stability and its color and clarity. During the wine-making process, iron may form insoluble precipitates or colloidal forms which flocculate and result in undesirable turbidity (16–17).

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ABSTRACT

Metals in wine occur at the mg/L level or even less and, though not directly related to the taste of the final product, their content should be determined because excess is undesirable and in some cases restricted by legislation to guarantee consumer health protection.

Seven elements were determined in 14 white and 33 red wines from nine Uruguayan wineries.

Several techniques have been approved for the determination of metallic ions in wine, but the most sensitive and rapid is atomic absorption spectroscopy.

In the present work, flame atomic absorption spectrometry (FAAS) was employed for the determination of Cu, Fe, Mn, and Zn, and graphite furnace-atomic absorption spectrometry (GF-AAS) was used for Cd, Cr, and Pb determination.

The following concentration (mg/L) ranges were obtained for Cd (0.002-0.003), Cr (0.004-0.052), Pb (0.006-0.057), Cu (0.034-0.65), Fe (0.73-4.6), Mn (0.74-2.2), and Zn (0.49–2.2). Mean recoveries of elements from fortified wines were: 98.3±2.6% for Cd, 101.5±1.7% for Cr, 99.1±2.7% for Pb, 96.9±1.4% for Cu, 97.3±3.1% for Fe, 98.1±1.9% for Mn and 95.7±3.8% for Zn. The detection limits (mg/L) were: 0.0005 for Cd, 0.001 for Cr, 0.003 for Pb, 0.006 for Cu, 0.020 for Fe, 0.008 for Mn and 0.007 for Zn.

The concentrations of all the metal ions analyzed in wines fall within the range typical of wines from around the world and none of them is above the limits established by the Office International de la Vigne et du Vin (OIV).

The origin of copper in wine can be attribued to exogenous origins or to the very nature of the grapes themselves. High concentrations of this metal can be attributed to the application of copper-based compounds (copper sulphate, dicopper chloride trihydroxide) to the grapevine as a plant fungicide. Copper is also responsible for turbidity and unfavorable flavor changes (17–18). Zinc is responsible for undesirable flavors in wine and its presence in the final product could be due to leaching from the equipment and containers or be the result of anti-fungi treatments of the grapes (17,19). Manganese affects the fermentation process and is characteristic of the production region (14,17).

Determination of the concentration of metallic elements in wine is also useful to calculate the daily intake of such elements. Several studies reveal that wine is an important source of iron (17).

On the other hand, some metal elements are to be investigated because of their toxicity and potential health effects.

Chromium is an essential element for the carbohydrate, cholesterol, and protein metabolism, while Cr toxicity depends on the metal's chemical form. Cr(VI) compounds show a toxic, mutagenic, and even carcinogenic character. Cr(III), which is the most frequently found form in foods and beverages, has low toxicity. Although humans can absorb Cr compounds by inhalation or dermal contact, Cr intake through diet is the most important route of entry into humans (20–23).



Cadmium is considered as toxic as lead and mercury, and its determination has gained attention as a result of its effect on health. High level Cd contamination in wine might be caused by the application of pesticides and fertilizers (24).

Health concerns regarding lead content in wines have been raised during the last decades. High levels of this metal in wine have been explained to be due to sources such as soil, lead-based insecticides (although now prohibited in most locations, it has been used as a caterpillar insecticide), and lead paint. The use of brass components such as pumps, valves, faucets, and piping also are large contributors to Pb contamination found in wine.There is some controversy concerning the uptake of Pb by vines grown in vineyards close to major highways (24–30).

Not surprisingly, the average concentration of some toxic elements, especially Pb, in wine has been decreasing worldwide due to improved wine-making techniques and equipment, and a decreased use of pesticides. But, interestingly, metals associated with stainless steel (Ni, Cr) have been rising (31–32).

Methods described for the determination of metal elements in wine include atomic absorption spectrometry (AAS) (33–36), inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry (37), potentiometric stripping analysis, and differential pulse anodic stripping voltammetry (38).

Among these methods, the most commonly used is AAS because of its versatility, precision, and accuracy. The recommended technique for the determination of Cu, Fe, Mn and Zn in wine is flame AAS. Trace element determination is performed with a more sensitive technique such as graphite furnace atomic absorption spectrometry (GFAAS). This methodology is employed by the OIV for the quantification of lead and cadmium, and is also suggested in the literature for chromium determination (15).

EXPERIMENTAL

Instrumentation

A PerkinElmer Model 5000 atomic absorption spectrometer: (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA), equipped with a deuterium arc background corrector.

For ETA-AAS determinations, the same spectrometer was used equipped with a PerkinElmer HGA®-500 graphite furnace and pyrolytically coated graphite tubes. Argon gas was used to protect and purge the graphite tubes.

The instrumental settings, furnace programs, and working conditions are listed in Tables I and II. Water purification was performed using a Milli-Q[™] Plus purifier system (Millipore Corp., Bedford, MA, USA).

Reagents and Solutions

All reagents were of analytical grade or better.

Standard stock solutions of elements were of 1000 μ g/mL Cd, Cr, Cu, Fe, Mn, Pb, and Zn (J.T. Baker, Inc., USA), certified by the manufacturer to ±1% (w/v) traceable to NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA).

Nitric acid, 65% (E. Merck). Nitric acid 1% was used for wine dilution.

All solutions were prepared with deionized water with specific resistivity of $18M\Omega$.cm.

A 10% (w/v) Triton® X-100 (Merck) solution was made by diluting 1 g of Tritron X-100 to 10 mL with deionized water.

Matrix modifier, ammonium dihydrogen phosphate (Suprapur®, Merck, 1.01440). The matrix modifier solution was prepared by dissolving 1 g NH₄H₂PO₄ in 50 mL 0.3% (v/v) HNO₃. The final solution was diluted to 100 mL with 0.3%(v/v) HNO₃.

The wine matrix consisted of 100 mL absolute alcohol, 7.0 g citric acid, 3.0 g sucrose, 2.0 g glycerol, 3.8 g tartaric acid, 1.5 mL phospohoric acid, and up to 1000 mL deionized water.(39)

Recovery solution test: In order to perform recovery studies of the these elements in wine, a known amount of Cd, Cr, Cu, Fe, Mn, Pb, and Zn was added to a wine sample. The metal concentrations were made to contain 2 ng/mL Cd, 8 ng/mL Pb, 8 ng/mL Cr, 0.3 mg/L Cu, 0.08 mg/L Zn, 1 mg/L Fe, and 2 mg/L Mn (the concentration was intended to be at the center of the

TABLE I							
Working Conditions for the Determination of Cu, Fe, Mn, and Zn							
lomont	Wavalangth	Slit	Flamo	Light	Linear		

Element	Wavelength	Slit Width	Flame Type	Light Source	Linear Working Range
	(nm)	(nm)	- J P0	504100	(mg/L)
Cu	324.8	0.7	AAOF	HCL	0.020-0.90
Fe	248.3	0.2	AAOF	HCL	0.050-4.0
Mn	279.5	0.2	AAOF	HCL	0.060-4.0
Zn	213.9	0.7	AAOF	HCL	0.010-0.25

AAOF = air-acetylene oxidizing flame; HCL = hollow cathode lamp.



matching method, which offers the ability to obtain a simple external calibration by preparing standard solutions as similar as possible to the samples (14,39,40).

The calibration curve covers the range of 20–1000 ng/mL Cu, 10–250 ng/mL Zn, 50–3000 ng/mL Fe, and 60–4000 ng/mL Mn.

RESULTS AND DISCUSSION

The results of the analysis of the wines examined are summarized in Table III and the analytical characteristics of the methodology used are shown in Table IV.

To calculate the detection limits, seven determinations were carried out in the wine matrix in accordance with the methodology suggested by EPA (41).The detection limits obtained are in good agreement with those reported previously using the same analytical technique (9,14,16,18,28).

The recovery study for the seven metals was performed by spiking three different wine samples with two different concentrations of standard solutions of each element. The recoveries obtained show very acceptable results (95.7% or higher) for the seven metals.

Iron

Mineral elements, such as iron, are natural constituents of wine and directly affect the final quality and characteristics of the wine. Iron normally appears in the grape as part of certain enzymes, but its concentration in wines can be increased by the type of soil, the maturity of the grape, climactic conditions, agrochemical residues, and especially by the processes involved in making the wine (44). Iron has the capacity to form compounds with a wide variety of substances, giving rise to turbidity or changes in color (blue or white shift). It also acts as a catalyst in the oxidation processes involved in

Instrumental Co for the Dete	onditions and Fu ermination of Cd	rnace Programs , Cr and Pb	
	Cd	Cr	
ength (nm)	228.8	357.9	
t setting (nm)	0.7	0.7	

TARIE II

Wavelength (nm)	228.8	357.9	283.3
Low slit setting (nm)	0.7	0.7	0.7
Light source	HCL	HCL	HCL
Drying temperature (°C)	110	110	110
Ramp (s)	5	5	5
Hold(s)	50	50	50
Flow rate (mL/min)	300	300	300
Ashing temperature (°C)	300	500	1000
Ramp (s)	5	10	15
Hold(s)	10	10	10
Flow rate (mL/min)	300	300	300
Atomization temperature (°C)	2100	2300	2700
Ramp (s)	1	1	1
Hold(s)	5	5	5
Flow rate (mL/min)	0	0	0
Cleaning temperature (°C)	2700	2700	2700
Ramp (s)	1	1	1
Hold(s)	2	2	2
Flow rate (mL/min)	300	300	300
Chemical modifier	NH ₄ H ₂ PO ₄	NH ₄ H ₂ PO ₄	0.5% HNO ₃
Injection volume			
sample/modifier (µL)	20/5	20/5	20/5
Background correction	D ₂ Lamp	D ₂ Lamp	D ₂ Lamp
Measurement mode	Peak Area/ Height	Peak Area/ Height	Peak Area/ Height
		8	8

calibration curve). The sample was spiked with a certified solution, Trace Metal Standard I (J.T. Baker Inc., USA).

Procedure

To obtain extensive data for this work, 47 different brands of fine Uruguayan wines were analyzed. The samples were homogenized in the original bottles for 15 min in an ultrasonic bath prior to sampling. This was done to ensure that the precipitate in some wines was dissolved. Wine bottle tops were scrubbed and rinsed prior to cork extraction. All sample manipulations were performed using autopipettes with disposable tips.

Determination of Cd, Cr and Pb

Pb

The wine samples were diluted 1 to 4 by mixing 200 μ L of wine with 800 μ L of 1% HNO₃. To each diluted sample, 3 μ L of a 10% solution of Triton X-100 was added. The samples were injected manually onto the wall of the graphite tube with a micropipet. The chemical modifier was injected soon after the sample and the method of standard addition was used.

Determination of Cu, Fe, Mn, and Zn

To avoid pre-treatment of wines, a calibration curve was prepared in a wine matrix simulator. Some authors reported using a matrix-

R	esults fo	r the De	terminati	on of Cd,	Cr, Pb, Cu, Fe, Mr	n, and Zn in U	ruguayan Wine	es ^a
Grape	Wine	Cd	Cr	Pb	Cu (mg/I)	Fe	Mn (mg/I)	Zn (mg/I)
Tannat	Type Pod		(IIIg/L)	$(\Pi g/L)$	(111g/L)	(IIIg/L) 2.54±0.22	(IIIg/L)	$(\Pi g/L)$
1 annat Morlot	Red	DL	0.037	0.024 DI	0.0332±0.0033	2.34 ± 0.22 2 10±0 17	n.u.	0.07 ± 0.10 1 10±0 17
Tennet	Reu Dod		0.017	DL 0.012	0.103 ± 0.012	2.10 ± 0.17	n.u.	1.10 ± 0.17
Talillat	ĸeu	DL	0.023	0.015	0.0713 ± 0.0009	2.34±0.10	11.u.	0.99 ± 0.15
Sauvignon	Red	DI	0.031	0.010	0 0580+ 0 0050	2 87+0 19	n d	0 74+0 11
Merlot	Rod	DI	0.001	0.010	0.0000 ± 0.0000	2.07 ± 0.15 2 31+0 15	n.d.	0.74 ± 0.11 0 97+0 15
Tannat	Rod	DI	0.002	0.020	0.140 ± 0.014 0.0704 + 0.0067	2.01 ± 0.10 2 15+0 43	n.d.	1 43+0 91
Merlot	Red	DI	0.014	0.000	0.0704 ± 0.0007 0.149+ 0.15	1.10 ± 0.10 1.91+0.23	n.d. n d	0.81 ± 0.21
Merlot	Red	DI	0.015	0.010	0.140 ± 0.10 0 101 + 0 010	4 64+0 37	n.d. n d	0.01 ± 0.12 0.643+ 0.096
Tannat	Red	DI	0.020	0.010	0.101 ± 0.010 0.0604 + 0.0060	2 50+0 23	1.d. 1 431+0 098	0.040 ± 0.000
Merlot	Red	DI	0.000	0.012	0.0004 ± 0.0000 0.0873 ± 0.0087	2.50 ± 0.20 2 55+0 21	2 20+0 15	0.000± 0.000
Cabernet.	ncu		0.010	0.021	0.0070± 0.0007	2.00±0.21	2.20±0.10	0.70±0.12
Sauvignon	Red	DL	0.009	0.006	0.0623 ± 0.00572	2.43±0.19	1.834 ± 0.13	0.566 ± 0.084
Cabernet-								
Sauvignon	Red	DL	0.038	0.057	0.331 ± 0.029	$4.40{\pm}0.35$	n.d.	0.653 ± 0.098
Shiraz	Red	DL	0.030	DL	0.0723 ± 0.0068	$2.34{\pm}0.21$	$1.431{\pm}~0.098$	0.653 ± 0.098
Cabernet-								
Sauvignon	Red	DL	0.020	DL	0.0691 ± 0.0073	1.35 ± 0.11	1.50 ± 0.13	$0.624{\pm}~0.093$
Merlot	Red	DL	0.027	DL	0.0860 ± 0.0077	1.33 ± 0.13	1.55 ± 0.11	0.77 ± 0.12
Merlot	Red	DL	0.026	DL	0.0543 ± 0.0054	$1.30{\pm}0.10$	$1.74{\pm}0.12$	0.495 ± 0.074
Shiraz-	_							
Tannat	Red	DL	0.031	DL	0.103 ± 0.010	2.35 ± 0.18	0.794 ± 0.055	0.92 ± 0.14
Merlot	Red	DL	0.029	DL	0.0873 ± 0.0086	1.41 ± 0.11	1.338 ± 0.091	0.78 ± 0.12
Tannat-	D. J	DI	0.020	DI	0.0500 . 0.0050	1 04 . 0 14	9.09.0.14	0 5 2 0 . 0 0 00
Meriot	Rea	DL	0.030	DL	0.0580 ± 0.0050	1.84 ± 0.14	2.03±0.14	0.538 ± 0.080
Cabernet-	Pod	Ы	0 030	Ы	0 0044+ 0 0080	1 74+0 14	1 233 - 0 084	0 600+ 0 000
Morlot	Red	n d	0.030 n d	DL nd	0.0344 ± 0.0003 0 104 + 0 019	1.74 ± 0.14 1.00±0.11	1.233 ± 0.004 1 216 \pm 0.085	0.000 ± 0.030 0.125 \pm 0.010
Tannat	Rod	n.u DI	n.u DI	n.u 0.017	0.104 ± 0.012 0.225 + 0.021	1.03 ± 0.11 1 8/1+0 1/	1.210 ± 0.000	0.125± 0.015 2 00±0 030
Tannat	Red	DI	0.004	0.017	0.223 ± 0.021 0.114 + 0.014	1.04 ± 0.14 9 19±0 17	1.44 ± 0.12 1 11+0 11	2.00 ± 0.030
Morlot	Rod	DI	0.004 DI	0.010 DI	0.114 ± 0.014 0.0765 + 0.0073	2.13 ± 0.17 1 43+0 11	1.44 ± 0.14 1 53+0 11	0.55 ± 0.14 0.68±0.10
Merlot	Rod	DI	DL 0.039	DI	0.0703 ± 0.0073 0.128+0.012	1.43 ± 0.11 2 01+0 20	1.33±0.11	0.00 ± 0.10 1 03±0 15
Morlot	Rod	0.003	0.002 n d	0.020	0.120 ± 0.012 0.03/0+0.0036	2.01 ± 0.20 2 0 2 + 0 2 3	1.75 ± 0.12 1 121 ± 0.000	1.05 ± 0.15 1 1/+0 9/
Morlot	Rod	0.005 n d	n.u. n d	0.020 n d	0.0340 ± 0.0030 0.102+0.020	2.52 ± 0.25 1 034 + 0 084	1.421 ± 0.000 1 82+0 13	1.14 ± 0.24 0 70+0 11
Tannat.	neu	n.u	n.u	n.u	0.132 ± 0.020	1.034± 0.004	1.02±0.15	0.70±0.11
Merlot	Red	n.d	n.d	n.d	n.d	2.03±0.17	1.54±0.11	0.66 ± 0.11
Tannat	Red	n.d	n.d	n.d	0.0713 ± 0.083	1.58 ± 0.13	1.79±0.14	0.66 ± 0.10
Merlot	Red	n.d	n.d	n.d	0.197 ± 0.013	1.61 ± 0.13	1.65 ± 0.10	0.606 ± 0.090
Cabernet-								
FrancMerlot	Red	n.d	n.d	n.d	n.d	$1.247 {\pm}~0.099$	1.50±0.11	0.488 ± 0.075
Cabernet-								
Sauvignon	Red	n.d	n.d	n.d	$0.120{\pm}\ 0.013$	1.43 ± 0.11	1.79±0.13	0.79 ± 0.11
Tannat	Red	n.d	n.d	n.d	$0.0746 {\pm}\ 0.0080$	$1.203{\pm}~0.096$	1.67 ± 0.12	$0.666 {\pm}~0.099$
Chardonay	White	DL	0.023	0.042	$0.0890 {\pm}\ 0.0089$	$1.033 {\pm}~0.081$	n.d.	1.43 ± 0.21

 TABLE III

 for the Determination of Cd, Cr, Pb, Cu, Fe, Mn, and Zn in Uruguayan

Table III continued on next page



I	Results :	for the De	eterminat	ion of Cd,	, Cr, Pb, Cu, Fe, M	n, and Zn in U	ruguayan Win	es ^a
Grape	Wine	Cd	Cr	Pb	Cu	Fe	Mn	Zn
Variety	Туре	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Chardonay	White	DL	0.022	0.012	0.170 ± 0.0017	1.30 ± 0.11	n.d.	$0.80 {\pm} 0.12$
Chardonay	White	DL	0.020	0.030	0.0360 ± 0.0030	$2.36{\pm}0.18$	n.d.	$0.594{\pm}\ 0.089$
Sauvignon-								
Blanc	White	DL	0.031	DL	0.0740 ± 0.0065	1.34 ± 0.14	0.943 ± 0.066	0.600 ± 0.090
Chardonay	White	DL	0.018	DL	$0.230{\pm}~0.023$	$0.850{\pm}\ 0.068$	$1.321{\pm}~0.091$	$2.00{\pm}0.30$
Chardonay	White	0.002	0.024	DL	n.d.	0.733 ± 0.058	1.65 ± 0.11	n.d.
Chardonay-								
Viognier	White	n.d	n.d	n.d	n.d	$2.55 {\pm} 0.20$	1.25 ± 0.10	$2.179{\pm}~0.33$
Sauvignon								
Gewürz-								
traminer	White	n.d	n.d	n.d	0.0713 ± 0.0069	1.155 ± 0.096	0.967 ± 0.067	0.458 ± 0.069
Botrytis-								
Noble	White	n.d	n.d	n.d	n.d	2.16 ± 0.18	0.799 ± 0.055	0.631 ± 0.089
Chardonay	White	n.d	n.d	n.d	n.d	1.65 ± 0.13	1.42 ± 0.11	$0.609{\pm}\ 0.091$
Chardonay	White	DL	0.006	0.006	$0.221{\pm}~0.018$	$0.954{\pm}~0.076$	$1.435{\pm}~0.078$	$2.00{\pm}~0.030$
Sauvignon	White	n.d	n.d	n.d	$0.0317 {\pm}~0.0032$	$0.522 {\pm}~0.042$	1.45 ± 0.12	0.83 ± 0.13
Chardonay	White	n.d	n.d	n.d	0.0923 ± 0.011	0.144 ± 0.011	1.43 ± 0.11	$1.59 {\pm} 0.24$
Chardonay	White	n.d	n.d	n.d	0.0844 ± 0.0076	0.493 ± 0.039	1.82 ± 0.14	$0.79 {\pm} 0.12$
Typical								
rånge ^b		0.00025	0.030	0.030	0.060-0.40	0.90-10.0	0.37-5.0	0.50-3.5
		- 0.0007	- 0.060	- 0.100				

TABLE III (continued)

^a Each value is the average of 3 replicates.

^b Typical values of metallic ions in wines informed before (37, 43).

DL = Detection limit.

n.d.= not determined.

aging and it has an important effect on the sensorial evaluation of the product (16).

Iron levels in the samples investigated vary between 0.73 and 4.6 mg/L. These concentrations are among the lowest reported in the literature for wines (37) and indicates that no contamination occurred during the wine-making process.

Since the Fe concentration in wines does not exceed 10 mg/L, there should be no danger of ferric cloudiness and the stability of these wines should be assured (45).

Copper

Copper occurs naturally in grapes, but treatment of the vine with copper-based pesticides can result in higher concentrations of this element in wines.

This metal is found in wine at concentrations varying between 0.1 and 0.5 mg/L (46), although other authors have estimated copper levels to be closer to 1 or 3 mg/L (47). It is generally believed that the mean values taken between 0.2 and 0.4 mg/L create no problems in stability with respect to cupric cloudiness (18, 48).

The legal limit for Cu according to OIV regulations is 1 mg/L. It was found that all of the samples analyzed did not exceed 0.33 mg/L nor did they show any cupric cloudiness.

Zinc

The determination of zinc in wines has been documented extensively in the literature. Table III shows that the zinc levels in the samples analyzed were between 0.49 and 2.2 mg/L, which is well below the OIV established limit for this element in wine (5 mg/L). These values fall within the range 0.15-4.0 mg/L and are considered to be normal. The low levels found can be attributed to the specific techonological methods employed, the aging procedures of the product, and storage of the wine in

	Analytical Characteristics of Method to Determine Cd, Cr, Pb, Cu, Fe, Mn, and Zn							
	Detection Limit (mg/L)	Recovery (%)	Precision CV (%)	Range (mg/L)				
Cd	0.0005	$97.8 {\pm} 2.5$	10	0.001-0.0090				
		$97.9 {\pm} 2.5$						
		$99.2 {\pm} 2.6$						
Cr	0.001	98.4±1.7	3.9	0.002-0.010				
		102.7 ± 1.7						
		$103.4{\pm}1.8$						
Pb	0.003	98.2 ± 2.7	7.5	0.008-0.020				
		98.7 ± 2.7						
		100.4 ± 2.7						
Cu	0.0055	$95.9{\pm}1.3$	3.6	0.020-0.090				
		$97.0{\pm}1.4$						
		$97.8 {\pm} 1.4$						
Fe	0.021	96.5 ± 3.1	4.0	0.050-4.0				
		97.0 ± 3.1						
		$98.4 {\pm} 3.2$						
Mn	0.0077	96.9 ± 1.8	2.3	0.060-4.0				
		$97.9 {\pm} 1.9$						
		99.5 ± 1.9						
Zn	0.007	$95.0{\pm}3.6$	2.0	0.010-0.25				
		$95.8 {\pm} 3.6$						
		96.3 ± 3.7						

TABLE IV

wooden containers. Wines kept in metallic containers usually have higher levels of zinc and other elements as well. (19)

Manganese

Manganese levels in wine are generally low. Some authors believe that they are characteristic of a specific wine-growing region, since the amount of Mn in soil is reflected in the final wine content (37). Manganese concentrations in these wines varied between 0.74 and 2.2 mg/L.

The manganese content in wines depends on the type of vinification. It is higher in red wines because during the wine-making process the must remains in contact with the solid part of the grapes for a longer period of time and dissolves the mineral salts. (49)

Chromium

Although the chromium content in wine is not regulated by the OIV, it is important to know the chromium level in wines because of its toxicity. The presence of this metal can be attributed to the use of stainless steel equipment during the wine-making process.

Chromium concentration levels were as high as 0.052 mg/L in only one sample. The other wines presented concentration levels lower than 0.034 mg/L Mn.

Taking into account that the maximum tolerance limit established by the U.S. Food and Drug Administration for drinking water is 0.100 mg/L (50), the chromium concentration found for all the samples tested in this study were far below this limit. Thus, the consumption of this fine Uruguayan wine presents no health threat.

The low concentration of this metal found in this project suggests that leaching from stainless steel is very slight.

Cadmium

From the 32 wine samples investigated, only two samples showed detectable amounts of cadmium. However, they were below the limit legislated by the OIV.

Lead

Lead content in wines deserves special consideration because of its toxicity and cumulative character (51). Health concerns regarding lead in wine have increased over the past deacade. Surveillance excercises during this period have shown that the lead content is variable (14). However, improved industrial practices in wine-making have caused a gradual reduction in lead content, which is reflected in lowering the limits set by leading organizations (52). The OIV has prescribed the limit to 0.2 mg/L Pb, with a recommendation for further reduction (15).

All the wines tested showed lower lead concentrations than the maximum limit permitted by the OIV. The highest concentration found was 0.057 mg/L for one red wine while all other wines showed concentration levels lower than 0.042 mg/L. These low lead levels found in the Uruguayan wines confirms the good production practices employed.

Further analysis of the results listed in Table III shows that there exists a correlation between wine color and metal content. Several studies indicate that element concentrations in wine are related to whether the wines were red or



white. This implies a connection with processing and/or grape variety. It is assumed that the element variability between red and white wines is reflected in the differences between grape varieties. Wines of the same color may have similar element concentrations due to processing. The grape skins contact the must during red wine fermentation which causes the extraction of anthocyanins and tannins. Higher concentrations of some metals may be related to a more efficient extraction of the elements from the skins and pulp during fermentation (9).

Iron concentrations in red wines are higher than in white wines, even for wines from the same winery. It did not seem to matter whether the wine came from the same winery or not, the iron levels appeared to be higher in red than in white wines.

In contrast, zinc concentrations in white wines are higher than in red wines. This tendency was reported before but no further explanation was given (9).

Manganese levels are frequently associated with the production region. In all of the samples for which manganese was determined, the same mean value of 1.4 mg/L was found regardless of the wine color or the winery. This may be attributed to the fact that the vineyards were located in the same area and thus the soil was of similar manganese compositon.

The reasons why the elemental composition of wines from the same winery appear to be very similar are that (a) the wines came from grapes grown on similar soil, (b) they came from the grapes of vines irrigated with water from the same source, (c) they were crushed, stored, and aged with similar equipment, or (d) they were purified and filtered by similar processes (9).

CONCLUSION

This type of project is very important since the determination of elements in wines may help protect prestigious wineries from counterfeit wines and permit source confirmation for government certification.

The methodology employed for the determination of Cd, Cr, and Pb by GFAAS, and Cu, Fe, Mn, and Zn by FAAS was appropiate and the results obtained were as expected.

Fine Uruguayan wines have received many awards and their excellence is recognized worldwide. In this work, the quality of the Uruguayan wines studied was demonstrated and confirmed with regard to their metal content. The data generated show that the cadmium, copper, lead, and zinc concentrations in the wines tested are significantly lower than the maximum tolerance limits established by the Office International de la Vigne et du Vin. Apart form this, the concentrations of all the elements determined fall within the range typical of wines from around the world.

It can also be concluded that the wines tested are stable with regard to ferric and cupric cloudiness.

ACKNOWLEDGMENTS

The author is especially grateful to Raquel Huertas for her support, guidance, and help throughout this research.

I would also like to thank to Elena Darre for her helpful review of an earlier version. I acknowledge all persons who so kindly provided helpful and pertinet comments.

I would also like to thank the staff of the Wine Department of LATU who collected and kindly donated the wine samples used for the present work. The author also thanks the Head of the Analytical Department of the Laboratorio Tecnológico del Uruguay for his permission to use the facilities and the equipment of the laboratory to carry out this project.

Trade names are used for informational purposes only.

Received November 23, 2003.

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