Determination of Transition Metals in Wine by IC, DPASV-DPCSV, and ZGFAAS Coupled with UV Photolysis

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In the present work ion chromatography (IC), differential pulse anodic (DPASV) or cathodic stripping voltammetry (DPCSV), and Zeeman graphite furnace atomic absorption spectroscopy (ZGFAAS) were applied to the determination of heavy and transition metals in wine. The matrix is degraded by oxidative UV photolysis in a digester equipped with a high-pressure mercury lamp. The temperature of the sample is maintained at 85 ± 5 °C by a combined air/water cooling system. This procedure has decisive advantages if compared with other sample pretreatment techniques. Most organic wine constituents degrade in <1 h, whereas metals quantitation remains unaffected by UV radiation, with the exception of manganese. The clear solution is directly analyzed for most common heavy and transition metals such as cadmium, cobalt, copper, iron, lead, nickel, and zinc. In the absence of standards, the results obtained by different techniques are compared and are found in good agreement. All of the considered techniques appear to be equivalent, but ZGFAAS is more time-consuming because it does not permit multielement analyses.

Keywords: *Ion chromatography; metals; UV photolysis; voltammetry; wine; Zeeman graphite furnace atomic absorption spectroscopy*

INTRODUCTION

The determination of metals in wine is very valuable from both the technological and the hygienic points of view; the uptake of aluminum, cobalt, iron, nickel, or silicon leads to unwanted turbidity or conspicuous taste (Wuensche et al., 1986), whereas toxic elements such as cadmium, copper, lead, or zinc are strictly limited by health regulations (Republic of Italy, 1986; European Economic Community, 1990). Despite the availability of official methods for the determination of heavy metals in wine based on atomic absorption spectroscopy (i.e., Office International de la Vigne et du Vin and American Society of Enologists), the demand for sensitive, simple, and rapid instrumental analytical techniques devoted to multielement control of micro- and macrocontaminants and/or constituents of wine is continuously increasing. This not only satisfies wine regulation requirements, but it also is basic for developing good quality products.

Metals determination in complex matrixes, such as wine, has traditionally been a challenging analytical task because of the interference due to the matrix. Sample pretreatment is usually required to destroy the organic matrix and/or to extract the metal ions bound in inorganic and organic complexes. The procedure must take into account the analytes of interest, the sample matrix, and the speed requirements of the analytical technique considered. Dry ashing and wet digestion are widely used for food sample pretreatment. In the wine industry, dry ashing dates from the very beginning of

wine analysis; it involves the complete combustion of all the organic matter at high temperature, but the factors controlling the volatilization and retention mechanisms are not always easy to assess and cause low recoveries when trace analysis is performed (Allen et al., 1989).

The wet digestion technique involves the treatment of the matrix with mixed acids and is widely adopted (Gorsuch, 1959). This technique is time-consuming and not prone to automation; in addition, the use of large amounts of reagents generates a lot of waste.

As an alternate to these, a microwave oven digestion technique has become popular due to the reduced reagents amount, temperature, and time required for sample treatment; however, the decomposition of the wine organic matrix is delicate, and its progress must be strictly controlled. In addition, the nonvolatile residues, remaining after the treatment, are significative for analytical techniques sensitive to organic interference (Reid et al., 1995).

The present work deals with oxidative UV photolysis as a simple and reliable sample preparation method, useful for analyzing metals at all steps in wine preparation and aging with different analytical techniques. Among the wide range of modern techniques that has been used in the determination of trace metals in wine (Linskens and Jackson, 1988; Ough and Amerine, 1988), ion chromatography, voltammetry, and atomic absorption spectroscopy have been selected as the most relevant and widely adopted ones.

EXPERIMENTAL PROCEDURES

Apparatus. *UV Photolysis.* The wine samples were subjected to UV photolysis in a 705 UV digester (Metrohm, Herisau, Switzerland) equipped with a high-pressure 500 W lamp. The temperature of the sample was maintained at ~85

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Table 1. Ion Chromatographic Conditions

	Pb, Cu, Cd + Mn, Co, Zn, Ni	Fe, Cu, Ni, Zn, Co, Cd, Mn
column	IonPac CG5A + CS5A	
eluent	80 mM oxalic acid	7 mM PDCA
	50 mM KOH	66 mM KOH
	100 mM TMAOH	5.6 mM K_2SO_4
	(pH 4.7)	74 mM HCOOH
		(pH 4.2)
eluent flow rate	1.2 mL min^{-1}	
injection volume	150 μL	
detection	visible absorbance (530 nm)	
postcolumn	0.3 mM PAR	
reagent	1 M 2-dimethylaminoethanol	
	0.5 M NH_4OH	
	0.3 M $NaHCO_3$	
	(pH 10.4)	
PCR flow rate	0.6 mL min^{-1}	

± 5 °C with the help of the combined air/water cooling system built in the digester.

Chromatography. Chromatographic analyses were performed on a metal-free high-pressure ion chromatograph, model Dionex DX-300 (Dionex, Sunnyvale, CA), which included one gradient pump AGP, a postcolumn pneumatic controller for postcolumn reagent addition, and a DSA UV−vis multiple wavelength detector operating at 530 nm. Trace of metals in the chromatographic system were removed by flushing all flow paths, pump, and columns with 5× concentrated eluent at 1 mL/min prior to use.

The 250 × 4 mm i.d. IonPac CS5A (Dionex) analytical column was used for the separation of transition metals. The 50 × 4 mm i.d. IonPac CG5A guard column is placed prior to the IonPac CS5A to prevent potential fouling of the analytical column.

Mixed-Bed Ion Exchange Column. The IonPac CS5A has been designed to separate a broad range of chelated metal complexes by anion and cation exchange chromatography (Riviello et al., 1996). The column has a 55% cross-linked, microporous, hydrophobic poly(ethylvinylbenzene−divinylbenzene)-based resin core that has been agglomerated with two layers of permeable ion exchange latex particles. The first sulfonic latex layer is attached to the surface of the structural polymer by a quaternary amine graft. The outer aminated latex layer is electrostatically bonded to the sulfonic layer. Hydrated and weakly complexed metals can be separated as cations on cation exchange sites. When a chelating carboxylic acid is added to the eluent, the net charge on the metal is reduced, and if the chelating agent concentration is high and the β constant is >10^3, then the net charge of metal complexes is negative and the metal ion complexed can be separated by anion exchange.

All measurements were made isocratically and at room temperature. In all cases, injection of the sample was done at least in triplicate. All of the samples were filtered through a 0.2 μm filter *before injection*. Chromatographic conditions are summarized in Table 1. Data manipulation and the operation of all the components in the system were controlled by AI-450 Dionex chromatographic software interfaced via an ACI-2 Advanced Computer Interface to an 80386 based computer (Epson, Sesto S. Giovanni, Italy).

Voltammetry. Voltammetric measurements were performed on a Metrohm (Herisau, Switzerland) 646 VA processor equipped with a 647 VA stand, a 675 VA sample changer, a 677 drive unit, and Dosimat 665 automatic addition burets. A conventional three-electrode arrangement consisting of a multimode electrode (MME) working electrode, an Ag/AgCl [3 M KNO$_3$] reference electrode, and a 6.5 cm long platinum wire auxiliary electrode was used. All of the voltammetric conditions are listed in Table 2.

Atomic Absorption Spectrometry. A Zeeman 3030 (Perkin-Elmer, Beaconsfield, PQ, Canada) atomic absorption spectrometer, equipped with an HGA 400 (Perkin-Elmer) furnace module, was used. A pyro/platform tube in an argon stream was used, with a slit of 0.7 nm (for copper, cadmium, lead,

and zinc) or 0.2 nm (for iron, cobalt, and nickel), at the resonance lines reported in Table 3. Lead only was analyzed in an uncoated tube. The results were obtained by computerized graphic evaluation of the standard addition method, taking into account the matrix modifier dilution when required.

Reagents. Sodium hydrogencarbonate, potassium hydroxide, potassium sulfate, oxalic acid, tetramethylammonium hydroxide (TMAOH), 2-dimethylaminoethanol, 4-(2-pyridylazo)resorcinol monosodium salt (PAR), and pyridine-2,6-dicarboxylic acid (PDCA) were of chromatographic grade (Novachimica, Milan, Italy). Hydrogen peroxide (30% m/m), ammonium hydroxide (30%), and nitric acid (70%) were of Erbatron electronic grade (Carlo Erba Reagenti, Milan, Italy). Formic acid, ammonium acetate, ammonium dihydrogen phosphate, magnesium nitrate, dimethylglyoxime, and ethyl alcohol (95°) were of ACS reagent grade, and 2 M ammonium acetate (pH 5.5) was of chelation grade (Dionex, Sunnyvale, CA). Ultrapure water with conductivity <0.1 μS (DI water) was obtained from a Milli-Q (Millipore, Bedford, MA) deionization system.

Working standards were prepared daily by diluting Carlo Erba Reagenti Normex atomic absorption standards (1.000 g L^{-1}).

Quartz test tubes and all glassware were cleaned by refluxing in hot and concentrated nitric acid, then carefully washed with DI water, and finally dried with filtered air in a clean atmosphere. Details of cleaning procedures and apparatus are reported in the standard texts. Normal precautions for trace analysis were observed throughout. Manipulations were done on a laminar-flow clean bench to avoid fortuitous pollution.

Voltammetric Complexing Solutions. For the determination of nickel(II) and cobalt(II), a 43 mM dimethylglyoxime solution was prepared in ethyl alcohol (95°).

Postcolumn Reagent. The postcolumn reagent was 0.3 mM PAR, 1 M 2-dimethylaminoethanol, 0.5 M ammonium hydroxide, and 0.3 M sodium bicarbonate. The pH of the reagent was 10.4. Prior to use, the reagent must be filtered on a 0.2 μm filter. Because PAR is readily oxidized by oxygen, the reagent was degassed and store under nitrogen. The reagent flow rate was set at 0.6 mL min^{-1}.

Procedure. The wine sample (0.5 mL) is treated with 1 mL of hydrogen peroxide and subjected to UV photolysis. Five aliquots of 0.2 mL each of hydrogen peroxide are added after every 5−10 min, followed by the addition of 10 μL of 1 M nitric acid.

At the end of the UV photolysis period, which varies from 30 to 90 min depending on wine characteristics (see Table 4), the sample is adjusted to a pH between 5 and 6 by adding 50 μL of 2 M ammonium acetate, and the solution is then diluted to 5 mL and analyzed by IC.

For DPASV-DPCSV analysis, at the end of the UV photolysis period the sample solution is simply diluted to 10 mL with DI water and transferred to the voltammetric cell. The equipment operations must be programmed for a 300 μL addition of 2 M ammonium acetate, followed by the determination of zinc, lead, cadmium, and copper, and a successive addition of 300 μL of 5 M ammonia/ammonium acetate buffer (pH 9.5) and 50 μL of 43 mM dimethylglyoxime solution for the determination of nickel and cobalt.

Zeeman graphite furnace atomic absorption spectroscopy is applied to the same photolyzed samples, simply diluted to 5 mL with DI water. Each analysis calls for 20 μL of sample, and 10 μL of the matrix modifier is added if necessary, according to Table 3.

RESULTS AND DISCUSSION

UV Photolysis. For making the proposed method amenable for the widest range of applicability, samples of wines of different origins and variable constitutions were chosen and the effect of UV radiation on various cations has been investigated in detail. Matrix matching ethanol solutions as well as wine samples have been

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Table 2. Voltammetric Conditions

	Zn, Cd, Pb, Cu	Ni, Co
electrode type	MME operated as HMDE, Hg drop size 0.60 mm²	
electrode stirring speed[a]	1920 rpm	
measuring conditions	pre-electrolysis (at −1.45 V) 120 s, quiet time before potential sweep 20 s, DPASV from −1.45 to −0.10 V, pulse amplitude 60 mV, potential sweep rate 10 mV s⁻¹	pre-electrolysis (at −1.10 V) 35 s, quiet time before potential sweep 30 s, DPCSV from −1.10 to −1.45 V, pulse amplitude −40 mV, potential sweep rate 10 mV s⁻¹

[a] During pre-electrolysis time.

Table 3. Zeeman Graphite Furnace Atomic Absorption Spectrometric Conditions

element	wavelength (nm)	temp (°C) pretreatment	temp (°C) atomization	matrix modifier[a]
Zn	213.9	700	1800	A
Cd	228.8	900	1600	B
Ni	232.0	1400	2500	C
Co	242.5	1400	2500	C
Fe	248.3	1400	2400	C
Pb	283.3	900	1800	B
Cu	324.8	900	2000	

[a] A, 6 μg of $Mg(NO_3)_2$; B, 200 μg of $NH_4H_2PO_4$ + 10 μg of $Mg(NO_3)_2$; C, 50 μg of $Mg(NO_3)_2$.

spiked with various amounts of heavy and transition metal ions and subjected to UV photolysis for 6 h prior to instrumental analyses as reported in the procedure. It has been found that cadmium(II), cobalt(II), copper-(II), iron(III), lead(II), nickel(II), and zinc(II) are not affected by UV photolysis, and the recovery of these species is between 97 and 103% in matrix matching ethanol solutions as well as in wine samples. The results of the photolytic study are summarized in Table 4 and show that wines with low organic content are degraded in less time than those with a higher one.

Also, increasing the amount of hydrogen peroxide can further reduce the photolysis time. The purpose of using hydrogen peroxide in the course of photolysis is to supply free OH• radicals, which accelerate the decomposition of organic components present in the wine; in addition, the decomposition products of this reagent are water and oxygen, which do not interfere. Hence, depending upon the analytical requirements and the type of wine to be analyzed, the best compromise can be made between the photolysis time and the amount of hydrogen peroxide added.

pH Effect. The quantitative analysis of metals in wine was found to be dependent on the pH of the analyte. After UV photolysis, the sample pH generally rises to ~9, suggestive of the decomposition of the carboxylic and other acids present in the wine. At this pH, metals present in the wine get hydrolyzed/precipi-tated and losses take place. It is therefore necessary to lower the pH to ensure that all of the metals present remain in soluble ionic form. When 10 μL of 1 M nitric acid is added to a 0.5 mL sample, the pH is lowered to ~2, so that all of the metals present remain in unbound/free form and insoluble oxides formation is prevented. When using IC, the instrumental response at this pH is found to be lower than expected, noticeably when a weak complexing eluent (such as oxalate) is used. Therefore, a systematic study for the response of the considered metals in wine matrix has been conducted at various pH values for the different analytical techniques selected.

The results showed that no pH problem exists when the photolyzed sample is analyzed by ZGFAAS, whereas the use of IC revealed that the best pH range for the

Table 4. UV Photolysis Time and Amount of H_2O_2 Added for the Complete Recovery of the Element

low-tannin wine H_2O_2 added (mL)	low-tannin wine photolysis time (h)	medium-tannin wine H_2O_2 added (mL)	medium-tannin wine photolysis time (h)	high-tannin wine H_2O_2 added (mL)	high-tannin wine photolysis time (h)
		Pb[a]			
0	>8.0	0	>8.0	0	>8.0
0.5	3.0	0.5	4.2	0.5	5.0
1.0	1.0	1.0	2.5	1.0	3.2
1.5	0.8	1.5	2.0	1.5	2.5
2.0	0.5	2.0	1.1	2.0	1.5
		Cd[b]			
0	>8.0	0	>8.0	0	>8.0
0.5	3.1	0.5	4.0	0.5	5.2
1.0	1.2	1.0	2.5	1.0	3.3
1.5	0.8	1.5	1.9	1.5	2.4
2.0	0.4	2.0	1.1	2.0	1.5
		Fe[c]			
0	>8.0	0	>8.0	0	>8.0
0.5	2.8	0.5	4.1	0.5	4.9
1.0	0.9	1.0	2.5	1.0	3.1
1.5	0.7	1.5	1.8	1.5	2.4
2.0	0.4	2.0	1.0	2.0	1.5
		Cu[d]			
0	>8.0	0	>8.0	0	>8.0
0.5	2.9	0.5	4.2	0.5	5.0
1.0	1.0	1.0	2.4	1.0	3.1
1.5	0.7	1.5	1.9	1.5	2.4
2.0	0.5	2.0	1.0	2.0	1.5
		Ni[e]			
0	>8.0	0	>8.0	0	>8.0
0.5	3.3	0.5	4.5	0.5	5.5
1.0	1.3	1.0	3.0	1.0	3.5
1.5	1.0	1.5	2.5	1.5	2.8
2.0	0.6	2.0	1.4	2.0	1.7
		Zn[f]			
0	>8.0	0	>8.0	0	>8.0
0.5	2.9	0.5	4.2	0.5	4.8
1.0	1.0	1.0	2.3	1.0	3.0
1.5	0.7	1.5	2.0	1.5	2.2
2.0	0.5	2.0	1.0	2.0	1.4
		Co[g]			
0	>8.0	0	>8.0	0	>8.0
0.5	3.3	0.5	4.5	0.5	5.5
1.0	1.4	1.0	3.0	1.0	3.5
1.5	1.0	1.5	2.5	1.5	2.8
2.0	0.6	2.0	1.4	2.0	1.7

[a] Wine sample, 0.5 mL; spikes, 50 and 100 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, DPASV, ZGFAAS. [b] Wine sample, 0.5 mL; spikes, 100 and 200 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, DPASV, ZGFAAS. [c] Wine sample, 0.5 mL; spikes, 50 and 100 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, ZGFAAS. [d] Wine sample, 0.5 mL; spikes, 50 and 100 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, DPASV, ZGFAAS. [e] Wine sample, 0.5 mL; spikes, 100 and 200 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, DPCSV, ZGFAAS. [f] Wine sample, 0.5 mL; spikes, 50 and 100 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, DPASV, ZGFAAS. [g] Wine sample, 0.5 mL; spikes, 50 and 100 μL; average of five replicates each; recovery, 97−103%; analytical techniques, IC, DPCSV, ZGFAAS.

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Table 5. Comparison of Results for Different Types of Wine

		wine type: color and geographical origin								
		white, Emilia		white, Romagna		red, Umbria		red, Campania		red, Piemonte	
element	test[a]	μg L^{-1}	s[b]	μg L^{-1}	s[b]	μg L^{-1}	s[b]	μg L^{-1}	s[b]	μg L^{-1}	s[b]
Cd	IC	<25		<25		<25		<25		<25	
	DPASV	<5		<5		<5		<5		<5	
	ZGFAAS	<5		<5		<5		<5		<5	
Co	IC	<10		<10		<10		<10		<10	
	DPCSV	<10		<10		<10		<10		<10	
	ZGFAAS	<50		<50		<50		<50		<50	
Cu	IC	287	±3	167	±2	344	±4	362	±4	485	±5
	DPASV	290	±4	170	±2	350	±4	360	±4	490	±5
	ZGFAAS	290	±4	165	±2	347	±4	362	±4	487	±5
Fe	IC	365	±3	257	±3	675	±5	881	±9	978	±10
	ZGFAAS	365	±5	254	±5	670	±8	875	±10	986	±10
Ni	IC	<20		<20		<20		35	±5	60	±4
	DPCSV	<5		<5		20	±1	32.4	±1.1	57.2	±1.7
	ZGFAAS	<20		<20		<20		35	±4	55.3	±4.5
Pb	IC	< 10		< 10		< 10		34.5	±0.6	149	±1.0
	DPASV	< 10		< 10		< 10		34.2	±0.6	148	±1.5
	ZGFAAS	< 15		< 15		< 15		37	±7.9	143	±5.4
Zn	IC	350	±3	277	±3	503	±4	789	±7	980	±10
	DPASV	348	±6	280	±5	500	±8	795	±10	975	±10
	ZGFAAS	348	±5	278	±4	495	±6	800	±8	990	±10

[a] Procedures as previously reported. [b] $n = 5$.

analysis of the selected metals in wine after UV degradation is between 5 and 6. It is therefore advisable that the wine sample after UV photolysis is buffered in the required pH range. The addition of 50 μL of 2 M ammonium acetate to the sample was found to be quite effective. It should be noted that the large quantity of nitric acid, as required by official methods (Helrich, 1990) for sample digestion, should not be used for the acidification of the sample, as this in turn would require larger amount of ammonium acetate, which just increases the size of a peak located in front of the lead one, interfering in this way with its determination.

The same pH range was found to be effective both for ZGFAAS and for the simultaneous analysis of copper, cadmium, lead, and zinc by DPASV, whereas nickel and cobalt dimethylglyoximates are better formed at pH 9.5. So, after the determination of copper, cadmium, lead, and zinc, an ammonia/ammonium acetate buffer is added before the dimethylglyoxime solution and nickel and cobalt DPCSV determinations are carried out. Some results obtained on wines of different origins are summarized in Table 5.

The detection limits have been determined by spiking matrix matching ethanol solutions as well as wines of different origins with various amounts of different cations and subjecting them to oxidative UV photolysis as reported in the procedure. The detection limit, calculated according to the method of Long and Winefordner (1983), and concentration ranges, in which calibration curves are linear, with correlation coefficients >0.995, for the different cations determined by ion chromatography, voltammetry, and Zeeman graphite furnace atomic absorption spectrometry are summarized in Table 6. As evident from Table 6, the proposed sample pretreatment technique is highly suitable for the determination of very low amounts of cadmium(II), cobalt(II), copper(II), iron(III), lead(II), nickel(II), and zinc(II).

Ion Chromatography. Separation of transition metals can usually be accomplished via complexation with eluent and anionic or cationic exchange (Riviello and Pohl, 1983, 1984). The main problem with strong complexing eluents such as pyridine-2,6-dicarboxylic

Table 6. Detection Limits and Concentration Ranges

Ion Chromatography

element	eluent	detection limit (μg L^{-1})	range (μg L^{-1})
lead(II)	oxalate	10	25−2000
cadmium(II)	oxalate	25	50−1500
iron(III)	PDCA	5	15−2000
copper(II)	PDCA	5	10−1500
nickel(II)	PDCA	20	100−1500
zinc(II)	PDCA	10	25−2000
Cobalt(II)	PDCA	10	20−2000

Voltammetry

element	technique	detection limit (μg L^{-1})	range (μg L^{-1})
copper(II)	DPASV	10	20−10000
cadmium(II)	DPASV	5	10−10000
lead(II)	DPASV	10	20−10000
zinc(II)	DPASV	20	40−10000
nickel(II)	DPCSV	5	10−10000
cobalt(II)	DPCSV	10	20−5000

Zeeman Graphite Furnace Atomic Absorption Spectrometry

element	wavelength (nm)	detection limit (μg L^{-1})	range (μg L^{-1})
zinc(II)	213.9	20	40−100
cadmium(II)	228.8	5	10−50
nickel(II)	232.0	20	50−100
cobalt(II)	242.5	50	100−300
iron(III)	248.3	10	20−50
lead(II)	283.3	10	20−50
copper(II)	324.8	10	20−50

acid (PDCA) or oxalate is that they interfere with the metallochromic indicator used for postcolumn reaction; thus, sample dissolution technique, pH, complexant, and metallochromic indicator concentrations are optimized to permit the forming of the complexes with the eluent and their consequent separation by ion exchange. These complexes must be sufficiently weak so that, in the postcolumn reaction coil, the metallochromic indicator can rapidly substitute the ligand and give a stable complex monitored by the spectrophotometric detector.

An excess over 1000:1 of sodium, potassium, calcium, or magnesium does not interfere in the determination;
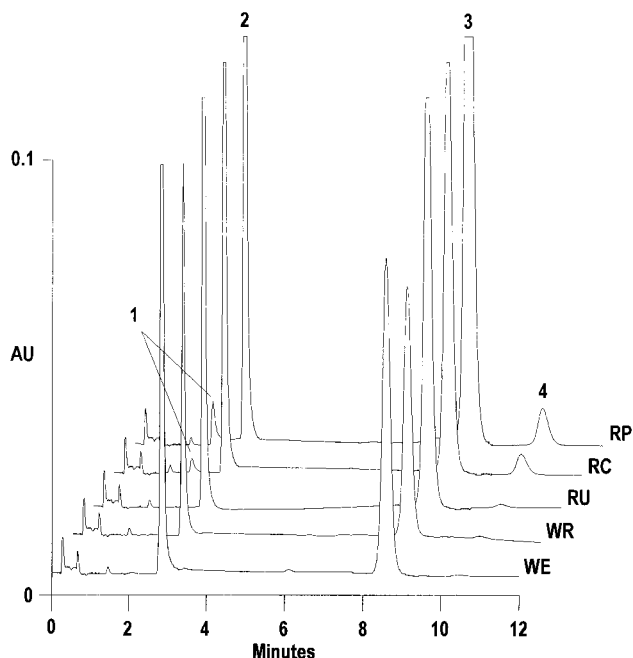
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Figure 1. Isocratic elution of metals in different wine samples after UV photolysis treatment as described: WE, white Emilia; WR, white Romagna; RU, red Umbria; RC, red Campania; RP, red Piemonte. Peaks: 1, Pb; 2, Cu; 3, Zn; 4, Ni. Eluent: Oxalic acid. Chromatographic conditions were as in Table 1.
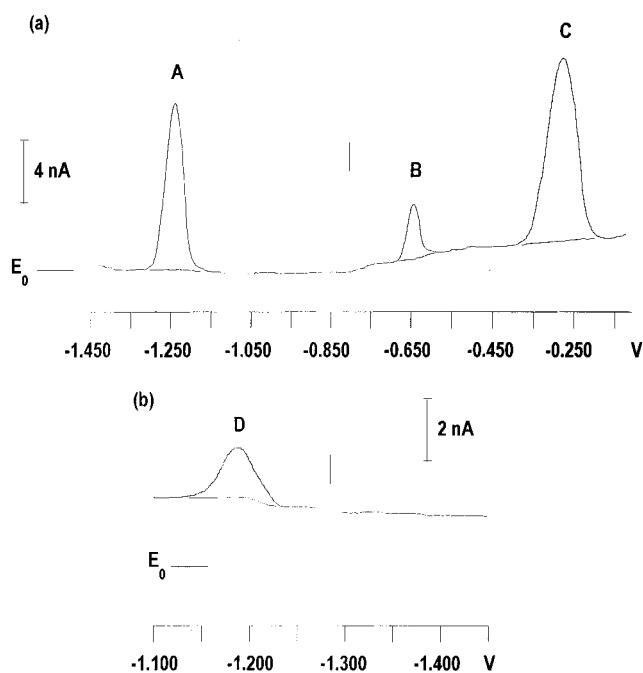

Figure 2. Voltammogram of cations in RP wine sample after UV photolysis treatment as described: (a) peak A, Zn (-1.240 V); peak B, Pb (-0.650 V); peak C, Cu (-0.270 V); Cd (-0.800 V), not found; (b) peak D, Ni (-1.180 V); Co (-1.280 V), not found. Blank values are reported as peak baseline. Polarographic conditions were as in Table 2.

cadmium(II) and manganese(II) coelute with oxalic eluent, whereas cadmium(II) is well separated from other metals with PDCA eluent. A series of chromatograms of different wine samples obtained with PDCA eluent are shown in Figure 1. Manganese(II) cannot be completely recovered because of its oxidation due to the influence of UV radiation.

The advantage of the ion chromatographic approach to the transition metals determination is that the

instrumentation is cheap and widespread and the same system with minimal modification can be used in the food analysis for the determination of the other ionic components (i.e., alkaline, alkaline-earths, and inorganic and organic anions) (Buldini et al., 1997).

Voltammetry. ASV has been used for trace metals determination in wine (Garrido et al., 1997; Baldo et al., 1997; Sanllorente et al., 1998), but the proposed method performs simultaneous and completely automatic analyses of a wide range of metals by microprocessor-controlled voltammetry. Data processing for copper and zinc DPASV peaks area does not reveal any interference as shown in Figure 2, whereas the couple of cadmium and lead DPASV peaks, as well as that of nickel and cobalt DPCSV ones, has been evaluated by taking into consideration only the front half of the first peak (cadmium or nickel) and the rear half of the second one (lead or cobalt), to avoid any interference that might occur in the presence of a very large excess (>1000-fold) of an element over the other one.

More than 40 elements were tested for possible interfering effect (Buldini et al., 1991). Interferences were found in the presence of an excess of bismuth(III) (on copper), titanium(IV) (on copper, cadmium, and lead), indium(III) (on Camden), chromium(VI) (on lead), molybdenum(VI) (on lead), and tungsten(VI) (on zinc), but their occurrence in a wine matrix is unusual, especially in excess over the interfered species.

A particular advantage of the voltammetric techniques lies in performing the preconcentration steps directly into the voltammetric cell without risk of sample contamination; on the other hand, electrochemical techniques usually require a more highly trained staff.

Atomic Absorption Spectroscopy. This technique has been widely used for trace metals determination in wine (Gonzales et al., 1988; Probst-Hensch et al., 1992; Jaganathan et al., 1997), and it is officially adopted (European Economic Community, 1990). Despite this, it was found to be more time-consuming, not permitting multiple analyses, and its short linearity range requires multiple dilution steps, especially when unknown samples of different origins are analyzed.

Conclusions. Oxidative UV photolysis has been found to be superior compared to dry-ashing and wet digestion sample preparation techniques because of the simple procedure, minimal reagent requirement, complete automation, and very low blank values that minimize interferences. The capability of coupling this sample treatment method with a wide range of analytical techniques has been evaluated by taking into consideration ion chromatography, voltammetry, and atomic absorption spectrometry.

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