

Article

Direct Determination of Zn, Cd, Pb and Cu in Wine by Differential Pulse Anodic Stripping Voltammetry

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Abstract: Metals in wine can originate from natural and anthropogenic sources and their concentrations have significant effects on wine properties as well in its conservation. In this work, direct and simultaneous determinations of Zn, Cd, Pb and Cu in wine samples were carried out by differential pulse anodic stripping voltammetry without any steps of previous pretreatment. The samples analyzed presented concentration levels from 4.64 to 69.3 $\mu\text{g L}^{-1}$ of Zn, from 1.74 to 5.25 $\mu\text{g L}^{-1}$ of Cd, from 4.57 to 17.9 $\mu\text{g L}^{-1}$ of Pb and from 1.0 to 10.3 $\mu\text{g L}^{-1}$ of Cu. Accuracy was evaluated with the standard addition method and recoveries ranged from 82.5 and 130.8% for Zn, from 85.7 to 107.0% for Cd, from 89.7 to 101.0% for Pb and from 81.4 to 105.9% for Cu. With the application of this method, it was possible to quantify the metals in a simple and easy way not requiring sample preparation or other approaches for the destruction of organic substances.

Keywords: direct analyses; differential pulse anodic stripping voltammetry (DPASV); metals; wine

1. Introduction

Wine is an alcoholic beverage, obtained from yeast fermentation of natural sugars present in grapes [1]. Wine chemical composition includes ethanol, sugars, organic acids, tannins, metals, aromatic compounds and coloring substances [1]. Such composition can be influenced by enological techniques, grape cultivar, and climatic factors [2].

The analysis for certain elements in wines is important due to their toxicity in case of excessive intake, and also for the effect they seem to have on organoleptic properties of wine [3]. Cd and Pb are known to be potentially toxic [3]. Cu is an essential micronutrient but toxic at high concentration which can increase during wine manufacturing, grape cultivation, and/or cellar processing [4]. Additionally, elements such as Fe, Cu and Mn play an important role in wine oxidation and stability affecting its organoleptic properties [3]. However, daily consumption of wine in moderate quantities can contribute significantly to the intake of essential elements such as Zn.

The content of trace metals in wine depends on several factors, such as the type of soil, the grapes' capacity to adsorb mineral substances from the soil, agrochemical treatments, environmental pollution, vinification processes (from fermentation reaction to the addition of substances), winery equipment, wine preservation and bottling [5,6]. However, the application of pesticides, fungicides, and fertilizers containing Cd, Cu, Pb, and Zn leads to increased amounts of such metals in wine [5,7]. The International Organisation of Vine and Wine (OIV) [8], Mercosur [9] and Brazilian Health Regulatory Agency [10] allow 1000, 1000 and 10,000 $\mu\text{g L}^{-1}$ of Cu in wine; and the OIV and Mercosur allow up to 10 $\mu\text{g L}^{-1}$ of Cd and 5000 $\mu\text{g L}^{-1}$ of Zn. The Pb concentrations accepted are 150 and 300 $\mu\text{g L}^{-1}$ for the OIV and Mercosur, respectively. However, the Brazilian Health Regulatory Agency does not present any legislation for Cd, Pb and Zn in wines. The determination of metals in wine

has been performed by atomic absorption spectrometry (AAS) [5,11,12], inductively-coupled plasma mass spectrometry (ICP-MS) [13] and inductively-coupled plasma optical emission spectrometry (ICP-OES) [14]. However, electroanalytical techniques, combining high sensitivity, precision and accuracy with inexpensive instrumentation are suited for metal determination in wine [4]. The electroanalytical methods most frequently used for this purpose are anodic stripping voltammetry, differential pulse anodic stripping voltammetry (DPASV) and linear sweep anodic stripping voltammetry [15–17], potentiometric stripping analysis [12,18–20] and square-wave anodic stripping voltammetry (SWASV) [4].

In general, voltammetric methods are used for individual and simultaneous determination of trace metals in wine and fish with low detection limits and high precision [4,12,16,21–26]. However, in some cases the sample pretreatment steps are needed [4,24,25]. The direct voltammetric determination of Zn, Cd, Pb e Cu in wine has been performed with a thick-film modified graphite-containing electrode [16] and with a mercury deposited in platinum microdisc electrode [26], but in both cases the solid electrode preparation as well the film deposition are necessary. However, to the best of our knowledge, the direct and simultaneous determination of metals such as Zn, Cd, Pb e Cu using an electrode with good reproducibility, small memory effect, and good analytical response such as mercury electrode, was not performed.

The direct determination of aluminum, copper, chromium, iron and nickel using graphite furnace atomic absorption spectrometry (GF-AAS) in soda were reported [27] as well as the determination of copper, manganese, lead and zinc in beer by AAS. However, there is a need for cheap, fast, safe and accurate analytical methods with a minimum or no sample preparation, allowing the determination of metals at low concentration in these kinds of samples.

In order to minimize the mineralization step, the present work intends to evaluate voltammetry as a technique to directly and simultaneously determine Zn, Cd, Pb and Cu in different wine samples by anodic stripping.

2. Material and Methods

2.1. Reagents, Equipment, and Instrumental Parameters

All reagents used in this work were of analytical grade. For preparation of samples and standard solutions ultrapure water (resistivity > 18.0 MΩ cm) obtained from Millipore Milli-Q system (Billerica, MA, USA) was used. Mixed standard solutions containing 4 mg L⁻¹ of Zn and Cu and 8 mg L⁻¹ of Pb and Cd were prepared daily by dilution of individual stock solutions of 1000 mg L⁻¹ of Zn (Assurance SprexCertiprex, Portland, EUA), Cd (Assurance SprexCertiprex, Portland, EUA), Pb (Merck, Darmstadt, Germany) and Cu (Assurance SprexCertiprex, Portland, EUA). Adequate amounts of acetic acid (55 mL, Synth, São Paulo, Brazil) and ammonium hydroxide (37 mL, Merck, Darmstadt, Germany) were used in the preparation of the electrolyte (0.1 mol L⁻¹) in ultrapure water (300 mL).

All materials used in this work were previously cleaned by immersion in 10% *v/v* HNO₃ (Merck, Darmstadt, Germany) solution for 24 h and rinsed with ultrapure water.

The pH measurements were performed using an expandable ion analyzer (EA-940, Orion, Houston, USA), employing a combined glass electrode with an Ag/AgCl (3.0 mol L⁻¹ KCl) external reference electrode. Voltammetric measurements were carried out on a Potenciostat/Galvanostat Metrohm Autolab PGSTAT 101 (663 VA Stand, Metrohm and Interface Autolab IME663, Herisau, Switzerland). All electrochemical measurements were performed in a three-electrode system configuration with a hanging mercury drop electrode, Ag/AgCl (KCl 3 mol L⁻¹) and platinum wire as working, reference and counter electrodes, respectively. DPASV measurements were performed in 0.1 mol L⁻¹ ammonium acetate solution (pH 4.6) [28]. The experimental conditions for DPASV technique were: start potential = -1.1 V, end potential = 0.2 V, deposition potential = -1.1 V, deposition time = 120 s, amplitude = 0.05 V, modulation time = 0.04 s and scan rate = 20 mV s⁻¹.

2.2. Voltammetric Determination in Wine Samples

Samples used in this work (seven samples of wine) were produced in Rio Grande do Sul state (Santa Maria, Brazil). All samples were stored in glass bottles at dark at room temperature and were named S12 and S13 (Shiraz), MA12 and MA13 (Malbec), ME12 and ME13 (Merlot) and PN12 (Pinot noir).

For voltammetric analysis, 1 mL of the electrolyte solution (pH 4.6), 1 mL of wine sample (without previous sample preparation steps) and 8 mL of ultrapure water were added in the voltammetric cell. DPASV measurements were performed in 0.1 mol L⁻¹ ammonium acetate solution (pH 4.6). The experimental conditions for the DPASV technique were: start potential = -1.1 V, end potential = 0.2 V, deposition potential = -1.1 V, deposition time = 120 s, amplitude = 0.05 V, modulation time = 0.04 s and scan rate = 20 mV s⁻¹. The quantification was carried out using standard addition calibration (5 additions of 100 µL of mixed standard solution containing 4 mg L⁻¹ of Zn and Cu and 8 mg L⁻¹ of Cd and Pb). For accuracy evaluation, the samples were spiked in two concentration levels (40 and 120 µg L⁻¹ of Zn and Cu as well as 80 and 240 µg L⁻¹ of Cd and Pb). The analyses were carried out in triplicate and basic statistical analyses (descriptive statistics, analysis of variance (ANOVA), Tukey post-hoc test) were performed with the Statistic 5.0 software (StatSoft Inc., Tulsa, OK, USA).

3. Results and Discussion

The direct and simultaneous determination of Zn, Cd, Pb and Cu were performed by DPASV as described and the concentration levels are shown in Table 1.

Table 1. Mean concentrations (µg L⁻¹) of Zn, Cd, Pb and Cu in wine.

Sample	Concentration (µg L ⁻¹)			
	Zn	Cd	Pb	Cu
S12	53.8 ± 0.45 ^d (0.84)	3.69 ± 0.29 ^d (7.81)	17.9 ± 0.97 ^e (5.44)	1.95 ± 0.06 ^d (3.27)
S13	4.64 ± 0.63 ^a (13.58)	5.25 ± 0.70 ^e (13.35)	4.57 ± 0.62 ^a (13.62)	6.76 ± 0.13 ^e (1.88)
MA12	57.9 ± 2.67 ^d (4.61)	2.09 ± 0.30 ^b (14.21)	8.46 ± 0.03 ^b (0.33)	1.31 ± 0.13 ^b (10.30)
MA13	16.3 ± 1.18 ^b (7.22)	1.78 ± 0.11 ^a (5.98)	5.02 ± 0.86 ^a (17.18)	1.00 ± 0.01 ^a (0.71)
ME12	22.5 ± 0.28 ^c (1.26)	1.74 ± 0.22 ^a (12.50)	5.42 ± 0.65 ^a (12.08)	1.64 ± 0.28 ^c (17.32)
ME13	69.3 ± 5.80 ^e (8.37)	2.04 ± 0.26 ^b (12.86)	13.5 ± 1.66 ^d (12.33)	2.00 ± 0.14 ^d (7.07)
PN12	15.0 ± 2.43 ^b (16.20)	2.71 ± 0.08 ^c (3.13)	10.8 ± 0.16 ^c (1.44)	10.3 ± 1.01 ^f (3.83)

Results in µg L⁻¹ (values represent the mean and standard deviation for triplicate). Means followed by equal letters do not differ significantly by Tukey test ($p \leq 0.05$); S12: Shiraz 2012; S13: Shiraz 2013; MA12: Malbec 2012; MA13: Malbec 2013; ME12: Merlot 2012; ME13: Merlot 2013; PN12: Pinot noir 2012.

The statistical analyses showed that Zn content was statistically equal to 95% of confidence level in MA13 (16.3 µg L⁻¹) and PN12 (15.0 µg L⁻¹) (different variety of grape and vintage) as well as between MA12 (57.9 µg L⁻¹) and S12 (53.8 µg L⁻¹) (different variety of grape). The same concentration of Cd was quantified in MA13 (1.78 µg L⁻¹) and ME12 (1.74 µg L⁻¹) as well as in MA12 (2.09 µg L⁻¹) and ME13 (2.04 µg L⁻¹). The Pb concentration was statistically equal in MA13 (5.02 µg L⁻¹) and ME12 (5.42 µg L⁻¹) as well as Cu concentration was the same in S12 (1.95 µg L⁻¹) and ME13 (2.00 µg L⁻¹). For all the other samples analyzed, the concentrations of metals were statistically different. These findings show that the type of grape and the differences in harvests can influence the metal concentration present in wine. The presence and the concentration of metals in wine derive from two different sources: natural (corresponding to the transfer of metals from the soil to the fruit through the roots) and anthropogenic (environmental pollution by the use of inorganic and organic fertilizers and pesticides used in agricultural practice and the deposition of the particulate material from the air on the grapes) [7].

Zinc was found in all analyzed wine samples in concentration levels smaller than the maximum accepted limit by the OIV [8] (5000 µg L⁻¹) and Mercosur [9] (5000 µg L⁻¹). However, the Brazilian Health Regulatory Agency [10] has no established limits for Zn. The amounts of Zn (vintage 2013)

found in this study ranged from 4.64 to 69.3 $\mu\text{g L}^{-1}$ (Shiraz and Merlot, respectively) and these concentrations are lower than those found by Lara et al. [3] for white (95 $\mu\text{g L}^{-1}$) and red wine (110 $\mu\text{g L}^{-1}$) from Argentina. Bentlin et al. [29] analyzed 15 samples of wine (Cabernet Sauvignon, Malbec, Shiraz, Merlot, Pinot Noir, Isabella and Bordeaux) from Brazil, 13 samples from Argentina (Cabernet Sauvignon, Malbec, Shiraz, Merlot, Pinot Noir and Assemblage), 13 samples from Chile (Cabernet Sauvignon, Malbec, Shiraz, Merlot, Carmenere and Pinot Noir) and 12 samples from Uruguay (Cabernet Sauvignon, Malbec, Shirz, Merlot, Tannat and Pinot Noir) by ICP-OES and ICP-MS, and the concentrations of Zn quantified were from 184 to 891 $\mu\text{g L}^{-1}$ (samples from Brazil), from 155 to 1239 $\mu\text{g L}^{-1}$ (samples from Argentina), from 140 to 1359 $\mu\text{g L}^{-1}$ (samples from Chile) and from 174 to 1359 $\mu\text{g L}^{-1}$ (samples from Uruguay). The authors affirm that several factors may contribute to these different concentrations, such as vine cultivation, the winemaker's knowledge, storage, fertilizers and fungicides. Blesic et al. [30] determined Zn in merlot wine from different locations by AAS and the concentrations quantified were 526 and 1856 $\mu\text{g L}^{-1}$ showing that the location influences the Zn concentration in the samples from the same grape variety and the same vintage (2010).

Cd was quantified in all samples analyzed in this work. The values were from 1.74 to 5.25 $\mu\text{g L}^{-1}$ and Shiraz (vintage 2013) had the highest concentration. It is known that the presence of Cd in wine may be directly associated with air pollution and the use of phytosanitary products [31]. Besides that, wineries located near roads or industrial areas, where emissions and vehicular discharges are intense, are susceptible to contamination by this element [32]. In addition, a significant amount of Cd present in wine, is due to contact with the apparatus used in the wine production and packaging process. Additionally, the values quantified by us are in agreement with those reported by Lara et al. [3] for white and red wine (concentration range from 1.0 to 4.7 $\mu\text{g L}^{-1}$) from Argentina by spectrometry. However, Bentlin et al. [29] found lower concentrations in samples from Chile (from 0.01 to 6 $\mu\text{g L}^{-1}$), Uruguay (0.01 to 0.5 $\mu\text{g L}^{-1}$), Argentina and Brazil (from 0.01 to 0.06 $\mu\text{g L}^{-1}$). All analyzed wine samples contained Cd to levels lower than established by the OIV [8] and Mercosur [9] (MSul) which tolerate 10 $\mu\text{g L}^{-1}$ (the Brazilian Health Regulatory Agency has no established limit to Cd [10]).

All the analyzed wine samples presented Pb levels lower than that established by the OIV (150 $\mu\text{g L}^{-1}$) [8], Mercosur [9] (300 $\mu\text{g L}^{-1}$) and the Brazilian Health Regulatory Agency has no established limits [10]. In the present study, Pb concentrations from 4.57 to 17.9 $\mu\text{g L}^{-1}$ were quantified and Shiraz (2012) had the highest concentration. These results are lower than those determined by Lara et al. [3] that were quantified from 50 to 90 $\mu\text{g L}^{-1}$. Bentlin et al. [29] quantified Pb in wine from 0.6 to 26 $\mu\text{g L}^{-1}$ (samples from Brazil), from 2 to 53 $\mu\text{g L}^{-1}$ (samples from Argentina), from 2.5 to 28 $\mu\text{g L}^{-1}$ (samples from Chile) and from 8 to 82 $\mu\text{g L}^{-1}$ (samples from Uruguay). Blesic et al. [30] determined Pb by spectrometry and found 30 and 47 $\mu\text{g L}^{-1}$ in Merlot (2010) cultivated in different places. Dessuy et al. [33] developed a method for Pb determination in wine by spectrometry without any sample preparation and the results obtained for seven samples using the proposed method as well as the analyses after an acid digestion procedure did not show any significant difference (using a Student's t-test). The Pb concentrations determined in seven arbitrarily chosen white and red wine, five from Brazil (Cabernet Sauvignon (red), Cabernet Franc (red), Merlot (red), Chardonnay (white), Semillon (white)), one from Chile (Sauvignon Blanc (white)) and one from Spain (Monastrell (red)) ranged from 6 to 60 $\mu\text{g L}^{-1}$ Pb with an average content of 11.4 $\mu\text{g L}^{-1}$ Pb for the wines from South America.

Copper was determined in all analyzed wine in concentrations below (from 1.0 to 10.3 $\mu\text{g L}^{-1}$) the maximum acceptable limit set by the OIV [8] (1000 $\mu\text{g L}^{-1}$), Mercosur [9] (1000 $\mu\text{g L}^{-1}$) and the Brazilian Health Regulatory Agency [10] (10,000 $\mu\text{g L}^{-1}$). The results obtained present lower values than that reported by Lara et al. [3] (from 23 to 28 $\mu\text{g L}^{-1}$) in red and white wine (10 samples for each one) in samples from Argentina. Sauvage et al. [11] determined Cu (330 $\mu\text{g L}^{-1}$) by AAS in white wine (24 samples) from four different regions (vintage 1997, 1998 and 1999). Bentlin et al. [29] analyzed 15 samples of wine (Cabernet Sauvignon, Malbec, Shiraz, Merlot, Pinot Noir, Isabella and Bordeaux) from Brazil, 13 samples from Argentina (Cabernet Sauvignon, Malbec, Shiraz, Merlot, Pinot Noir and

Assemblage), 13 samples from Chile (Cabernet Sauvignon, Malbec, Shirz, Merlot, Carmenere and Pinot Noir), and 12 samples from Uruguay (Cabernet Sauvignon, Malbec, Shirz, Merlot, Tannat and Pinot Noir) by ICP-OES and ICP-MS and the quantified values were from 28 to 222 $\mu\text{g L}^{-1}$ (samples from Brazil), from 20 to 249 $\mu\text{g L}^{-1}$ (samples from Argentina), from 73 to 346 $\mu\text{g L}^{-1}$ (samples from Chile), and from 21 to 1290 $\mu\text{g L}^{-1}$ (samples from Uruguay). Blesic et al. [30] determined Cu in Merlot wine (2010 vintage) by AAS and 169 $\mu\text{g L}^{-1}$ was quantified in the sample from Stolac (Bosnia) and 856 $\mu\text{g L}^{-1}$ in the sample from Trebinje (Bosnia). According to Green et al. [18] the presence of Cu in the wine can be attributed to application of fungicides in the vineyards, by spraying products containing Cu that are used for pests and disease control as well as by the contact of the must with utensils and equipment that incorporate this metal within their components.

Illuminati et al. [4] optimized the procedure for the sample pre-treatment by ultraviolet (UV) digestion and SWASV determinations was applied to samples of Podium wine (white wine of the certified brand of origin Verdicchio dei Castelli di Jesi Denominazione di Origine Controllata (DOC) Classico Superiore) from 2006 and 2009 vintages and Cd and Pb concentrations were similar in both vintages (around 0.18 $\mu\text{g L}^{-1}$ of Cd and 9.5 $\mu\text{g L}^{-1}$ of Pb). However, the Cu concentration in the 2016 vintage was higher than 2009 (35 and 19 $\mu\text{g L}^{-1}$, respectively).

For the evaluation of method accuracy, the spiked wine samples in different concentrations levels were analyzed and the recoveries obtained for Zn, Cd, Pb and Cu are shown in Table 2.

Table 2. Recovered levels (%) of Zn, Cd, Pb and Cu of seven wine with the proposed method.

Wine	Concentration Added ($\mu\text{g L}^{-1}$)							
	Zn		Cd		Pb		Cu	
	40	120	80	240	80	240	40	120
Recoveries (%)								
S12	100.3	106.0	86.4	94.2	93.6	97.7	81.4	97.1
S13	113.8	87.2	98.5	98.7	99.2	96.3	105.9	95.3
MA12	111.5	109.0	86.1	94.1	89.7	101.0	105.7	81.8
MA13	88.8	96.3	102.0	95.6	93.5	91.3	89.1	96.1
ME12	130.8	102.0	100.0	107.0	97.7	94.5	94.2	96.2
ME13	88.1	82.5	85.7	93.4	95.8	99.6	97.6	105.6
PIN12	104.5	92.6	89.5	92.3	94.7	97.5	89.2	91.1

S12: Shiraz 2012; S13: Shiraz 2013; MA12: Malbec 2012; MA13: Malbec 2013; ME12: Merlot 2012; ME13: Merlot 2013; PIN12: Pinot noir 2012.

The recovery values obtained were from 82.5 to 130.8% for Zn, from 85.7 to 107.0% for Cd, from 89.7 to 101.0% for Pb and from 81.4 to 105.9% for Cu. According to these results, we can consider the procedure used to be appropriate for the purposes of this work demonstrating that Zn, Cd, Pb and Cu can be directly and simultaneously determined in wine by voltammetry. Bentlin et al. [29] made a similar evaluation and the recoveries quantified were 99, 102 and 98% for Cd, Pb and Cu respectively, and in the work of Illuminati et al. [4] recoveries of 108% for Cd, 107% for Pb and 102% for Cu were obtained.

It should be noted that there are few studies in the literature which determine metals in wine by direct analysis, mainly using electrochemical techniques. The direct analyses of samples employed in this work present advantages such as: the sample is placed directly in the cell, there is lower risk of contamination from pretreatment steps, a small sample volume is needed, and less reagents are required.

4. Conclusions

This work described an efficient and effective procedure applied for the direct and simultaneous determination of Zn, Cd, Pb and Cu in wine by DPASV without previous sample preparation steps. The concentrations of Cu, Zn, Cd and Pb determined in the analyzed samples were lower than the maximum limit established by the OIV and Mercosur. Therefore, it can be assumed that the metal

concentrations quantified in the analyzed wine samples were influenced by viticulture and oenological practices rather than soil and other environmental conditions on the locations where grapes for wine production were grown. With the results presented here, it is possible to conclude that the method using anodic stripping voltammetry is efficient to directly and simultaneously determine Zn, Cd, Pb and Cu in different wine samples without any mineralization or pretreatment steps.

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