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An insight into the adsorption and electrochemical processes occurring during the analysis of copper and lead in wines, using an electrochemical quartz crystal nanobalance.

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ABSTRACT

Copper and lead in wine were quantified by anodic stripping voltammetry (ASV), performed onto the gold electrode of a piezoelectric quartz crystal. Both current or mass changes could be used as analytical signals, without a statistical difference in the results ($\alpha=0.05$). However, the plot of mass vs. potential provided an in depth understanding of the electrochemical processes and allowed studying adsorption phenomena. Copper interaction with fructose is an example of a process which was not possible to ignore by observing the mass change on the gold electrode of the piezoelectric quartz crystal.

1. Introduction

Copper and lead in wine may have natural sources, and rise due to their presence in the vineyard soil, and decrease during fermentation. However, copper and lead content in wine is strongly influenced by human activity. Grapes can be contaminated by atmospheric fallouts and treatment with pesticides containing metals. Metals can also be deliberately added to wine, as for instance in the form of copper sulphate, which is used to remove reduced sulphur malodour compounds [1]. Copper and lead can increase due to poor cellar practice, as for instance due to the use of lead or copper plumbing [2], and the use of reagents of enologic grade, which contain metals [1]. There was also the suspicion that lead could diffuse from the capsules through the moist cork [1,3] during storage which was proved by Gulson et al. [4] to be insignificant. Anyway, the use of those capsules is forbidden by the OIV since 1994 [5].

Copper can be responsible for oxidative spoilage of wine and its concentration must be kept bellow a recommended safe level (0.3–0.5 mg dm^{-3}) [2]. Besides, copper is toxic at high levels. Also lead, which is of no nutritional value, is very toxic, and needs to be controlled.

Spectrophotometer methodologies and flame atomic absorption spectrometry are the most used analytical methodologies for copper and lead analysis [5,6]. Lead is present in lower concentrations than copper, and a pre-concentration step or a graphite furnace is mandatory [5,7].

These methodologies can only provide total metal concentrations, but electrochemical stripping techniques, besides being sensitive enough for both copper and lead quantification in wine, can be used for speciation studies. Due to the low pH in the stomach, the total concentrations of metals are of health concern [8] and subject to legal limits (1 mg dm^{-3} for copper [9] and 0.2 mg Kg^{-1} for lead [10], which has been reduced by OIV to 0.15 mg dm^{-3} for wines produced after the harvest of 2007 [5]). However, the chemical form of the metal can be decisive for the stability of wines [11] and speciation studies are of utmost importance. Several authors refer the role of macromolecules in Pb complexation and in Pb assimilation [12].

Potentiometric stripping analysis (PSA) is based on the potentiostatic concentration of the metal on a mercury film and on its subsequent re-oxidation (stripping) [2,8,13–16]. PSA is based on the measurement of the solution potential as a response to physico-chemical changes, and does not require sample deoxygenation and it is little affected by the presence of surface active agents, as well as by electroactive organic matter. Therefore, no sample pre-treatment is needed. However, it was reported that discrepancies between values found by PSA and atomic absorption spectrometry can approach as much as 50% [17]. On the contrary, Salvo et al. [18] obtained results not significantly different from the ones obtained by AAS, by analysing Cu and Pb in wine by derivative potentiometric stripping analysis (dPSA). dPSA, in which E is ploted vs. dt/dE, allows the elimination of the capacitive current and reduces the influence of the adsorbed species [16]. In spite of the simplicity of PSA, McKinnon and Scollary [17]

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found that simple acidification of wine was not capable of detecting the total amount of copper in the majority of the analysed wines. Moreover, the use of mercury films and often the requirement of a high concentration of mercury (II) in the sample matrix to achieve fast stripping [2] pose serious environmental problems.

Voltametric methods, where potential is actively changed and the system responds in the form of a measurable current, are however not free from interferences from organic couples. Therefore, sample pre-treatments of varying complexity have been used in the analysis of metals in wine [19–21].

Using the gold electrode of a piezoelectric quartz crystal as the working electrode, allows one to know the mass deposited or stripped [22]. Through mass recording, phenomena undetected on the current vs. potential plots, could be noticed and related to the wine matrix complexity. The present work intends to show the importance of the new information gained with the introduction of the piezoelectric quartz crystal and to show that the mass deposited on the quartz, while giving an insight into non-faradaic processes, is also a direct consequence of electrochemical processes and that contains information directly correlated with the current measurements.

Therefore, mass vs. potential plot was used in the present work to investigate wine sample treatment methodologies, but also to perform quantitative analyses using the stripped mass. The metal concentration results were compared with the ones obtained from the usual current vs. potential plots, for several white and red wine samples.

Several experiments were conducted at several potential scan rates, in order to obtain data that would clarify some of the processes taking place during the anodic stripping voltametry (ASV) of copper and lead.

Fructose, sometimes regarded as a natural safe sugar, is known to interfere with the absorption of copper in rats [23]. There is some concern about its effect in humans, although there are studies showing no effect on copper balance in humans, after fructose consumption equivalent to 20% of the total energy [24]. Based on the evidences showing that fructose affects to some extent the bioavailability of copper, ASV experiments were performed with copper in aqueous solutions containing a few compounds known to be present in wine: glucose, fructose and gallic acid. New information provided by the mass vs. potential plot was obtained.

2. Experimental

2.1. Apparatus

An electrochemical quartz crystal nanobalance EQCN 700 and a potentiostat/galvanostat PS-205, both from Elchema, were used. Quartz crystals were 10 MHz AT-cut HC-6/U with gold electrodes deposited over a chromium layer (ICM-International Crystal Manufacturing Co., Inc.). Fig. 1 shows the cell layout. Cells were made of Teflon and allowed easy crystal assembling. A glass cup appropriate for holding volumes from 10 to 20 mL was easily connected to one face of the cell. Both crystal cells and cups were home-made according to a design conceived to allow changing of cups and of the crystal face in contact with the solution without dismounting the quartz crystal.

The counter electrode was a platinum wire and the reference was an Ag/AgCl (KCl sat) electrode.

2.2. Reagents

Two stock solutions, one with 1000 mg dm^{-3} of Cu^{2+} (Panreac 313178) and another one with 1000 mg dm^{-3} of Pb^{2+} (Panreac 313189) were used as standards.

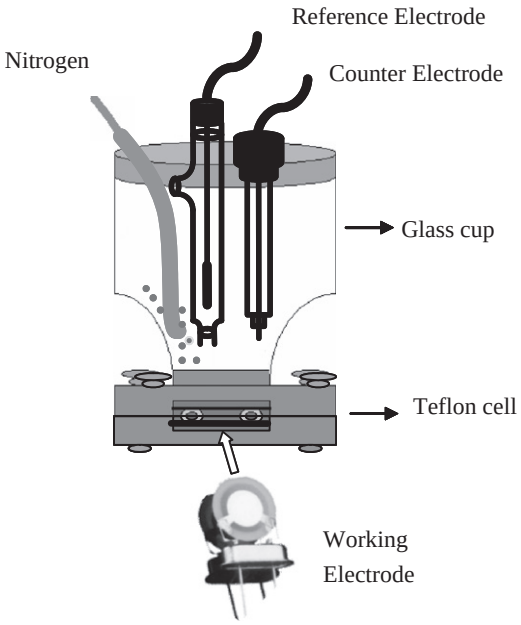

Fig. 1. New cell for the electrochemical quartz crystal nanobalance.

Gallic acid (Merck 159630), glucose (Panreac 131341.1211) and fructose (Riedel-de-Haën 15760) were used without further purification.

2.3. Procedure

All glassware, as well as the crystal cell and cup, have been soaked in nitric acid solution, rinsed with Milli-Q water and allowed to dry before the experiments.

A volume of 10.00 mL of the sample to be analysed was poured into the glass cup and contacted with one of the gold electrodes of the crystal. Reference and counter electrodes were then immersed into the solution and nitrogen was bubbled for a few minutes, in order to displace oxygen. Mass display was adjusted to zero, and the voltage was then set at the deposition potential and held at that value for 3 min. Different deposition potentials were initially used with wine samples in order to select the one which allowed an efficient copper and lead deposition (-800 mV).

A nitrogen flow of 215 mL min^{-1} was maintained inside the cell, in order to favour convective mass transport, but it was stopped 30 s before the starting of potential scanning towards the positive direction. A nitrogen blanket over the solution was maintained throughout the whole experiment. Potential was swept till $+600$ mV at a constant rate. Quantitative analysis were performed at 10 mV s^{-1}, although other scanning rates were used in some ASV experiments for clarification of some processes, namely complexation reactions. Both current and mass vs. potential were recorded.

Quantitative analysis of copper and lead in wine were performed by the standard addition method, using 10.00 mL of wine. Total copper and lead in wine were determined after an acidic pre-treatment of the wine, followed by UV irradiation.

A few experiments were also conducted in metal aqueous solutions.

3. Results and discussion

Fig. 2 shows the plot of mass and current vs. potential for a solution of 1.91 mg dm^{-3} of copper and 1.91 mg dm^{-3} of lead, prepared in MilliQ water, during an anodic stripping process (scan rate 50 mV s^{-1}). It can be seen that the mass on the gold

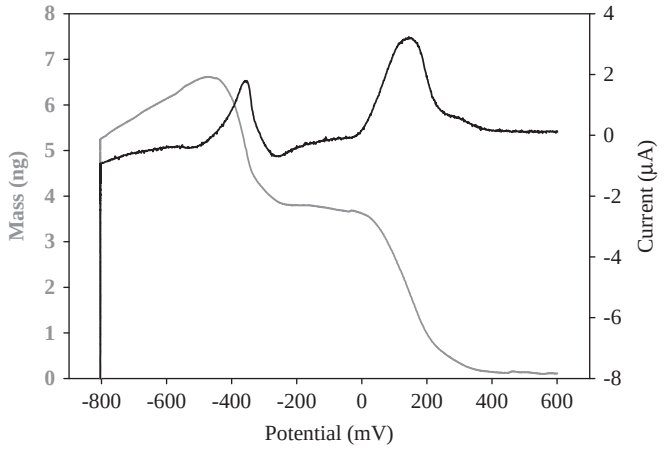

Fig. 2. Mass vs. potential and current vs. potential plots from ASV of an aqueous solution with 1.91 mg dm^{-3} of copper and 1.91 mg dm^{-3} of lead.

electrode increased during the deposition step, and that it continued to increase during the sweep of the potential towards more positive values, until the potential of oxidation of lead was achieved. At this point a simultaneous current increase and mass decrease could be noticed. Copper oxidation occurred only at about 0 V, when a marked loss of mass on the electrode was registered, simultaneously with a current flow due to copper oxidation. The complete reversibility of the deposition and stripping process was proved, as the mass on electrode returned to the initial value (zero).

Several experiments were performed at different deposition potentials in order to select the potential for the deposition of both metals from a wine sample. While copper could be deposited at a potential of −450 mV, a deposition potential of −800 mV would be necessary to obtain the maximum stripping currents for lead.

Fig. 3 (a) and (b) shows current and mass plots, respectively, vs. potential recorded during ASV analysis of a wine sample, performed with three different potential scan rates. The increase in the anodic currents with the scanning rate is a strong indication of the existence of adsorption processes [25]. Table 1 shows the anodic current of lead and copper for several scanning rates. Both for lead and copper, a correlation between current (i) and scan rate (ν) was found $i=0.096\nu+2.087$ ($r=0.998$), and $i=0.11\nu+0.83$ ($r=0.998$), respectively. The proportionality found between current and scan rate and the presence of small peaks following the main anodic peak towards more positive potentials can be explained by the adsorption of the oxidation product [26–28]. Product adsorption favours the oxidation reaction leading to the observed increase in the currents.

Mass plot of Fig. 3 (b) can give an inside picture of the adsorption and electrochemical processes that take place during the ASV. After the 3 min deposition at constant potential, copper and lead continues to be deposited until the stripping potential for each metal is attained, which happens first, in terms of potential, for the slowest scan rate, 10 mV s^{-1}, followed by the 20 mV s^{-1} scan rate and finally by the 50 mV s^{-1} scan rate. However, as the velocity increases, less time is spent reaching a certain potential and consequently, less mass is deposited. Concerning the amount metal which is deposited, these two factors act in opposite directions, and this is why the intermediate velocity, 20 mV s^{-1}, allows a higher amount of metal to be deposited, than the other two. At low scan rates, interactions with species in solution become possible, and some complexation reactions could take place. This can explain the increase in the mass which can be observed in the experiments

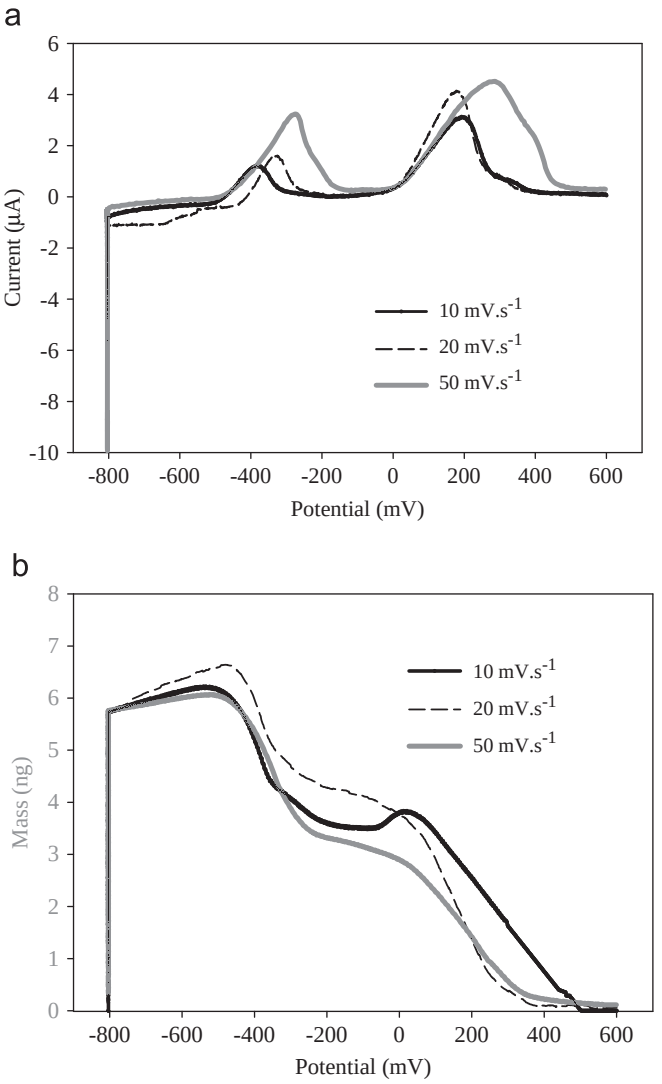

Fig. 3. ASV analysis of a wine sample, performed with three different potential scan rates. (a) current vs. potential plot, (b) mass vs. potential plot.

Table 1
Stripping currents for lead and copper in wine, obtained at several scan rates.

Scan rate (mV s^{-1})	Stripping current for copper (μA)	Stripping current for lead (μA)
10	3.0	2.0
20	4.1	3.1
30	5.2	4.2
40	5.9	4.8
50	6.7	5.9
60	7.8	6.9
70	8.5	8.0
80	9.8	9.4
90	10.7	10.5
100	11.9	11.5

with potential scan rate of 10 mV s^{-1}, approximately at the same potential at which copper oxidation starts. This mass deposition cannot be a result of an electrochemical reaction, as no current signal related with such deposition was registered. On the other side, hindered mass transport caused by organic matter adsorbed onto the electrode surface is known to be particularly effective with copper [29], and in fact, the cleaning of the electrode is particularly slow for the 10 mV s^{-1} scan rate. For higher scan rates, it is

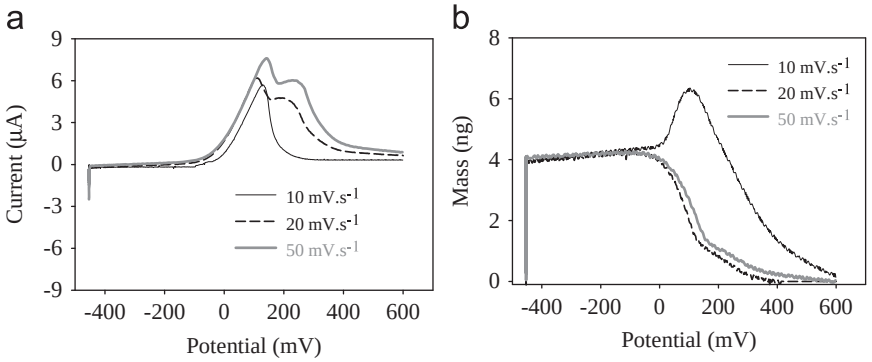

Fig. 4. ASV experiments of copper in fructose solutions, performed at different scan rates. (a) current vs. potential plot, (b) mass vs. potential plot.

expected that complexation would be kinetically hindered as well as diffusion and, in fact, the stripping at 20 mV s^{-1} is no longer more difficult than at 50 mV s^{-1}.

Fig. 4 (a) and (b) shows the current vs. potential and mass vs. potential plots, respectively, of ASV experiments of copper in fructose solutions performed at different scan rates. Marked differences can be found both in current and mass plots. These differences are remarkably similar to the previously discussed ones observed for wine. Once again, the small stripping peak attributed to adsorption is more important at higher scan rates, as little material diffuses away. The electroinactive processes, as complex formation, require time to take place and produce a mass increase on the electrode only at very slow scan rates.

ASV with a potential scan rate of 10 mV s^{-1} of copper in MilliQ water solutions containing fructose also showed a similar mass uptake around 0 V. When fructose was replaced by glucose the mass increase signal at 0 V disaperaed and it was also absent in metal aqueous solutions with gallic acid.

Fructose is present in a higher content than glucose in wines, which increases the importance of these observations on the mass plots. These observations are clearly in the direction of the modern concerns on the interaction between fructose and copper.

The anodic stripping voltammetry of wine samples requires sample pre-treatment in order to release the metal ions bound to inorganic and organic compounds. Several pre-treatments have been recommended for wine analysis by ASV [21]: acidification with HCl to pH 1.5, addition of H_2O_2 and UV irradiation for 2 h, or addition of HCl to pH 1.5 and UV irradiation for 4 h. The addition of H_2O_2 showed to be very aggressive and led to the deterioration of the piezoelectric quartz crystal. The other two methods were applied to the wine analysis. The marked mass uptake at the beginning of the stripping of copper in wine samples, which was described before, was absent in the ASV of copper in aqueous solutions displayed in Fig. 2, as well as after any of the performed pre-treatments to wine. More intense analytical signals (current or mass) were obtained after the double treatment (pH 1.5 and UV irradiation).

The mass plot is not useful just for diagnosing and to understanding the electrochemical processes, but it can be used for quantitative purposes, as long as one does remember that the first mass loss corresponds to the stripping of lead and the second mass loss to the stripping of copper.

Table 2 presents the results obtained by standard addition ASV choosing for analytical signal either the current or the mass. Copper and lead were determined in 5 bottles of Portuguese white wines and 5 bottles of Portuguese red wines. Four replicate samples of each bottle were analysed. The concentrations obtained using the mass and current were compared using a paired *t*-test. No significant differences were found ($\alpha = 0.05$).

Table 2
Results obtained by standard addition ASV, obtained monitoring the current or the mass.

Wine	Copper (μg L^{-1})		Lead (μg L^{-1})	
	Determined using the current measurements	Determined using the mass measurements	Determined using the current measurements	Determined using the mass measurements
A(white)	110.45 ± 0.01	110.43 ± 0.02	26.19 ± 0.03	26.18 ± 0.02
B(white)	106.34 ± 0.04	106.34 ± 0.02	15.84 ± 0.03	15.84 ± 0.06
C(white)	96.14 ± 0.03	96.15 ± 0.01	9.18 ± 0.01	9.17 ± 0.03
D(white)	70.70 ± 0.03	70.70 ± 0.02	18.02 ± 0.02	18.03 ± 0.01
E(white)	89.18 ± 0.03	89.18 ± 0.02	12.10 ± 0.02	12.10 ± 0.02
F(red)	99.65 ± 0.03	99.65 ± 0.05	22.82 ± 0.03	22.82 ± 0.02
G(red)	93.06 ± 0.02	93.06 ± 0.02	17.03 ± 0.01	17.03 ± 0.03
H(red)	86.86 ± 0.04	86.87 ± 0.03	30.02 ± 0.03	30.04 ± 0.03
I(red)	121.47 ± 0.03	121.47 ± 0.01	18.97 ± 0.02	18.96 ± 0.01
J(red)	107.32 ± 0.02	107.33 ± 0.04	24.50 ± 0.01	24.51 ± 0.02

4. Conclusion

The use of a piezoelectric quartz crystal as the working electrode in the ASV determination of copper and lead in wine, allowed to evidence both the role of the sample pre-treatment and the complexation of copper by matrix species, as, for instance, fructose.

This work showed that the mass vs. potential plot can provide a deeper understanding of the electrochemistry of complex samples than the ordinary current vs. potential plot, without any disadvantage from the quantitative point of view.

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