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Square-wave anodic-stripping voltammetric determination of Cd, Pb and Cu in wine: Set-up and optimization of sample pre-treatment and instrumental parameters

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ABSTRACT

For the first time, square-wave anodic-stripping voltammetry (SWASV) was set up and optimized for the determination of Cd, Pb and Cu in white wine after UV photo-oxidative digestion of the sample. The best procedure for the sample pre-treatment consisted in a 6-h UV irradiation of diluted, acidified wine, with the addition of ultrapure H_2O_2 (three sequential additions during the irradiation). Due to metal concentration differences, separate measurements were carried out for Cd (deposition potential −950 mV vs. Ag/AgCl/3 M KCl deposition time 15 min) and simultaneously for Pb and Cu (E_d −750 mV, t_d 30 s). The optimum set-up of the main instrumental parameters, evaluated also in terms of the signal-to-noise ratio, were as follows: E_{SW} 20 mV, f 100 Hz, ΔE_{step} 8 mV, t_{step} 100 ms, t_{wait} 60 ms, t_{delay} 2 ms, t_{meas} 3 ms. The electrochemical behaviour was reversible bielectronic for Cd and Pb, and kinetically controlled monoelectronic for Cu. Good accuracy was found both when the recovery procedure was used and when the results were compared with data obtained by differential pulse anodic stripping voltammetry. The linearity of the response was verified up to ~4 μg L^{-1} for Cd and Pb and ~15 μg L^{-1} for Cu. The detection limits for t_d = 5 min in the 10 times diluted, UV digested sample were (ng L^{-1}): Cd 7.0, Pb 1.2 and Cu 6.6, which are well below currently applied methods. Application to a *Verdicchio dei Castelli di Jesi* white wine revealed concentration levels of Cd ~0.2, Pb ~10, Cu ~30 μg L^{-1} with repeatabilities of (±RSD%) Cd ±6%, Pb ±5%, Cu ±10%.

1. Introduction

The content of trace metals in wine depends on several factors, such as the type of soil, the capacity of the grapes to adsorb mineral substances from the soil, the agrochemical treatments of the grapes and soils, the possible environmental pollution, the vinification processes (from fermentation reaction to the addition of substances to obtain a quality wine), the winery equipment, the wine preservation and bottling [1,2].

Trace metals (and trace elements in general) in wine are determined not only to guarantee wine quality, typicality and authenticity (especially using chemometric methods to identify the type of wine and/or its geographic origin) and in particular against fraud or adulteration [3–10], but also to evaluate possible contamination derived from environmental pollution [1,11,12], to monitor the content of substances added during the wine making process, and to demonstrate compliance with legal limits, especially for export purposes [2,13], as well as to assess the contributions the metals make to the organoleptic characteristics (flavour, aroma, colour, taste) of the wine [14].

At present, however, due to the enforcement of increasingly restrictive legal limits of metal contents in wine and to the constant quality control, there is an ever-increasing demand for sensitive, powerful and reliable analytical techniques.

Until now, determinations of trace metals in wine [13], also due to the requirements of official organizations such as the Office International de la Vigne et du Vin (OIV) [15] and of the European norms [16], have been based especially on atomic absorption spectrometry (AAS) [1,12,17–28] and, more recently, on inductively-coupled plasma mass spectrometry (ICP-MS) [29–37] or ICP-optical emission spectrometry (ICP-OES) [38–43]. Total reflection X-ray fluorescence (TXRF) has also been used [44–46]. Isotope dilution mass spectrometry was also applied to determine lead concentration and isotopic signatures in wine [47–49]. However, electroanalytical techniques, combining high sensitivity, precision and accuracy with inexpensive instrumentation, are eminently suited for heavy metal determinations in wine. In this field, with the exception of the very first application of differential pulse polarography [50], the most frequently used methods for the determination of trace metals in wine are anodic stripping

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voltammetry (ASV), in differential pulse mode (DPASV) and linear sweep mode (LSASV) [17,19,22,23,27,36,51–56], and potentiometric stripping analysis (PSA) [12,20,21,42,56–60]. To our knowledge, square-wave anodic-stripping voltammetry (SWASV), i.e. the most sensitive of all voltammetric methods [61–64] has been applied only in one work [60] and only for copper determination using a static mercury drop electrode. Moreover no general set-up of the instrumental parameters and their optimization have so far been reported.

The aim of the present work was to set up and optimize a SWASV procedure for the determination of Cd, Pb and Cu in wine (specifically a white wine) using a rotating thin mercury-film electrode (TMFE) to obtain the most sensitive system. At the same time a proper sample pre-treatment procedure by UV photo-oxidation was also set up to be applied before the voltammetric analysis. Cd, Pb and Cu were selected because they are the ideal metal ions to be determined by ASV approaches. Moreover, Cd and Pb, which are two hazardous priority pollutants, and Cu, which is an essential micronutrient but toxic at high concentrations, can be increased through vine treatments during grape cultivation and/or through cellar processing during wine making. The OIV [15] sets the following maximum levels for the three metals: Cd 0.01 mg L^{-1}, Pb 0.15 mg L^{-1} (starting from the 2007 harvest year) and Cu 1 mg L^{-1}. The voltammetric behaviour of the three metals was studied according to theoretical predictions for SWASV with TMFE [62,65].

2. Experimental

2.1. Laboratory, apparatus and reagents

Sample treatments and voltammetric measurements have been carried out in a clean room laboratory under ISO Class 5 (or US F. S. 209e Class 100) laminar flow.

The voltammetric instrumentation consisted of a Metrohm (Herisau, Switzerland) 746 VA Trace Analyser, equipped with a 747 VA Stand, a Teflon PFA cell, which includes an epoxy-impregnated graphite (Ultra Trace) rotating disc working electrode (as a support for the TMFE), an Ag/AgCl/3 M KCl reference electrode (to which all potentials are referred throughout) and a glassy carbon rod counter electrode. Details in the potential waveform used, the current sampling scheme in square-wave (SW) mode and the measurement process are reported elsewhere [66].

A Metrohm UV digestion apparatus (Mod. 705, equipped with quartz vessels and a 500 W mercury lamp) and an Orion (Beverly, MA, USA) pH meter (Mod. 290A, equipped with an Orion epoxy pH electrode Sure-Flow) were used.

The polyethylene bottles, the quartz vessels and all other plastic containers were decontaminated as reported elsewhere [64,67].

Ultrapure H_2O_2 (ca. 30%) was from Romil (Cambridge, England), while other reagents and standards were reported previously [66].

2.2. Wine samples and UV digestion

The *Podium* dry white wine of the certified brand of origin *Verdicchio dei Castelli di Jesi DOC Classico Superiore* was selected for the study. It is a wine of substantial longevity due to delayed harvesting of selected grapes and maturation of at least one year before bottling.

Bottled samples of the 2006 and 2009 vintages kindly provided by the Garofoli winery (Loreto, Italy) were analyzed. The wine of the 2009 vintage was used for all the set-up and optimization procedures.

To avoid any possible contamination, after removing the capsule and the cork (stainless steel cork-screw), the bottle neck was washed with 2 + 1000 diluted ultrapure HCl. Then the wine was sampled with a micropipette directly from the bottle.

To obtain a complete mineralization of samples, to free the bound metal ions and to destroy the organic materials which interfere with the voltammetric analysis, an UV digestion procedure was set up and used. This procedure was optimized by varying the volume of H_2O_2 added, the irradiation time, and the addition/digestion mode (in one or more steps).

For this purpose, 1 mL of wine and 10 μl of concentrated ultrapure HCl were pipetted into a 12-mL quartz vessel, and variable volumes of ultrapure H_2O_2 (1–3 mL) were then added either in a single addition at the beginning of the UV digestion, or in sequential additions during the digestion (see details below in Table 1). The solutions obtained were brought to a 10-mL total volume with ultrapure water and UV-irradiated at a temperature of ∼90 °C for periods varying between 1 and 6 h. After this treatment the digested solutions (pH 1.89) were stored at +4 °C in 50-mL polyethylene containers until analysis.

2.3. Preparation of the thin mercury film electrode

As previously described [66] the mercury film electrode was prepared by electrochemical deposition from a 6×10^{-5} mol L^{-1} $Hg(NO_3)_2$ and 1.2×10^{-4} mol L^{-1} KCl solution. For the best results the literature suggests electrochemical pre-treatments of the electrode which make use of sine wave and triangular wave scans or square-wave pulses [68–70]. The procedure used here, modified from that recommended by the manufacturer, was as follows. With electrode rotation at 3000 rpm, three sets of fast cyclic, triangular wave potential scans were applied from −1000 mV to 0 mV at a rate of 1 V/s and from 0 mV to −1000 mV at 10 V/s, one set of 100 cycles and two sets of 10 cycles, alternating with short depositions at −1300 mV for 60 s and followed by square wave scans (initial potential −1100 mV, SW amplitude 25 mV, frequency 100 Hz, step height 8 mV, step time 150 ms, measurement time 3 ms, total no. of SW cycles in each step 4, final potential −20 mV). Then, the electrochemical deposition of the mercury film was carried out at a potential of −1000 mV for 20 min (rotation 3000 rpm). Film cleaning followed at −150 mV for 5 min (3000 rpm) and finally a square-wave voltammetric (SWV) scan was carried out from −900 mV to −150 mV to check for mercury film performance (instrumental parameters as above in the electrode pre-treatment).

The thickness (l) of the film, computed from the geometric area of the graphite disc support and from the mean current measured during the Hg deposition, was $3.5 \times 10^{-5} \pm 0.3 \times 10^{-5}$ cm [66]; so, according to the literature [62,65], our electrode can be regarded as a thin mercury film electrode (TMFE).

2.4. Voltammetric analysis and optimization

The general procedure used to determine Cd, Pb and Cu in wine digested solutions was SWASV, and the background-subtraction mode was applied since significant improvements in precision of peak-current measurements have been reported [66,71–73]. Because of the very high concentrations of Pb and Cu, compared with that of Cd, unless differently stated two separate analyses, one for Cd, and one for Pb and Cu simultaneously, were carried out with different deposition potentials and times. Using 10-mL sample digested solutions purged with N_2 the metal depositions were carried out at potentials of −950 mV (t_d = 15 min) for Cd and at −750 mV (t_d = 30 s) for Pb and Cu, respectively, with electrode rotation at 3000 rpm. The deposition potentials were selected from pseudopolarographic experiments (see Section 3.2.4). After a 15-s quiescent time, the anodic stripping voltammetric scan was carried out from −950 mV (Cd) or −750 mV (Pb and Cu) to a final potential of +10 mV in SWASV mode (potential modulation conditions and