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Measurement of labile copper in wine by medium exchange stripping potentiometry utilising screen printed carbon electrodes

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ABSTRACT

The presence of copper in wine is known to impact the reductive, oxidative and colloidal stability of wine, and techniques enabling measurement of different forms of copper in wine are of particular interest in understanding these spoilage processes. Electrochemical stripping techniques developed to date require significant pretreatment of wine, potentially disturbing the copper binding equilibria. A thin mercury film on a screen printed carbon electrode was utilised in a flow system for the direct analysis of labile copper in red and white wine by constant current stripping potentiometry with medium exchange. Under the optimised conditions, including an enrichment time of 500 s and constant current of 1.0 μA, the response range was linear from 0.015 to 0.200 mg/L. The analysis of 52 red and white wines showed that this technique generally provided lower labile copper concentrations than reported for batch measurement by related techniques. Studies in a model system and in finished wines showed that the copper sulfide was not measured as labile copper, and that loss of hydrogen sulfide via volatilisation induced an increase in labile copper within the model wine system.

1. Introduction

The presence of copper(II) ions in wine can lead to oxidative, reductive and colloidal instability [1]. The source of copper in wine can stem from the use of copper-containing sprays in the vineyard, contamination in wineries and via the addition of copper(II) to wine for removal of sulfidic-off odours [1–3]. A recent review provides an in depth discussion of the importance of each of these sources of copper in wine [1]. Paradoxically, in the 1950 s, text books described the addition of sodium sulfide to wine, forming hydrogen sulfide, to remove copper(II) ions as copper sulfide precipitate, whilst in the last 30–40 years copper(II) has been added to wine to remove hydrogen sulfide [1,4,5]. In more recent times, certain wines with access to minimal oxygen and with high copper concentrations have been linked to increased concentrations of hydrogen sulfide in the wines during aging in bottle [6].

A diverse range of analytical instrumentation and methodologies have been utilised for the measurement of total copper concentration in wine [1], including electrochemical, colorimetric and flame/furnace/plasma spectroscopic techniques. However, with total concentrations in wine generally within the range of 0.02–0.5 mg/L [7], often the more sensitive techniques are required to accurately determine the copper at low concentrations.

In addition to measures of total concentration, techniques have been developed to measure different forms of copper(II) in wine [7–11] with the ultimate aim of relating specific forms to the likelihood of copper-induced wine spoilage. The main variation in measuring the different forms of copper(II) compared to total measures, was the removal of digestion steps, and the need for a fractionation pretreatment step for the flame/furnace/plasma spectroscopic techniques [8,9,12]. For other techniques, such as colorimetric and electrochemical analysis, the methodology was generally developed to involve minimal manipulation or adulteration of the sample. Extensive dilution of sample and addition of supporting electrolyte and/or colorimetric reagents were still necessary to enable measurement [11,13], leading to possible perturbation of the balance of copper between its various forms. In this sense, the measurement of the different forms of copper(II) in wine with added reagents generated results that were methodology dependent or operationally defined. For electrochemical techniques, the broad categories of 'labile' and 'non-labile' copper were defined as forms of copper able to be detected or not-detected, respectively, by the combined electrochemical technique and any necessary pretreatment of the sample. In general, it was anticipated that the labile measure would equate to loosely bound

Abbreviation: ICP-OES, Inductively Coupled Plasma – Optical Emission Spectroscopy

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and reactive metal species, while the non-labile fraction would be more tightly bound and inert metal species. For the electrochemical stripping techniques with sufficient sensitivity to measure the low concentration of labile copper in wine, the biggest challenge was the compromise between minimal perturbation of the sample and limiting the interference caused by organic compounds adsorbing on the working electrode (typically a thin mercury film).

One approach to overcome this complication utilised stripping potentiometry [14,15] with a 3-in-1 electrode and a medium exchange step [7]. This technique enabled enrichment of copper(II) from wine into a thin mercury film, then washing the organic compounds from the film before final stripping into an optimised 4.0 M ammonium acetate solution. Consequently, the unadulterated wine was analysed and interference from surface adsorbing organic compounds minimised. This technique, however, had the disadvantage of batch analysis whereby an open container and rapid stirring (~3000 rpm) of sample was required. Given that copper in wine is known to bind sulfide [2], the loss of hydrogen sulfide in the open container during rapid stirring could lead to an increase in labile copper concentration during the measurement. Further, the constant exposure of the same wine sample to the mercury electrode at low potential values (−700 to −900 mV) may well disturb the binding of copper to wine components.

The advance in screen printed electrodes with combined working, reference and counter electrodes presents an alternative to the earlier designed 3-in-1 electrode hardware. Not only is there the possibility for medium exchange in batch mode but also their utilisation in closed flow cell systems. Such screen printed electrodes, in conjunction with a thin mercury film, have been utilised for total copper measurements by square wave anodic stripping voltammetry in seawater and marine samples [16,17]. Furthermore, screen printed electrodes have been utilised with medium exchange for the analysis of total lead and cadmium concentrations in water by differential pulse anodic stripping voltammetry [18,19].

This study was conducted to afford the measurement of labile copper in wine on a thin mercury film with commercially available screen printed electrodes. The technique was designed in such a way as to allow direct measurement of labile copper in unadulterated wine and to minimise disturbance of the sample during measurement, including measurement in a closed flow cell. Analysis of 52 red and white wines was conducted, and the ability of the technique to discriminate labile copper from copper sulfide in wine and model wine systems was investigated.

2. Material and methods

2.1. Reagents and instrumentation

All glassware was soaked overnight in 10%(v/v) nitric acid and then rinsed with copious amounts of 18.2 MΩ water prior to usage. Working standard solutions were prepared by dilution of an ICP standard solution (1001 mg/L, Sigma-Aldrich). Dilution of standards was performed with model wine, consisting of 12%(v/v) aqueous ethanol, 0.011 M potassium hydrogen tartrate, and 0.007 M tartaric acid and pH of 3.2. Wine and model wines with variable hydrogen sulfide to copper mole ratios were prepared with copper(II) sulfate pentahydrate (>99%, BDH) and sodium sulfide (>98%, Sigma-Aldrich).

All electrochemical experiments were performed with a 797 VA Computrace (Metrohm, Herisau, Switzerland) and managed with the VA Computrace 797 PC Software (v1.3). A DropSens 110 screen printed carbon electrode (DropSens, Llanera, Spain) was utilised, which consisted of a 4 mm carbon working electrode, carbon counter electrode and silver reference electrode, and the electrode was connected to the 797 VA Computrace system via a CAC connector cable (DropSens). Based on the comparison of potentials for the copper stripping signals on the thin mercury film upon the (DropSens 110) screen printed carbon electrode with those obtained in previous studies [7] under identical stripping conditions, the screen printed Ag reference electrode reported potentials 0.25 V more negative than the traditional Ag/AgCl electrode. For batch analysis, the electrode was transferred using a Radiometer SAC80 Sample Changer (Copenhagen, Denmark) that was operated manually, and stirring was achieved with the standard propeller stirrer (10.0 mm propeller blade, speed setting 3) on the SAC80. For flow analysis, a methacrylate (transparent) wall-jet flow-cell (DropSens) was used. Sample flow into the cell was controlled with a Waters Reagent Manager pump (Waters, Milford, USA), whereby the restrictor coil was 120 mm in length to provide a back pressure of 100–200 psi. Stripping solutions were controlled with either an Ismatec peristaltic pump (Zurich, Switzerland), using PVC tubing (2.05 mm i.d.), or a Finnigan MAT Spectra System P4000 HPLC pump (Waltham, USA), and the stripping solutions were passed through an on-line Alltech Elite Degasser. A six channel Rheodyne TPMV valve was used to switch between sample and washing/stripping solutions. A second six channel Rheodyne TPMV valve was used to switch between the 60%(v/v) aqueous ethanol wash solution and the 4.0 M ammonium acetate stripping solution when the peristaltic pump was used. Stripping potentiograms were plotted as dt/dU vs U, by the VA Computrace 797 PC Software (v1.3), where U represents potential (V) and t represents time (s).

2.2. Medium exchange stripping potentiometry: batch analysis with mercury film screen printed carbon electrodes

All sample, rinse, wash and stripping solution volumes were 25 mL during batch analysis. The electrode plating solution consisted of 0.13 M HCl and 800 mg/L $HgCl_2$. The electrode was placed in the plating solution, the potential set to −300 mV and stirring commenced. The stirring rate was a compromise between speed, limiting bubble formation and exposure of the electrode to air upon vortex formation. The electrode potential was set to −300 mV for 2 min, then −500 mV for 1 min, −700 mV for 1 min, and −1000 mV for 4 min. The potential was then set to −250 mV and the electrode was transferred via two rinse solutions of 0.1 M KNO_3 to a solution of 4.0 M ammonium acetate.

During analysis the electrode was initially transferred via two rinse solutions (0.1 M KNO_3) to the sample. Enrichment was performed at −900 mV with stirring for typically 375 s and then no stirring for 5 s, after which the electrode was transferred via one 0.1 M KNO_3 rinse solution, and one wash solution (60% (v/v) ethanol, 0.25 M acetic acid and 0.25 M ammonium acetate) to another wash solution. Stirring was performed for 8 s and no stirring for 2 s in the wash solution. After this the electrode was transferred via a 4.0 M ammonium acetate rinse solution to the final 4.0 M ammonium acetate stripping solution. This solution was stirred for 5 s and not stirred for 15 s, after which stripping occurred as control of the potentiostat was released [20] and the potential monitored from −900 mV to −200 mV and a constant current of 3.0 μA applied. A cleaning step consisted of −300 mV being applied with stirring for 10 s in the 4.0 M ammonium acetate solution before transfer via two 25 mL 0.1 M KNO_3 rinse solutions to the plating solution. The potential was then set to −900 mV for 8 s with stirring before 2 s without stirring. This final step was conducted to repair any deterioration of the thin mercury film by particulate matter in the wine. Quantification was performed with an external calibration graph in the model wine