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Electrochemistry applied to the analysis of wine: A mini-review

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ABSTRACT

Many redox species in wine are amenable to electroanalytical monitoring. This review focuses on voltammetric approaches, with some mention of potentiometric measurements. Particular attention is given to carbon-based electrodes, and the voltammetric signals obtained in red and white wines, along with electrodes modified with various agents including conducting polymers. The analytical targets include wine phenolics, and antioxidant additives such as sulfites and ascorbic acid. Further approaches to create 'electronic tongues' are also introduced, where the range of targets expand to include several chemical constituents and sensory descriptors.

1. Introduction

Quality winemaking is all about redox reactions. While the underlying aroma and taste potential is established in the vineyard, decisions around the extent of oxygen exposure, and the application of antioxidants to juices and wines, contribute enormously to the final wine style [1,2]. At the extremes, an excessively oxidised wine is brown in colour and depleted in fruity aromas, while so-called unwanted "reductive", or rubbery/flinty aromas develop in certain wines where the oxygen content is low. The modern understanding of wine chemistry centres on phenolic compounds as the initial substrate of oxidation, in processes catalysed by metals such as Fe and Cu, leading to reactive quinones and hydrogen peroxide. These compounds promote reactions that are frequently desirable in red wines and undesirable in white wines [3,4].

Given that key redox-active species can also be oxidised and reduced at electrodes, applications of electrochemistry have been developed both to quantify such species, and to probe wine maturation processes. Target species that can be oxidised include phenolics, sulfites (SO_2 in solution), ascorbic acid, glutathione and ethanol, while species that can be reduced include oxygen, H^+, quinones and metals ions. Different electrodes will respond to varying extents to these species, while further choices involve the methodology to be applied, such as potentiometry or voltammetric techniques.

One procedure with a long history in enology is the measurement of the open-circuit potential at bright platinum electrodes, known as the redox potential of wine [5,6]. However, studies at a variety of electrode surfaces, including platinized platinum [7,8] raised questions about the origin of the value, which was ascribed to a mixed potential involving coupling of ethanol oxidation and reduction of oxygen, with minor contributions expected from the phenolics and metal ions [9,10]. At best the value provides a broad measure of oxygen content, which can be made more accurately with alternatives such as the Clark electrode [11]. Platinum electrodes have also been used during potentiometric titrations, typically starting with a pre-reduction step with trichlorotitanium to a potential of −400 mV (Ag/AgCl), then oxidation with dichloroindophenol to a potential of +400 mV, to obtain a measure of the 'resistance to oxidation' [12]. However, concerns have been raised about the slowness of the reaction with reduced components in wine [13].

This review will focus on voltammetric techniques that have been developed for the electrochemical characterisation of wines, including modified electrodes. However, the review will not cover biosensors based around the inclusion of enzymes developed for the analysis of phenolics [14], and other beverage components, but will briefly touch on approaches to develop 'electronic tongues' for wine analyses.

2. Voltammetry at carbon electrodes

Carbon-based electrodes have proven to be very suitable for the reversible oxidation of common phenolic compounds with an *ortho*-diphenol (catechol) group [15], while showing little background current due to ethanol oxidation [16]. Glassy carbon electrodes set at 400 mV (Ag/AgCl) are effective electrochemical detectors for the more easily oxidisable phenolics to provide a total 'antioxidant power' measure in Flow Injection Analysis, [17] and for the quantification of individual phenolics in HPLC [18]. The flexibility of adjusting the electrode

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potential to higher values allows a progressively wider range of phenolic compounds to be monitored.

The electrochemical properties of wine phenolics, and relative reducing strengths, have also been examined using cyclic voltammetry (CV). Phenolic standards are often prepared in a 'model wine solution' (typically 0.033 M tartaric acid in a 12% ethanolic solution with pH adjusted in the 3.3 to 3.6 range) [16]. Likewise well-defined voltammetric peaks are obtained for wines, once these have been diluted sufficiently to obtain peak currents that change linearly with wine dilution, which requires around 10-fold dilution for white wines, but up to 400-fold with red wines. Wines show an anodic peak at around 400 mV due to the oxidation of catechol and galloyl-containing phenolics (Fig 1), and the peak current provides a measure of caffeic acid-type hydroxycinnamic acids in whites wines [19]. Further current at higher electrode potentials is due to compounds with more isolated phenolic groups. Red wines usually show a major peak at around 650 mV, associated with the malvidin anthocyanins not present in white wines.

Owing to the diversity of phenolic compounds that contribute to peaks and shoulders in wine voltammograms, quantification of the phenolics can be made either with peak current, or with the integrated charge over a certain potential range, e.g. to 500 mV (Q_{500} value) for the stronger reducing agents present. The extent of adsorption of phenolics at glassy carbon electrodes has also been examined, with particularly strong adsorption seen with phenolics in the flavonol class [19]. Voltammetric approaches with glassy carbon and graphite electrodes have been undertaken by several groups to obtain total phenolic measures [20–23], and have even been compared to perceived astringency involving phenolics [23]. Methods based upon disposable electrodes have also been developed, including screen-printed graphite electrodes [24], and carbon paste electrodes with undiluted wines to provide an "oxidation signature" given by the changes in the voltammetry after saturation with oxygen [25].

The first anodic peak can also contain contributions from ascorbic acid, sulfites and glutathione [21]. While ascorbic acid on its own shows an anodic peak in the 200 to 250 mV (Ag/AgCl) range, the presence of adsorbed phenolics was found to raise the overpotential for ascorbic acid oxidation to overlap with that due to phenolic compounds [26]. The response given by sulfites is also affected by the presence of phenolics. Very little oxidation current is seen for sulfites on their own at potentials less than 500 mV [16,26], but the ability of free SO_2 to reduce the quinones formed by the oxidation of catechol-containing phenolics, results in a current increase in the 400 mV peak [26]. To obtain the more accurate measure of the phenolic compounds, a drop of acetaldehyde can be added prior to taking a voltammetric scan to bind up the free SO_2 [19]. The difference in voltammograms obtained with and without acetaldehyde can also be used to obtain a measure of the free SO_2 present in white wines [19]. Glutathione also interacts with quinones in a similar manner to sulfites and can increase the current due to the oxidation of catechol-containing phenolics [26].

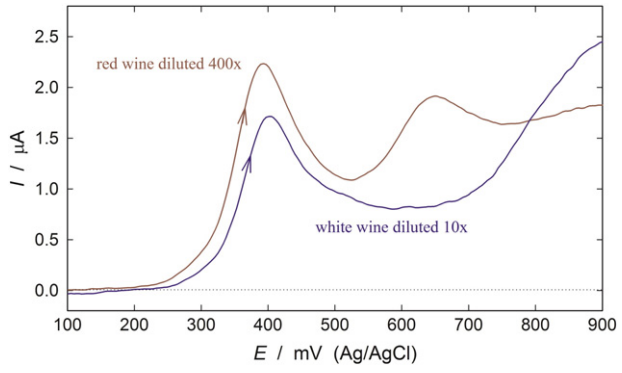

Fig. 1. Typical linear sweep voltammograms of red and white wines, at 100 mVs^{-1} taken at a 3 mm dia. Glassy carbon electrode for wines diluted in a model wine solution (adapted from [16]).

Sensitive and well-resolved voltammetric signals for the oxidation of wine phenolics can be obtained through the use of differential pulse voltammetry (DPV) [27–29]. The first anodic peak was used to quantify polyphenols in terms of catechin-equivalents for red wines diluted 400-fold [28]. DPV was found to be more resistant to effects of electrode poisoning than CV for wines with a higher phenolic content [29]. Voltammetric measures of total phenolics tend to be lower in value compared to those obtained with the conventional Folin-Ciocalteau reagent, an observation that has been ascribed to the ability of the regeant to react with a wider set of oxidisable species [27,30–32].

3. Voltammetry at modified electrodes

Alternative electrode materials have been tested for the voltammetric analysis of wines, to improve sensitivity and response selectivity. Modification of a carbon paste electrode with carbon nanotubes allowed the antioxidant capacity of wine to be evaluated using DPV in terms of gallic acid equivalents [32]. DPV and a chronocoulometric method was used to assess wine phenolic antioxidants using an electrode modified with multi-walled carbon nanotubes [33]. The oxidation current was enhanced 5-fold compared to bare glassy carbon, with three to four main anodic peaks matching the different types of phenolic compounds present. A phenolic-based electrode was obtained through the prior oxidation of caffeic acid to produce a poly(caffeic acid) thin film with its own internal redox processes [34]. DPV and a standard additions method was used to obtain a total polyphenols measure with the poly(caffeic acid) electrode [34], and in a further study with a gold-chitosan nanocomposite electrode [35].

Among further modified electrodes, the conducting polymer poly-3,4-ethylenedioxythiophene (PEDOT) has received particular attention due to improved sensitivity and antifouling properties. Multiple voltammetric scans obtained with DPV and CV were used to classify different types of undiluted white [36] and red wines [37,38], through the application of particular signal acquisition protocols. Separation of the response due to ascorbic acid, sulfites and wine polyphenols has been achieved at PEDOT electrodes [37,38], which can merge at glassy carbon electrodes [26]. With phenolics such as caffeic acid, the current peak returned to the background PEDOT response soon after the current peak, pointing to voltammetry of an adsorbed species rather than to one under diffusion control [39]. The current due to added sulfites continued at potentials greater than 600 mV when the caffeic acid peak was already completed (Fig. 2A), and could be used to quantify the SO_2 present [39]. In the presence of both caffeic acid and sulfites, an earlier peak at 240 mV due to ascorbic acid can be clearly seen and used for quantification purposes (Fig. 2B). The methodology holds promise for the analysis of white wine phenolics, while recognising the need to control pre-analysis holding time when the phenolic compounds adsorb on the PEDOT electrodes [40]. Levels of caffeic acid in white wines have been determined at PEDOT electrodes using CV and a standard additions method without interference from ascorbic acid [41].

Electrode modification has also been considered for the analysis of sulfites, including various metal complexes such as ferrocenes and porphyrin macrocycles, as previously reviewed [42]. While these may lower the potential for sulfite oxidation below that of the phenolics present, interference from ascorbic acid is still expected. Another electroanalytical approach with sulfite has been to pursue reduction of the anion and the generation of a cathodic signal [42]. A cathodic current at a glassy carbon electrode has been used to monitor the reagent 5,5-dithio-bis(2-nitrobenzoic acid), as the reagent was titrated with the sulfite in wines [43]. While small amounts of sulfhydryl compounds may interfere, the methodology does not suffer interferences from phenolics and ascorbic acid.