



## Comparative study of the antioxidant capacity and polyphenol content of Douro wines by chemical and electrochemical methods



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### ABSTRACT

A comparative study of the antioxidant capacity and polyphenols content of Douro wines by chemical (ABTS and Folin–Ciocalteu) and electrochemical methods (cyclic voltammetry and differential pulse voltammetry) was performed. A non-linear correlation between cyclic voltammetric results and ABTS or Folin–Ciocalteu data was obtained if all types of wines (white, muscatel, ruby, tawny and red wines) are grouped together in the same correlation plot. In contrast, a very good linear correlation was observed between the electrochemical antioxidant capacity determined by differential pulse voltammetry and the radical scavenging activity of ABTS. It was also found that the antioxidant capacity of wines evaluated by the electrochemical methods (expressed as gallic acid equivalents) depend on background electrolyte of the gallic acid standards, type of electrochemical signal (current or charge) and electrochemical technique.

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### 1. Introduction

Cyclic voltammetry (CV) has become a widely used tool to screen the antioxidant properties of beverages (Pisoschi, Danet, & Kalinowski, 2008), plant extracts (Barros, Cabrita, Boas, Carvalho, & Ferreira, 2011) and biological fluids (Kohen, Vellaichamy, Hrbac, Gati, & Tirosh, 2000), providing information on the potential redox and antioxidants content from the peak potential and current intensity, respectively.

The application of cyclic voltammetry to wine analysis dates back to 1988 (Lunte, Blankenship, & Read, 1988). In that work, CV was used to evaluate the suitability of using an electrochemical detection method coupled to HPLC, to detect and identify flavonoids and procyanidins in wine extracts. However, the first application of CV to characterise antioxidant properties in red and white wines was only reported in 2001 (Kilmartin, Zou, & Waterhouse, 2001). It was shown that CV provides a qualitative and quantitative assessment of wine phenolics based on their reducing strength, and charge passed to 500 mV (vs Ag/AgCl). The same research group also demonstrated the coherence of the cyclic voltammetric response with the information provided by HPLC, Folin–Ciocalteu assays and absorbance at 280 nm on white and red wines (Kilmartin, Zou, & Waterhouse, 2002). Analogous conclusions were obtained on monitoring the evolution of some phenolic compounds during the fermentation of red wine musts (Zou, Kil-

martin, Inglis, & Frost, 2002). Cyclic voltammetry was also used to investigate the influence of sulfur dioxide, glutathione and ascorbic acid on polyphenol oxidation processes relevant to wine oxidation (Makhotkina & Kilmartin, 2009).

Despite the utility of cyclic voltammetry, differential pulse voltammetry (DPV) is particularly suitable to study electrochemical systems involving adsorbing species that are not electroactive, which may mask the electrode response, due to the better discrimination between background electrolyte current and faradaic current (Brett & Brett, 1993). Regardless of the DPV advantage, the first application of this technique to the evaluation of the antioxidant capacity of wines was only reported in 2010 (Aguirre et al., 2010). It was applied to determine anthocyanin composition in Chilean red wines. Recently, the same group demonstrated that DPV was also a suitable technique to differentiate between young and aged red wines (Aguirre et al., 2011). This electrochemical technique was also applied to different Croatian red wines and a good correlation was found between the total polyphenols content determined by DPV, Folin–Ciocalteu assays and HPLC (Seruga, Ivana, & Jakobek, 2011). The use of a modified electrode, a carbon paste electrode modified with carbon nanotubes, was also successfully applied for the estimation of antioxidant capacity in red and white wines by DPV (Souza, Calegari, Zarbin, Marcolino-Júnior, & Bergamini, 2011).

So far, the results obtained by CV have never been compared with those obtained by DPV, nor correlated simultaneously with other conventional techniques for determination of the wine antioxidant capacity and total polyphenols content. Therefore, this

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work aims to perform such a comparative study using typical 2009 Douro region wines. In this region, considered a World Heritage region, there are three types of Port wine: tawny, ruby and white. In addition, muscatel and red wines of Douro region will be also studied.

## 2. Materials and methods

### 2.1. Chemicals

Gallic acid, 2,2'-azino-bis(3-ethyl-benzothiazoline-6-sulfonic acid) diammonium salt (ABTS 98% pure) and pure ethanol were purchased from Sigma–Aldrich (St. Louis, MO). Acetic acid, sodium hydroxide, sodium carbonate, potassium persulfate (99% pure) and Folin–Ciocalteu reagent were purchased from Panreac (Barcelona, Spain). Sodium acetate (99%) and L-tartaric acid were purchased from Merck (Darmstadt, Germany). Alumina (0.3  $\mu\text{m}$ ) powder was obtained from Buehler, Lake Bluff, IL. All solutions were prepared using high-purity water from a Milli-Q system.

### 2.2. Samples and standards

The samples used in this study were selected from various types of wines available in the Douro Region of Portugal: two red wines – Porca de Murça (RM) and Fialhoza (RF), two tawny Port wines – Essentia (PE) and Quinta do Infantado (PI), one ruby Port wine – Quinta do Infantado (PR), one white Port – Quinta do Infantado (W) and two muscatel – Favaíto (M) and Vista Alegre (MVA).

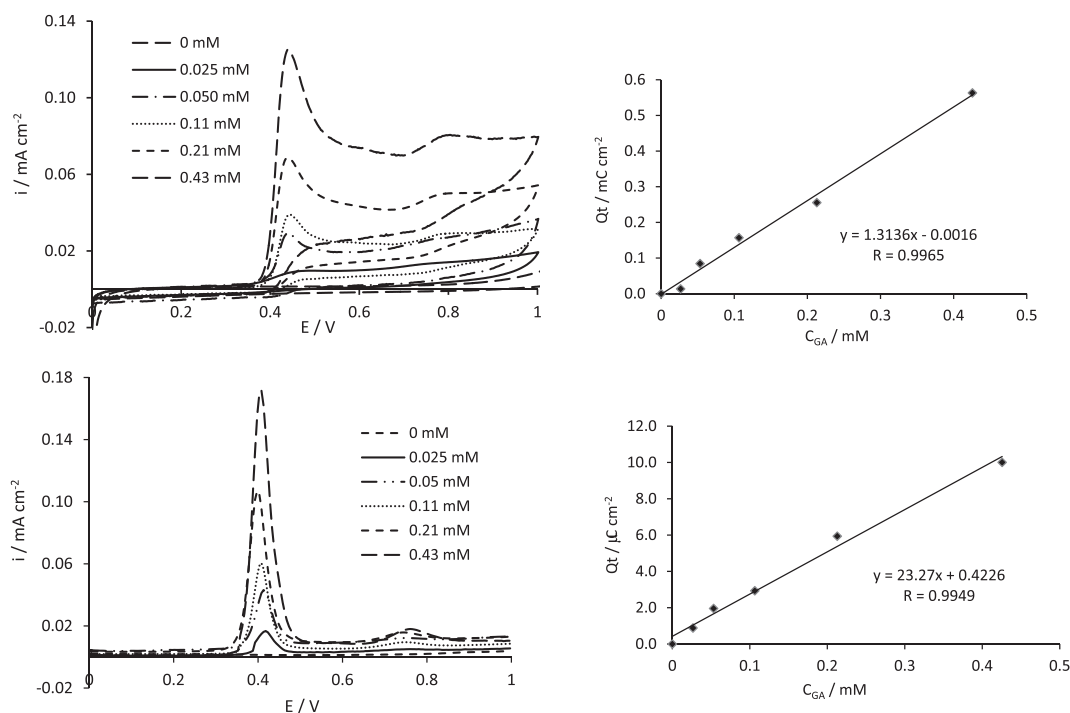
For the electrochemical experiments wine solutions were diluted with an alcoholic solution, composed of 33 mM L-tartaric acid, a volume of ethanol corresponding to the concentration of alcohol in each type of wine (12% v/v for RM and RF; 17% v/v for M, 19.5% v/v for PE, PI, W and PR) and NaOH solution to give a pH of 3.6. For quantitative analysis, gallic acid standard calibration curves were constructed for the cyclic voltammetric and differen-

tial pulse voltammetric data. Unless otherwise stated, the gallic acid standards were freshly prepared from a gallic acid stock solution (26.6 mM) by diluting it with 0.1 M sodium acetate–acetic acid buffer (pH 3.6).

### 2.3. Electrochemical assays to evaluate antioxidant capacity

The wine antioxidant capacity was determined by CV and DPV experiments and expressed as milligram of gallic acid equivalents per millilitre of wine (mg GAE/mL wine). The gallic acid standard calibration curves were obtained by plotting the total charge of the anodic oxidation peaks versus the concentration of gallic acid (0.025–0.426 mM), Fig. 1. The voltammetric experiments were carried out at room temperature in an electrochemical cell of three electrodes. The working electrode was glassy carbon with 0.196  $\text{cm}^2$  of area, the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum foil. Glassy carbon electrode was polished before any electrochemical measurement in an aqueous suspension of alumina 0.3  $\mu\text{m}$  (Buehler), washed with Milli-Q water and then sonicated for 2–3 min. Prior to the measurements, the electrolyte solutions were de-aerated with an inert gas ( $\text{N}_2$ ) for approximately 10 min. This step allows removing free  $\text{SO}_2$  from the diluted wines. The electrochemical experiments were performed using a potentiostat/galvanostat (Autolab Model 100) controlled by GPES 4.9 software (Metrohm Autolab B.V., Utrecht, The Netherlands).

For the wine samples a 50-fold dilution was required to reach a range in which the anodic peaks charge was directly proportional to the volume fraction of the wines. The cyclic voltammograms were recorded on freshly polished glassy carbon electrode by scanning the potential from 0.0 to 1.0 V at a scanning rate of 25 mV/s. On the differential pulse voltammetric assays the potential was scanned from 0.15 to 1.0 V with a step potential of 5.0 mV, a modulation potential of 25 mV and a pulse width of 50 ms ( $\nu = 10$  mV/s).



**Fig. 1.** Cyclic and differential pulse voltammograms of gallic acid standards prepared in a 0.1 M acetic acid/acetate solution, adjusted to pH 3.6. The corresponding calibration curves (charge vs concentration of gallic acid) are also shown its better to not mention the scan rate because such value is only related to the cyclic voltammograms, not to the differential pulse voltammograms.

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