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Evaluation of total polyphenol content of wines by means of voltammetric techniques: cyclic voltammetry vs differential pulse voltammetry

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Abstract

Taking advantage of the low oxidation potential of polyphenolic compounds, voltammetric techniques, such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are used rather indiscriminately. In this work, we report Total Polyphenols results (TPP) obtained by these two techniques from a set of nine samples of red and Tawny Port wine. The CV and DPV voltammograms display significant correlations with the physical-chemical parameters used to characterize red and Tawny Port wines, particularly with polyphenols. Although data obtained from CV and DPV for a single polyphenol are directly proportional, important deviations are found between voltammetric results from wines. Results from CV tend to be larger than those from DPV. This difference, that can reach 50 % of the TPP value, was related to the presence of total sulphur dioxide. In view of the present study, the polyphenol quantification in wines should be performed by DPV to minimize the interference of SO_2.

Keywords

Polyphenols; Sulphur dioxide; Wine characterization; Voltammetric techniques; Chemometrics

1. Introduction

Grapes are one of the most important natural source of phenolic compounds. In wine, polyphenols play a central role, affecting its organoleptic properties, aging capacity and shelf life(Lissi et al., 2014). In quality control these class of compounds may be appraised by absorbance measurement at 280 nm or by the Folin-Ciocalteu colorimetric assays. The simplicity of both procedures justifies the acceptance of these approaches, notwithstanding the recognized limitations associated with overestimation of the polyphenol content due to the contribution of non-polyphenolic substances(Blasco et al., 2005).

Voltammetric methods are being increasingly applied in the evaluation of polyphenols in foodstuff(Sochor et al., 2013),(Hoyos-Arbeláez et al., 2017). Some examples regarding the use of voltammetric assays are the evaluation of the total phenolic content of wine(Kilmartin et al., 2001),(Kilmartin, 2016) (Rebelo et al., 2013), teas(Piljac-Žegarac et al., 2010),(Głód et al., 2014), and fruit juice(Makhotkina and Kilmartin, 2012), the discrimination between different classes of polyphenols in complex samples(Głód et al., 2014),(Blasco et al., 2004),(Šeruga et al., 2011), monitoring of wine accelerated aging(Rodrigues et al., 2007), (Martins et al., 2008) and classification of wines regarding variety and vintage(Ugliano, 2016).

In these assays, polyphenols are quantified from current generated at an electrode when the potential is take to a range where oxidation occurs. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are among the most widely used electroanalytical techniques.

Voltammograms from natural samples result from the overlapping of current responses from a large number of polyphenols, originating bands by CV and broad peaks by DPV. Despite the technique, the quantification is mostly performed by means of the integration of voltammograms in predefined potential ranges and using calibration curves from a standard polyphenol. The polyphenols content is expressed by parameters, such as the Electrochemical Index(Blasco et al., 2005), Total Polyphenol Index(Cetó et al., 2012), Total Polyphenolic Content(Bisetty et al., 2011) or Total Antioxidant Potential(Głód et al., 2014).

CV and DPV are used for the quantification of total polyphenols in an almost indiscriminate way. However, the electrochemical responses obtained using these two techniques are substantially different regarding some fundamental aspects namely: i) the susceptibility to residual current; ii) the time base of the experiments and iii) the shape of the voltammetric curve. First, DPV as a differential technique is immune to residual current while CV is sensitive to residual current. This difference is even more significant when the measurement involves the integration of voltammograms. Second, as the electrochemical oxidation of polyphenols are coupled to homogeneous chemical reactions, the extent of charge transfer tends to increase for lower scan rates. Therefore, the relative contribution of polyphenols with slower coupled chemical reactions is higher for DPV (that is typically performed using a step potential of 5 mV and a modulation potential of 25 to 100 mV, corresponding to a scan rate of about 5 to 10 mV s^{-1}) comparatively to CV (performed using a scan rate typically between 50 to 100 mV s^{-1}). Third, the contribution of each polyphenol to a total phenolic parameter does not depend on the peak position by DPV. This is a consequence of the peak shape of DPV voltammogram where the current response is essentially confined to potentials

between E_p- $W_{1/4}$ and E_p+ $W_{1/4}$ (E_p is the peak potential and $W_{1/4}$ is the peak width at ¼ of its height). For cyclic voltammograms the situation is completely different as current becomes important for potentials close to $E_{p/4}$ and keeps substantial values for potential higher than the E_p (current tends to a steady-state value). Therefore, the extent of the contribution of each polyphenol depends on its position in the integration range of potentials, increasing with decreasing E_p values.

These aspects are associated with a different sensitivity to interferences, and may lead to substantial differences between results from these two techniques regarding the quantification of a total polyphenols parameter. As far as we are aware, there is only one publication that compares CV and DPV data from the same set of wine samples. In this work Rebelo et al. (Rebelo et al., 2013) found significant differences (from 70 % to 170 %) between the total polyphenol evaluated by these two electrochemical techniques. This difference cannot be *a priori* justified by any theoretical principle and the results do not clarify the origin of the difference. As the equivalence of results of total polyphenols in wine from the two techniques was not demonstrated, the question regarding the most adequate technique for this application remains without answer. In this work, the characteristics of CV and DPV are compared in terms of sensitivity, detection limits and bias. Voltammograms from samples of red and Tawny Port wines by CV and DPV are analyzed using chemometric tools to determine the more suitable technique for the analysis of polyphenols in wines.

2. Reagents and methods

2.1 Samples characterization

Wine samples were supplied by *Sogrape Vinhos S.A.* Five samples of red wine originated from different demarcated wine regions, were assigned by VT1, VT2, VT3, VT4. The region, harvest year and grape varieties from each wine used is listed below.

VT1- Dão; 2012; 30 % Touriga Nacional, 29 % Tinta Roriz, 24 % Alfrocheiro, 17 % Jaen. VT2 – Douro standard; 2013; 30 % Touriga Franca, 30 % Tinta Roriz, 20 % Touriga Nacional, 20 % Tinta Barroca; VT4 – Douro; 2014; 35 % Tinta Roriz, 30 % Tinta Barroca, 30 % Touriga Franca, 15 % Touriga Nacional. VT5 – Douro; 2013; 80 % Touriga Franca, 15 % Touriga Nacional, 5 % Tinta Roriz. VT3 – Alentejo; 2012; 50 % Trincadeira, 40 % Aragonês (Tinta Roriz), 10 % Alfrocheiro.

The four samples of Tawny Port wines were assigned the labels VP1, VP2, VP3 and VP4. Port wines are made from grapes grown in the Douro demarcated region in northern Portugal. The region covers 250 000 ha, of which about 45 000 ha are under vine; it is the world's oldest demarcated wine area, the original boundaries dating from 1761. Port wine is prepared with a blend of several grape varieties. Furthermore, blending of Ports from different origins (within Douro Wine Region) and years achieve each producer's individual profile, characterized by physical, chemical and sensory parameters. Tawny Ports have aged in oak casks to acquire delicious nuttiness and aromas of butterscotch and fine oak wood for different times: 10 years (VP1, VP2 and VP3) and 30 years (VP4).

All samples were characterized regarding current quality control parameters of red and of Tawny Port wines, following normalized methods described in the "Compendium of International Methods of Analysis" (OIV-MA, 2015) namely: total acidity, TA (OIV-MA-F-AS313-01); non-reducing extract, NRE (OIV-MA-AS2-03B); volatile acidity, VA, and reducing sugars, RS (OIV/Oeno 390/2010). Pigments, P, polyphenols, PP, tannins pigments, TP, and free anthocyanins, FA, were evaluated by UV-Vis spectral readings

123 and using calibrations maintained by the AWRI through the WineCloudTM
124 (www.thewinecloud.com.au). Free sulphur dioxide, FSD, and total sulphur dioxide, TSD,
125 were evaluated by potentiometric titration following a methodology adapted from
126 Ripper method. These parameters were evaluated at the laboratories of ADVID
127 (*Associação para o Desenvolvimento da Viticultura Duriense*). Results from physical-
128 chemical parameters are reported in Table 1.
129 In Tawny Port wine the FSD is below the threshold detection (9 mg/L) and thus its
130 analysis is not relevant. Moreover, as Port wines analyzed in the present work have aged
131 under oxidative conditions, for more than 3 years, TP, PP and FA are present in trace
132 amounts and the available wet chemistry methods will not provide appropriate accuracy
133 to characterize these parameters. Furthermore, for Port wine the AWRI has only
134 optimized the method for T evaluation.
135
136 2.2 Voltammetric assays
137 Electrochemical measurements were performed at room temperature (25 ± 2 °C) using
138 a potentiostat (Autolab type PGSTAT30, Ecochemie) controlled by GPES 4.9 software.
139 Cyclic voltammograms were obtained at scan rate of 100 mV s^{-1} and the anodic scan
140 corresponds to the direct scan. Differential pulse voltammograms were obtained with a
141 pulse amplitude of 100 mV, a potential step of 5 mV and a modulation time of 0.05 s.
142 Three or four scans were registered for each sample and the reported data correspond
143 to the average of at least two replicates. The working electrode was a glassy carbon
144 electrode, GCE, (3 mm diameter; *BAS M-2012*) and the secondary and reference
145 electrodes were a platinum wire and Ag / AgCl (3 M KCl; *CH Instruments, Inc*),
146 respectively. All potentials are quoted against the reference electrode used. Before each

147 scan the working electrode was polished on a polishing cloth with diamond suspension
148 (MetaDi Supreme 3 µm; *Buehler*). After polishing, the electrode was washed with
149 ultrapure water and dried with absorbent paper.

150

151 **Table 1.** Chemical characterization of red wines (VT) and Tawny Port wines (VP).

	VT1	**VT2**	**VT3**	**VT4**	**VT5**	**VP1**	**VP2**	**VP3**	**VP4**
Non-reducing extract (NRE, g/L)	29.6	36.3	27.8	30.9	34.4	30.7	30.2	21.2	25.6
Reducing sugars (RS, g/L)	2.2	2.2	2.7	2.4	2.6	101.2	101.9	132.5	131.7
Total sulphur dioxide (TSD, mg/L)	125	102	134	68	99	22	17	32	19
Volatile acidity (VA, g /L acetic acid)	0.54	0.56	0.57	0.54	0.52	0.19	0.25	0.39	0.47
Total acidity (TA, g /L tartaric acid)	5.1	5.2	5.9	5.2	5.2	3.8	3.9	5.7	6
Tannins (T, g/L eq. Epicatechin)	1.96	2.11	3.67	2.07	3.59	0.61*	0.5*	0.43*	0.26*
Polyphenols (PP, absorbance units)	59.32	61.91	94.71	67.6	94.1	-	-	-	-
Free sulphur dioxide (FSD, mg/L)	43	45	40	30	43	-	-	-	-
Tannins pigments (TP, absorbance units)	3.07	3.01	5.25	2.69	5.06	-	-	-	-
Free anthocyanins (FA, absorbance units)	12.73	11.23	22.33	23.56	23.88	-	-	-	-
Pigments (P, absorbance units)	17.84	16.25	31.08	28.04	32.31	-	-	-	-

152 * Values obtained by the AWRI Methodology for the determination of tannins in
153 fortified wines (Herderich and Smith, 2005)
154 - Not evaluated

155

156 2.3 Solutions and samples preparation for voltammetric assays

157 Solutions of gallic acid (GA, *Sigma-Aldrich*) and of sulphur dioxide (obtained from sodium
158 metabisulphite; *Sigma*) were prepared in 0.033 M tartaric acid (*Merck*) solution pH 3.20.
159 Ultrapure water (18 MΩ cm^{-1}) from Millipore Milli-Q system was used and pH was
160 adjusted using 1.0 M NaOH solution (*Acros Organics*). All chemicals were used without
161 further purification.

162 The wine samples were collected from the wine bottles. The original cork stopper was
163 substituted by a rubber septum stopper and wine was kept under an argon atmosphere
164 in the dark. Sample solutions were prepared from 25 mL aliquots transferred to
165 erlenmeyers under an argon atmosphere by dilution (1:25) in 0.033 M tartaric acid, pH
166 3.20. The dilution factor of 1:25 was chosen for all wine samples, considering the
167 linearity range of the current response and voltammetric area under the
168 voltammograms (by CV and DPV). All measurements were comprised between the 2^{nd}
169 (10 μM) and the 5^{th} (200 μM) standard solution of a set of 8 standard solutions.

170

171 2.4 Chemometric analysis

172 Chemometric analysis was performed by using the software Matlab R2007b and the PLS-
173 Toolbox 5.2.

174 Voltammetric data were organized in a matrix (9 x 560) for VC and a matrix (9 x 196) for
175 DPV, where nine is the number wine samples and 560 and 196 are the number of current
176 points acquired from a CV and from a DPV assay, respectively.

177 In the correlation analysis of physical-chemical parameters common to all wines, the
178 first six matrix columns are the physical-chemical parameters: NRE, RS, TSD, VA, TA and
179 T, the other variables are the current at each potential from voltammograms by CV and

by DPV. In the correlation with physical-chemical parameters of red wines, the first five matrix columns are the physical-chemical parameters: PP, FSD, TP, FA and P, the other variables are also the current at each potential from the voltammograms by CV and by DPV.

The correlation is defined for a pair of random variables (for example, x and y), where a correlation coefficient (r) between them is defined by the equation (1) (Bruns et al, 2006):

$$r(x,y) = \frac{\sum\left(\frac{x_i-\bar{x}}{s_x}\right)\left(\frac{y_i-\bar{y}}{s_y}\right)}{N-1} \quad (1)$$

where, *x* are the physical chemical parameters, *y* are the potentials from the voltammetric analysis, *s* is the standard deviation, *N* is the number of samples.

Based on equation 1, when *r* is equal to 1 the correlation is maximum, when *r* is equal to zero there is no correlation. Negative value of *r* means an antagonistic correlation between the variables.

3. Results and discussion

3.1 Voltammetric characterization of wine samples

Cyclic voltammograms and differential pulse voltammograms from nine different diluted samples (1:25) of red and Tawny Port wines, obtained with a glassy carbon electrode, are displayed in Figure 1. By CV, two overlapped bands, at about 0.73 V and 0.93 V, are noticeable (Figure 1-A for red wines and Figure 1-C for Tawny Port wines). The first band may result from the overlap of the voltammetric responses of the most easily oxidizable polyphenols, such as those with a flavonoid structure with a catechol or a galloyl group (Kilmartin et al., 2001). The second band may result from the oxidation

of anthocyanins and stilbene derivatives overlapped with the second oxidation process of flavonoids (Kilmartin et al., 2001; Kilmartin et al., 2010).

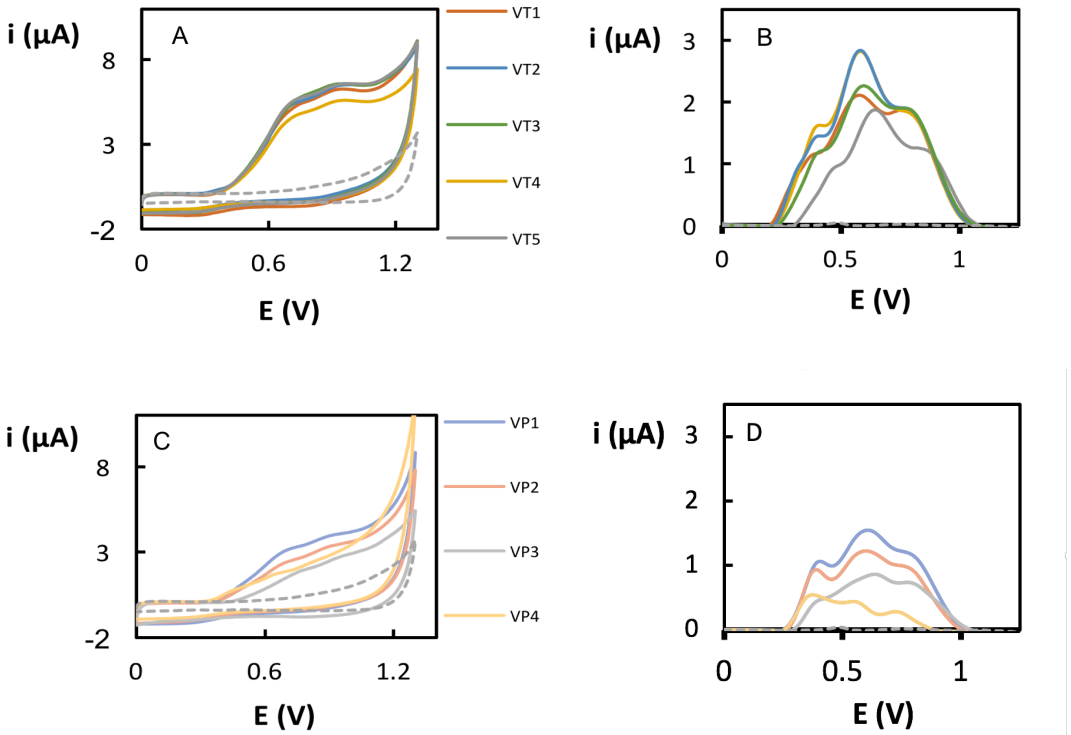


Figure 1. Cyclic (A, C) and pulse differential (B, D) voltammograms in wine samples: red wine (A, B) and Tawny Port wine (C, D). Dot dashed curve correspond to blank solution (0.033 M of tartaric acid at pH 3.20)

Four of the five voltammograms of the red wines are overlapped (VT1, VT2, VT3, VT5) and do not differ substantially from the voltammogram of VT4, either in shape or in current (ca. 10 % higher). These results may indicate that red wines have similar chemical composition regarding the total concentration of oxidizable species. Regarding Tawny Port wines, their voltammograms are much lower than those of red wines. In opposition to red wine samples, there are significant differences between the responses from the different samples.

By DPV three peaks, at about 0.40, 0.60 and 0.80 V, are displayed (Figure 1-B for red wines and Figure 1-D for Tawny Port wines). Although voltammograms of red wines display identical features, marked differences are noticed regarding the relative height of each peak in a voltammogram and the absolute value of the peaks height.

Given the differences between voltammograms from all samples, from red and Tawny Port wines, their chemical composition is expected to be distinct. This interpretation is not completely in agreement with results from CV, namely regarding the red wines samples. These results seem to indicate that the two voltammetric techniques are not equally sensitive to the same chemical species present in this set of samples.

3.2 Chemometric analysis of voltammograms

A correlation analysis between voltammetric data by CV and by DPV and the chemical composition of the wines were carried out in order to understand the origin of the observed discrepancy.

The chemometric analysis of the voltammograms of red and Tawny Port wines, obtained by CV and DPV was performed regarding the most relevant chemical parameters used to characterize each type of wine (red or Tawny Port wine). The correlation maps for the physical chemical parameters that are common to red and Tawny Port wines (NRE, RS, TSD, VA, TA and T) with respect to CV and to DPV data are displayed in Figure 2-A and Figure 2-B, respectively. These correlation maps identify the potential ranges in the voltammograms that are correlated with the physical-chemical parameters. The potential ranges where current increases concomitantly with a physical-chemical parameter are assigned in red tones. Blue tones assign antagonistic correlations, corresponding to potential ranges where current variations are opposed to the variation

of the physical-chemical parameter. Potential ranges in white mean that there is no correlation between current and the physical-chemical parameter.

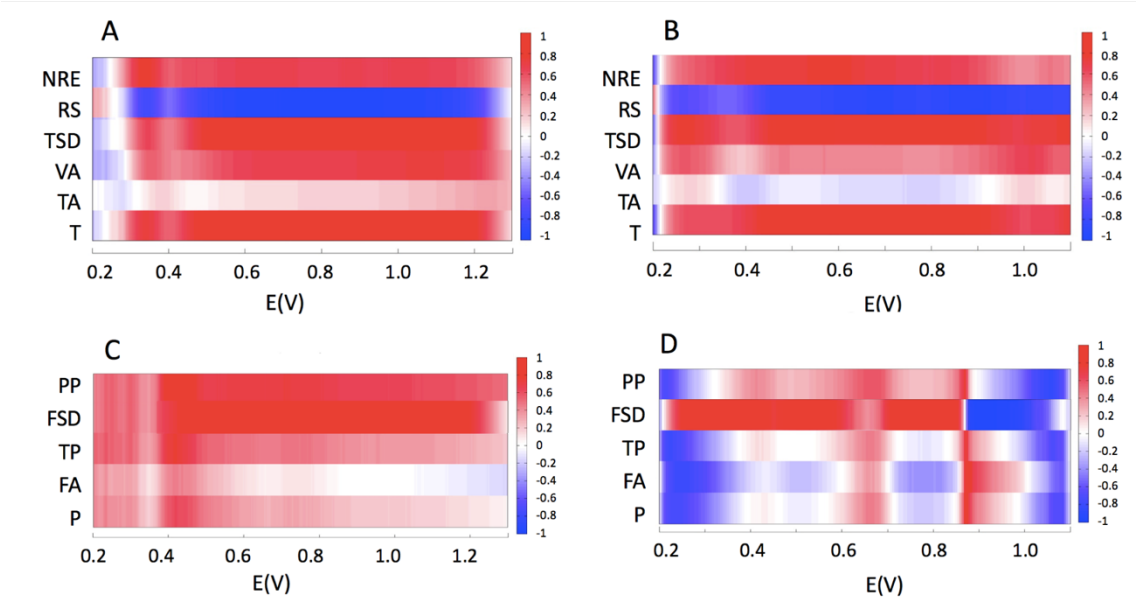


Figure 2. Chemometric analysis of correlations between physical-chemical parameters of red and Tawny Port wines and CV voltammograms (A) and DPV voltammograms (B) and between the physical-chemical parameters evaluated only for red wines and CV voltammograms (C) and DPV voltammograms (D).

These correlation maps show that T is the chemical parameter that presents the highest correlation with the data from CV and DPV, whereas for TA practically no correlation with CV and DPV is observed. For RS, an antagonistic correlation is observed in both techniques. The NRE presents a higher correlation with CV voltammograms around 0.35 V. The correlation for VA with CV voltammograms is around 0.5 to 0.6 from 0.6 to 1.2 V. TSD presents higher correlation with CV voltammograms from 0.5 to 1.2 V. With respect to DPV voltammograms VA presents the lower correlation (about 0.4). The higher correlations are obtained for the parameters NRE and TSD from 0.45 to 0.90 V. The correlation maps for the physical-chemical parameters measured only in red wine (PP,

261 FSD, TP, FA and P) and CV and DPV voltammograms are presented in Figure 2-C and
262 Figure 2-D, respectively.
263 The FSD is the physical-chemical parameter more correlated with both voltammetric
264 data. For all parameters the higher correlations with CV data are observed at about 0.45
265 V. For DPV all parameters display the higher correlations close to at 0.65 V and 0.87 V,
266 except for FSD that exhibits maximum correlations at 0.40 V and 0.75 V.
267 Based on correlation maps it is possible not only to identify the physical-chemical
268 parameters more closely related with data from voltammetric techniques, but also
269 identify the potentials ranges where correlations are higher. These results show that
270 both voltammetric techniques may be considered as an alternative approach to get
271 information on some of the physical-chemical parameters used for the quality control
272 of wines.
273
274 3.3 Comparison of integrated voltammetric responses of CV and DPV using a model
275 polyphenol
276 The integration of the area under voltammograms is an usual procedure used for the
277 evaluation of TPP of complex samples containing multiple polyphenols, as wine. The
278 value obtained from the integration of the voltammograms corresponds to a total
279 parameter that accounts for the contribution of the species that are oxidized at different
280 potentials, defining a response with the shape of a band, rather than of a peak.
281 The TPP content is evaluated by interpolation of voltammetric data of integrated area
282 under voltammograms of the wine samples in calibration curves of gallic acid (GA).
283 Figure 3-A and 3-B show the voltammetric response obtained from GA solutions by CV
284 and by DPV, respectively. GA is one of the most used reference phenolic compound. Its

285 voltammograms display two processes, corresponding to the sequential electron
286 transfer characteristic of GA oxidation(Abdel-Hamid and Newair, 2011). From these two
287 sets of voltammograms two calibrations curves were constructed using the integrated
288 area under the voltammograms (IA). For CV voltammograms, integration was performed
289 for a fixed potential range of 900 mV, while for DPV voltammograms the integration was
290 carried out for the entire voltammogram.
291 The calibration curves for the integrated area under voltammograms (IA) are
292 significantly different: IA (µA V)= (175 $\pm$ 3) c_{GA} (mM) + 2.8 $\pm$ 0.6, r = 0.9993 for CV and
293 IA (µA V)= (7.3 $\pm$ 0.1) c_{GA} (mM) + 0.01 $\pm$ 0.03, r = 0.9994 for DPV. This difference arises
294 from two main sources. First, the dissimilar shapes of the peaks obtained by each
295 technique. The peaks from CV are broad and decay slowly in opposition to the peaks
296 from DPV that are narrower and more symmetrical. Second, the integration ranges of
297 potentials are not exactly the same. For DPV, the range is defined from the beginning of
298 the first peak to the end of the last (second) peak, while for CV the range was selected
299 considering the start of the first peak until the rise of the current due to the medium
300 oxidation. Furthermore, the intercept of the calibration curve for CV is 280 times larger
301 than that of DPV, due to the contribution of residual current that affects the current
302 response of CV, but does not affect that of DPV. The detection limits, estimated by the
303 higher diluted standard that fits the calibrations (that exhibits a deviation from the
304 calibration curve lower than 20 %), are 5 µM for both techniques. Similar values (6 µM
305 and 10 µM for CV and DPV, respectively) were estimated by 3 s_a/b (where b is the slope
306 and s_a is the standard deviation of the calibration curve intercept). These detection limits
307 are comparable with the reported values obtained using bare GCE (4 µM) (Ziyatdinova
308 and Budnikov, 2014).

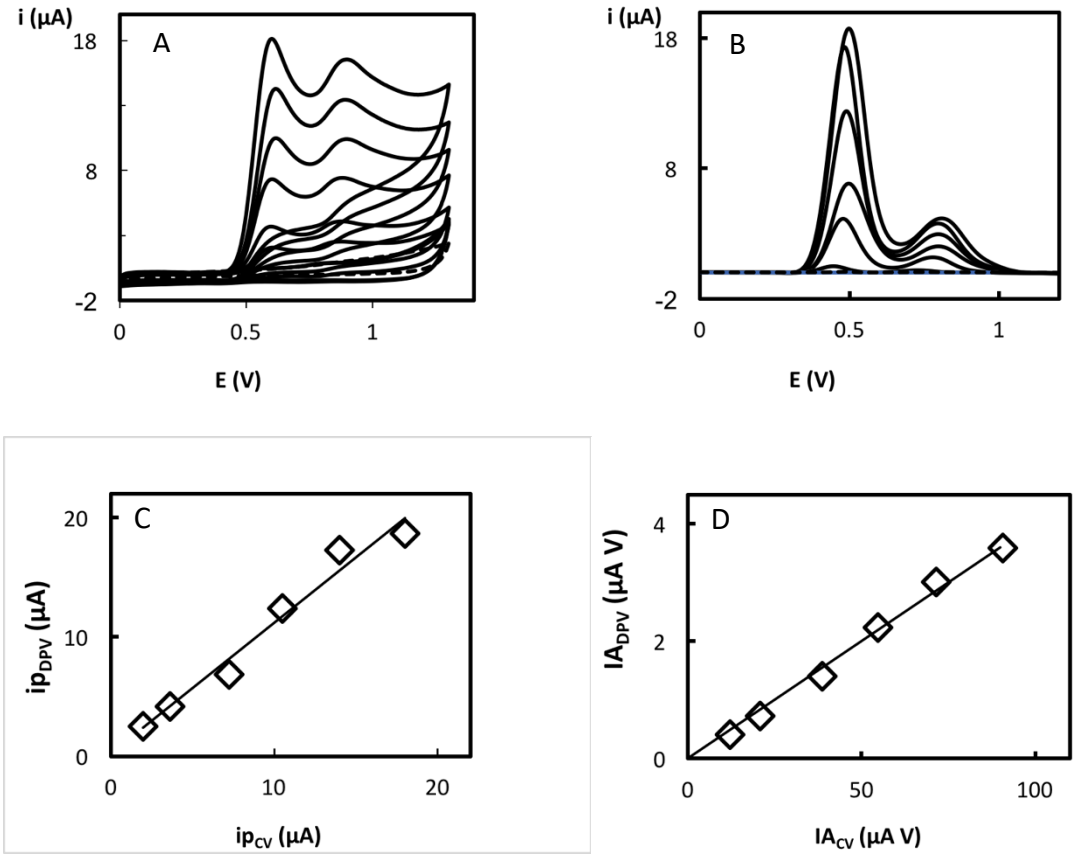


Figure 3. CV voltammograms (A) and DPV voltammograms (B) obtained using a GCE from GA solutions (0.010 mM, 0.050 mM, 0.10 mM, 0.20 mM, 0.30 mM, 0.40 mM and 0.50 mM) containing 0.033 M tartaric acid (pH 3.20). Comparison of I_p values, measured at the first peak, from DPV and CV (C). Comparison of *IA* values from DPV and CV (D).

The comparison between I_p values from both techniques are represented in Figure 3-C. The slope of the correlation straight line that compares I_p values from both techniques is close to 1 (y = 1.1 x + 0.2, r = 0.99) indicating that current values represented in both axes are similar, despite the different time bases of these two experiments (100 mV s^{-1} for VC and 9.9 mV s^{-1} for DPV). Figure 3-D compares *IA* values obtained from both techniques. The slope of the correlation straight line is ca. 24. This value is a consequence of the higher sensitivity of results from CV (175 mA V M^{-1}) in relation to

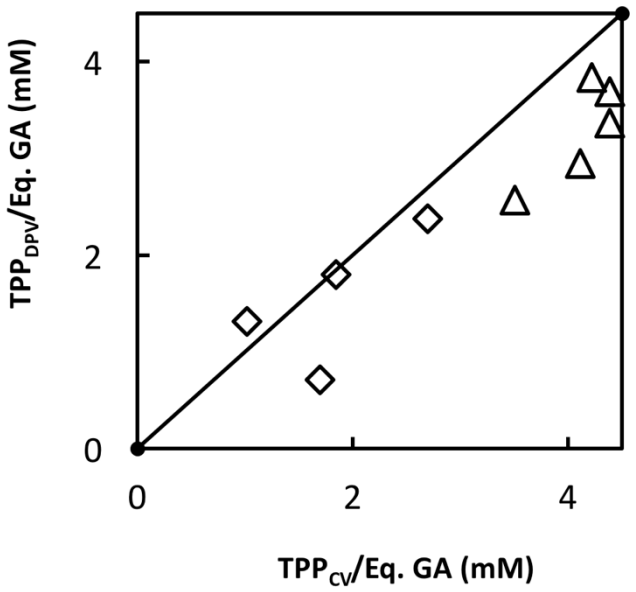
those from DPV (7.3 mA V M^{-1}) associated to the dissimilar shape of voltammograms from both techniques. Values of TPP expressed in GA equivalents, were evaluated by interpolation of *IA* values from voltammograms of the wines presented in Figure 1 in the corresponding calibration curves. Results for TPP obtained by the two techniques are represented in Figure 4, where triangles represent red wines and diamonds Tawny Port wines.

3.4 Comparison of TPP results obtained from the two voltammetric techniques

Results of TPP obtained by CV and by DPV can be compared in Figure 4, where the represented straight line, $y = x$, stands for the equivalence between values represented in the two axes. The TPP values of Tawny Port wine samples are lower than those of all red wines, regardless of the technique used. The majority of the points are under the equivalence line indicating that the TPP values evaluated by CV tend to be higher than those evaluated by DPV. This effect is more pronounced for red wine samples with differences between 10 % (VT-2) to 39 % (VT-1). Results from Tawny Port wines tend to distribute more evenly along the equivalence line, except for VP4 for which the TPP value from DPV is about 40 % of that from CV.

The presence of interferences, such as sulphur dioxide, that are oxidized in the working potential range, can be in the origin of these differences if the sensitivity of the two techniques for its detection are different. The extent to which sulphur dioxide contributes to the observed difference between results of TPP from the two voltammetric techniques is analysed in the following. The difference between the TPP values from CV and from DPV (TPP_{CV} - TPP_{DPV}) was plotted against TSD. In Figure 5, it can be observed that there is a correlation between TPP_{CV} - TPP_{DPV} and TSD with a coefficient

348 of 0.79. This important correlation demonstrates that CV is less selective than DPV
349 regarding the presence of total sulphur dioxide.
350 The difference in sensitivity between the two techniques concerning free sulphur
351 dioxide was evaluated in assays using sodium metabissuphite solutions (0.20 and 0.40
352 mM) in tartaric acid solution, pH 3.20. The sensitivity of the determination regarding the
353 integration of the area under CV and DPV voltammograms was compared with the slope
354 of GA calibration curves from the corresponding techniques. While for CV, the sensitivity
355 of free sulphur dioxide is about 141 % of the sensitivity of GA, for DPV the relative
356 sensitivity decreases to 64 %. This difference between the two techniques sensitivity
357 corroborates the observed differences between the TPP values obtained by the two
358 voltammetric techniques.
359



360
361 **Figure 4.** Comparison of the TPP values of red and Tawny Port wines evaluated by CV
362 and DPV. The straight line corresponds to the equivalence of methods ($y = x$).

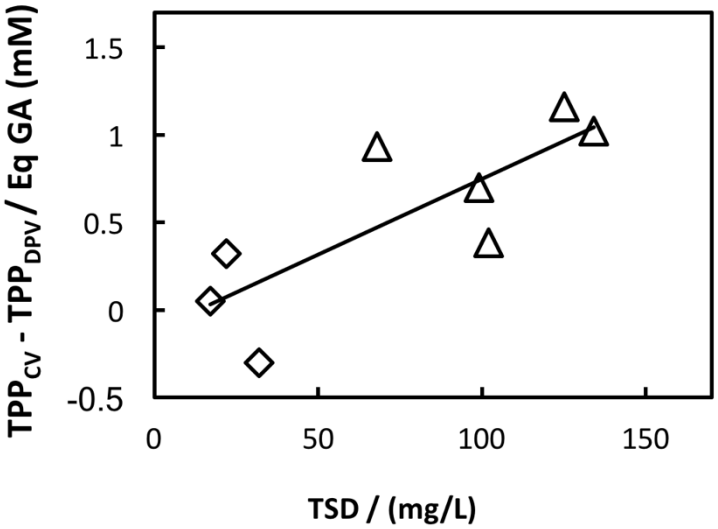


Figure 5. Correlation between the difference of TPP values from CV and from DPV (TPP_{CV} - TPP_{DPV}) with total sulphur dioxide (TSD) for all wines samples, except VP4. The straight line corresponds to fitting of experimental points to a linear model (y = 0.0086 x - 0.11, r = 0.79).

4. Conclusion

High correlations were obtained between CV and DPV voltammograms and the majority of the physical-chemical parameters used in quality control of red and Tawny Port wines. The exceptions were total acidity that was not correlated with voltammetric data and the reducing sugars that presented an antagonist effect. In this sense, the voltammetric techniques may be used as an alternative methodology to evaluate some of the physical-chemical parameters used in quality control of wines.

Polyphenols, free sulphur dioxide and total sulphur dioxide display high correlations with CV voltammograms in the potential range where faradaic current has the major contribution, whereas with DPV voltammograms these correlations are more dependent on potential. Nevertheless, it was not possible to identify specific potential

ranges where polyphenols can be evaluated without the interference of free sulphur dioxide and total sulphur dioxide.

The difference between the values of total polyphenols obtained by the two techniques was higher for wine samples with higher content of total sulphur dioxide. A correlation of 0.79 was obtained between these two quantities.

Results in this work indicate that DPV is most adequate for the quantification of total polyphenols due to its lower sensitivity to sulphur dioxide. Furthermore, the combination of CV with DPV data can be used to estimate the content of total sulphur dioxide.

In future work, the comparison of total polyphenols results obtained with the more friendly disposable screen-printed electrodes and with the traditionally glassy carbon electrodes is envisaged. This two works were designed with the aim of contributing to the establishment of simpler and universally accepted experimental variables for attaining meaningful values of total polyphenols in wine using electrochemical methods.

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Conflict of interest

The authors declare that they have no conflict of interest.

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