

1 **An assessment of voltammetry on disposable screen printed electrodes to predict wine**
2 **chemical composition and oxygen consumption rates**

3 Chelo Ferreira^{a,d}, María-Pilar Sáenz-Navajas^b, Vanesa Carrascón^a, Tormod Næs^c, Purificación
4 Fernández-Zurbano^b, Vicente Ferreira^{a*}

5 ^aLaboratorio de Análisis del Aroma y Enología (LAAE), Department of Analytical Chemistry,
6 Universidad de Zaragoza, Instituto Agroalimentario de Aragón (IA2) (UNIZAR-CITA),
7 Associate unit to Instituto de las Ciencias de la Vid y del Vino (ICVV) (UR-CSIC-GR), c/
8 Pedro Cerbuna 12, 50009 Zaragoza, Spain

9 ^bInstituto de Ciencias de la Vid y del Vino (ICVV) (Universidad de La Rioja-CSIC-Gobierno de
10 La Rioja), Carretera de Burgos Km. 6, Finca La Grajera, 26007 Logroño, La Rioja, Spain.

11 ^cNofima AS, Osloveien 1, P.O. Box 210, N-1431 Ås, Norway

12 ^dInstituto Universitario de Matemáticas y Aplicaciones (IUMA-UNIZAR)

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15 *Corresponding author: vferre@unizar.es

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17 **Abstract**

18 The present work aimed at determining the applicability of linear sweep voltammetry coupled to
19 disposable carbon paste electrodes to predict chemical composition and wine oxygen
20 consumption rates (OCR) by PLS-modeling of the voltammetric signal. Voltammetric signals
21 were acquired in a set of 16 red commercial wines. Samples were extensively characterized
22 including SO₂, antioxidant indexes, metals and polyphenols measured by HPLC. Wine OCRs
23 were calculated by measuring oxygen consumption under controlled oxidation conditions.
24 Chemical variables and wine OCRs were predicted from first order difference voltammogram
25 curves by PLS-regression.

26 A significant number of fully validated models predicting chemical variables from voltammetric
27 signals were obtained. This fast, cheap and easy-to-use approach presents an important potential
28 to be used in wineries for rapid wine chemical characterization.

29 *Key words: PLS; polyphenols; electrochemistry; oxidation; wine analysis*

30

31 1. Introduction

32 Wine is a complex beverage consisting of hundreds of several components that experiment
33 important changes during winemaking, many of which are definitely involved in wine quality
34 perception (Sáenz-Navajas, Avizcuri, Ballester, Fernández-Zurbano, Ferreira, Peyron, et al.,
35 2015). At present, wet chemistry and advanced chromatographic procedures are able to provide
36 reliable data that allow to monitor chemical evolution of wines during winemaking and thus, can
37 be useful tools to establish quality control programs (Ma, Bueschl, Schuhmacher, & Waterhouse,
38 2019; Márquez, Pérez-Navarro, Hermosín-Gutiérrez, Gómez-Alonso, Mena-Morales, García-
39 Romero, et al., 2019). However, these methods are expensive in terms of time, personal and
40 instrumentation resources, and therefore, are usually not affordable by small wineries. For this
41 reason, there is a great demand for rapid, cheap and easy-to-use analytical tools that can be used
42 to monitor wine composition and predict wine maturation processes (Kilmartin, 2016). Given the
43 importance of wine exposure to oxygen during winemaking, modern chemistry has focused on
44 understanding redox reactions, in which phenolic compounds are the main substrate (Singleton,
45 Orthofer, & Lamuela-Raventós, 1998). To this concern, voltammetric approaches are presented
46 as interesting tools for determining the content of electroactive molecules and thus monitoring
47 oxidation-related processes involved in wine evolution (Dhroso, Laschi, Marrazza, & Mascini,
48 2010; Kilmartin, 2016). These methods have been applied to measure a range of antioxidants,
49 including phenolic acids and flavonoids, ascorbic acid, SO₂ and the general resistance to
50 oxidation (Gonzalez, Vidal, & Ugliano, 2018; José Jara-Palacios, Hernanz, Escudero-Gilete, &
51 Heredia, 2014; Kilmartin, Zou, & Waterhouse, 2001, 2002; Martins, Oliveira, Bento, Geraldo,
52 Lopes, De Pinho, et al., 2008; Samoticha, Jara-Palacios, Hernández-Hierro, Heredia, & Wojdyło,
53 2018; Ugliano, Slaghenaufi, Picariello, & Olivieri, 2020). Glass-carbon electrodes have shown to
54 be suitable in the characterization of reducing ability of red and white wines mainly because this
55 material minimizes ethanol interferences which dominate the signals in platinum and gold
56 electrodes (Kilmartin, Zou, & Waterhouse, 2001, 2002; Martins, et al., 2008; Vilas-Boas,
57 Valderrama, Fontes, Geraldo, & Bento, 2019). In recent times, disposable screen-printed
58 graphite-based sensors are becoming more widely accessible and appear as an interesting

Kommentert [TN1]: General comment. You use the term PC's for PLS components. This is not fully correct. I suggest changing to PLS components.

Kommentert [cf2R1]: Ok!!

59 alternative to monitor and diagnose wine oxidation effects by direct sample measurement with no
60 sample dilution (Dhroso, Laschi, Marrazza, & Mascini, 2010; Gonzalez, Vidal, & Ugliano, 2018;
61 Ugliano, 2016; Ugliano, Slaghenaufi, Picariello, & Olivieri, 2020).

62 Even if the combination of voltammetric signals with multivariate statistical tools has been little
63 explored, principal component analysis (Gonzalez, Vidal, & Ugliano, 2018; Ugliano, 2016) and
64 partial least square regression modeling (Martins, et al., 2008) have been suggested –to be
65 interesting approaches to provide valuable information when monitoring wine oxidation effects
66 or providing wine fingerprinting.

67 In this context, it was hypothesized that relationships between voltammogram regions and
68 specific phenolic compounds as well as overall wine oxygen consumption rates (OCR) could be
69 established by multivariate analysis following an untargeted voltammetric approach. Thus, the
70 present work aimed at evaluating the applicability of linear sweep voltammetry coupled to
71 disposable carbon paste sensors to predict chemical composition and wine oxygen consumption
72 rates (OCR) by PLS-modeling in a set of commercial red wines.

73

74 **2. Material and methods**

75 *2.1. Wine samples*

76 A set of 16 red Spanish wines were studied. They were all purchased at a local store and were
77 from different regions, grape varieties and vintages (detailed information is provided in Table S1
78 of Supporting Information).

79 *2.2. Oxidation experiment*

80 Oxygen consumption rates of wines were determined from data collected in an oxidation
81 experiment consisting of five consecutive air-saturation cycles as described in Ferreira,
82 Carrascon, Bueno, Ugliano, and Fernandez-Zurbano (2015). Air saturations were carried out by
83 gentle shaking 500 mL of wine contained in a closed 1-liter glass bottle, then the cap was opened
84 to allow fresh air to enter the bottle. This procedure was repeated for each saturation until a final
85 concentration of $5.6 \pm 0.1 \text{ mg L}^{-1}$ of dissolved oxygen was reached. Then, wine samples were
86 incubated in the dark ($25 \pm 0.5 \text{ }^\circ\text{C}$) and dissolved oxygen was monitored at least once a day with a
87 non-destructive Nomasense oxygen analyzer (Namacorc S.A., Thimister-Clermont, Belgium)
88 until 90% of oxygen was consumed or during 7 days. This cycle was repeated five times.

89 *2.3. Voltammetric measurements*

90 Electrochemical measurements were performed with a commercial Nomasense Polyscan
91 electrochemical analyzer (Namacorc, Belgium) using disposable screen printed sensors. The
92 system consisted in three sensors: working and counter electrodes both screen printed carbon
93 paste electrodes and reference electrode consisting of an Ag/AgCl electrode. A drop of sample
94 was loaded onto the sensor, and linear sweep voltammograms were acquired between 0 and 1200
95 mV at a scan rate of 100 mV s^{-1} . A total of 122 voltammetric signals for each wine in duplicate
96 were recorded, and further worked with averaged data. A new sensor was used for each
97 measurement. Repeatability of the measurement was tested by three consecutive measurements
98 of the same wine.

99 *2.4. Chemical characterization*

100 *Metals.* Fe, Cu, Mn, Zn and Al were quantified by inductively coupled plasma optical emission
101 spectroscopy (ICP-OES) with previous microwave-assisted digestion of samples as described by
102 González, Armenta, and De La Guardia (2008).

103 *Low molecular-weight polyphenols by GPC-UPLC.* Compounds were analyzed in the first
104 fraction eluting (55:45:1, ethanol:water:formic acid) from a Gel Permeation Chromatography
105 (GPC) column filled with TSK Toyopearl gel (HW-50F) as described in Gonzalez-Hernandez,
106 Avizcuri-Inac, Dizy, and Fernandez-Zurbano (2014). Accordingly, a total of 21 anthocyanins
107 were quantified by UPLC-MS-DAD and 21 flavonols, 24 acids and derivatives and 11 flavanols
108 by UPLC-MS.

109 *Other polyphenol-related measurements.* Trolox equivalent antioxidant capacity (TEAC) was
110 measured (Rivero-Pérez, Muñiz, & González-Sanjosé, 2007) as well as total polyphenolic content
111 by both Folin-Ciocalteu method (Singleton, Orthofer, & Lamuela-Raventós, 1998) and total
112 polyphenol index (TPI) estimated as absorbance at 280 nm (Ribéreau-Gayon, 1970) of samples
113 diluted 1:100 in deionized water in 1-cm-quartz cuvettes. Mean degree of polymerization was
114 calculated as the ratio of total flavanol units (extension + terminal) to terminal units (calculated
115 as the difference between before and after thiolyis) by acid-catalyzed degradation in the presence
116 of toluene- α -thiol according to the method described by Labarbe, Cheynier, Brossaud, Souquet,
117 and Moutounet (1999) but with some modifications as described by Gonzalo-Diago, Dizy, and
118 Fernandez-Zurbano (2013). Determination of monomeric (MP), small polymeric pigments (SPP)
119 and large polymeric pigments (LPP) was carried out as described elsewhere (Harbertson,
120 Picciotto, & Adams, 2003). MPs were the group of compounds bleachable with bisulphite, while
121 SPP and LPP were resistant to bisulphite bleaching. SPP did not precipitate with ovoalbumin,
122 different to LPP. Levels of MP, SPP, and LPP were expressed as absorbance at 520 nm.

123 *Absorbance measurements.* Absorbance at 420, 520 and 620 nm of undiluted wine was measured
124 using glass cuvettes with optical paths of 1, 2, 5 or 10 mm. Measurement which provided
125 absorbance readings between 0.3 and 0.7 were considered as recommended by the OIV (2009a).
126 Measurements were carried out in a Shimadzu UV-1800 (Shimadzu Corporation, Tokyo, Japan)
127 spectrophotometer.

128 *Conventional oenological parameters.* pH was determined by Infrared Spectrometry with Fourier
129 Transformation (IRFT) with a WineScan™ FT 120 (FOSS), which was calibrated with wine
130 samples analyzed in accordance with official OIV (International Organization of Vine and Wine)
131 practices; free and total sulfur dioxide were determined by the aspiration/titration method
132 (Rankine method) recommended by the OIV.

133 *Measured Redox potential.* This parameter, which is not a truly redox potential as recently
134 discussed (Danilewicz, Tunbridge, & Kilmartin, 2019), was measured using a Pt electrode fitted
135 to a Ag/AgCl reference electrode model 50 58 from Crison (Alella, Barcelona) and a
136 microprocessor 6230N from Jenco Instruments (San Diego, CA). Measurements were recorded
137 in a glove chamber (Jacomex, France) with a level below 0.002% (v/v) of oxygen in gas phase.
138 Therefore, wine was firstly poured in a 4 mL vial where the electrode was introduced (with no
139 agitation) and measurement was recorded after 35 min. Then, the electrode was cleaned with
140 milliQ water and introduced in a solution containing equimolar amounts (0.01 M) of ferro- and
141 ferricyanide supplied by Panreac (Barcelona, Spain). This solution has a known redox potential
142 of 220 ± 10 mV at 25°C (vs. Ag/AgCl(s)). If the measured redox potential was in this range, the
143 electrode was rinsed again with water and was then ready for subsequent measurements. In case
144 the measured redox potential differed more than 10 mV from the expected 220 mV value, the
145 diaphragm of the electrode was cleaned with a solution of thiourea (<6%) and HCl (<2%) (Crison,
146 Alella, Barcelona). All analyses were performed in duplicate.

147 Chemical data (average, maximum and minimum) are presented in Table S2 of Supporting
148 Information.

149 2.5. Data treatment

150 2.5.1. Determination of wine oxygen consumption rates

151 The oxygen consumed in the five saturation cycles was calculated for each wine (as the average
152 among three independent saturation cycles per sample) as the difference between the dissolved
153 oxygen at the beginning and at the end of each cycle. Then, the oxygen consumed for each
154 saturation was plotted against the days employed to consume the oxygen. The five points
155 (accumulated O₂ consumed at the end of each saturation, time in which saturation ended)

156 followed a straight line which was adjusted by least square regression. The ordinate at time 1 day
157 was taken as the initial oxygen consumption rate. The slope was taken as the average oxygen
158 consumption rate (Ferreira, Carrascon, Bueno, Ugliano, & Fernandez-Zurbano, 2015). Data are
159 available in Table S3 of Supporting Information.

160 2.5.2. Exploration of raw voltammetric signals

161 First derivative voltammograms allow to improve the separation between anodic waves in
162 comparison with raw voltammograms (Gonzalez, Vidal, & Ugliano, 2018). Thus, first order
163 difference voltammograms curves were calculated for all wines. Further Principal Component
164 Analysis (PCA) was calculated in order to analyze the dominating types of variability for these
165 curves and, if possible, to reduce the initial number of variables.

166 2.5.3. Modeling OCRs and chemical variables from voltammetric signals

167 The main purpose was the prediction by regressing calibration of the chemical variables from the
168 voltammograms. The general model is given by

$$169 \quad Y = XB + F$$

170 where, for a sample size n ($n = 16$), $X_{(16,121)}$ represents the input matrix with the differences
171 between two consecutive voltammetric measurements, $Y_{(16,97)}$ the output matrix with the
172 chemical variables, $B_{(121,97)}$ is the matrix of regression coefficients and $F_{(16,97)}$ the matrix of
173 residuals.

174 Single response models are analyzed. Then, Ssingle Y - variable Partial Least Square regression
175 method is used for every chemical variable and the whole spectrum of voltammograms (X).

176 Therefore, the prediction by regressing for one single y data on X was as follows:

$$177 \quad y_i = Xb_i + f_i,$$

178 where, $y_{i(16,1)}$ are the vectors that represent every one of the chemical variables $1 \leq i \leq 97$ for
179 the red wine sample set and, $b_{i(121,1)}$ and $f_{i(16,1)}$ are respectively, the vectors of regression
180 coefficients and residuals.

Kommentert [TN3]: Question. Do you analyse only single response models. Maybe highlight more explicitly.

Kommentert [cf4R3]: Ok!

181 Firstly, the input variables X are enhanced in two ways, they have been filtered applying a 7 points
182 window Savitzky-Golay smoothing; and, on the other hand they have been standardized to
183 comparable noise levels. Likewise, chemical variables $y_{i,1 \leq i \leq 92}$ have been standardized.
184 With this considerations, a first PLS model was computed. Taking the ratio between sample size
185 and number of variables into account, variable selection has not been considered, in order to avoid
186 the problem of overfitting. Therefore, for every single chemical variable, the whole spectrum on
187 the X has been considered in one PLS model. The model was validated using full cross validation.
188 Then, those models with validated explained variance greater than 25% and presenting root mean
189 squared error (RMSE) between the 9% and the 12% of the range were considered. Considering
190 the size of the sample, and the number of factors that explain the main information of the
191 X -variables, only models with less than or equal to four ~~PCs~~PLSs, have been considered.
192 All the analyses have been carried out with Unscrambler X 10.5.1, Matlab R2018a, R 4.0 and
193 XLStat v2018.
194

195 **3. Results and discussion**

196 *3.1. Voltammogram profiles*

197 Figure 1 shows the first derivative voltammograms for the sample set. Two characteristic anodic
198 waves with two maximal points and a minimal can be observed. The first maximal point and the
199 minimal are around 420 mV and 600 mV, respectively. Differently, the second maximal point is
200 around 730 mV. The derivative curve displays maximum values in the first maximal point (around
201 420 mV) with a derivative current reaching values of 220 nA/mV. This can be explained because
202 red wines contain high levels of components that are rapidly involved in oxidative reactions such
203 as anthocyanins, ortho-diphenols and triphenols of gallic acids (Table S2), which usually occur
204 at low potential (Kilmartin, Zou, & Waterhouse, 2002) and thus can be associated with this first
205 anodic wave. The derivative current of the second anodic wave, which corresponds to less readily
206 oxidizable compounds (Ugliano, 2016), has been associated with vanillic or coumaric acids, the
207 meta-diphenols on the A ring of flavonoids such as catechin, SO₂, certain amino acids and brown
208 pigments related to oxidation reactions (Kilmartin, Zou, & Waterhouse, 2002; Makhotkina &
209 Kilmartin, 2013).

210 In order to shed light on specific linkages between compounds and voltammetric signals, PLS-
211 models have been built and discussed.

212 *3.2. Predicting OCR from voltammetric signals*

213 PCA was calculated with the derivative voltammetric signals. The first three PCs retain 91% (82%
214 in validation) of original variance. This result shows that voltammetric information can be
215 retained by three independent and non-correlated variables. Remarkably, even big efforts were
216 invested in building PLS-models predicting chemical variables and OCRs from these three PCs,
217 validated models could not be obtained, which could have simplified the prediction task. [A
218 possible explanation is that ~~This is probably~~ because we have no guarantee that the selected
219 principal components are associated with the outcome. In fact, it is a possible drawback of PCR
220 method \(PCA + regression\), where the selection of the principal components to incorporate in the
221 model is not supervised by the outcome variable.](#)

222 As detailed in the material and methods section and in a previous reference (Ferreira, Carrascon,
223 Bueno, Ugliano, & Fernandez-Zurbano, 2015), two different OCRs were defined for red wines:
224 the initial OCR, that corresponds to the rate of oxygen consumption during the first 24 h, and the
225 average OCR, that refers to the average rate of consumption for the rest of the experiment. Initial
226 OCRs are significantly faster and far more variable (0.54 – 8.22 mg O₂/L/day) than the average
227 rates (0.365 -0.792 mg O₂/L/day). Interestingly, potentials in the first anodic wave, specifically
228 in the 355-475 mV range (marked in green in Figure 2), present a significant negative correlation
229 with the initial OCR ($r < -0.54$; $P < 0.05$ in all cases), while for the average OCR no significant
230 correlation with potentials (i.e., X variables) could be established. This is a surprising result,
231 because we had expected that higher potential signals would be related to higher contents of
232 readily oxidizable substrates and thus to higher oxygen consumption rates. However, this result
233 is completely equivalent to that obtained in a previous paper, in which chemical compositional
234 parameters were just poorly positively correlated or not correlated at all with initial and average
235 OCRs, respectively; while significant negative correlations with some chemicals were observed
236 (Ferreira, Carrascon, Bueno, Ugliano, & Fernandez-Zurbano, 2015). In a further attempt to
237 investigate the relationship between OCRs (initial and average) and voltammetric signals (first
238 derivative), PLS models were calculated. Unfortunately, modeling failed to capture validated
239 models for initial and average OCRs, thus we could not validate one of our initial hypothesis.
240 Conversely, if a previous step consisting in the prediction of initial OCR from voltammetric
241 potentials, but not considering the second voltammetric wave (600-1000 mV), which corresponds
242 to less readily oxidizable compounds (Ugliano, 2016)~~selection of variables, in which~~
243 ~~voltammetric signals belonging to to the second anodic wave were not considered (600-1000~~
244 ~~mV)~~, a validated model explaining 62% of original variance for initial OCR was obtained. The
245 model included 8 voltammetric signals with half of them displaying positive (at 20, 100, 1050
246 and 1130 mV: marked in orange in Figure 2) and the other half negative (300, 440, 520 and 1140
247 mV: marked in blue in Figure 2) relationships with initial OCR (Figure S4 of Supporting
248 Information). Not surprisingly, the highest positive contributions to initial OCRs correspond to
249 voltammetric signals measured at very low potentials (10 and 100 mV). It is not clear to which

Kommentert [TN5]: Potential. Is that the X variables?

Kommentert [UdW6R5]: Yes, they are

Kommentert [TN7]: Emphasise that this is not based on variable selection in the PLS models.

Kommentert [cf8R7]: Ok! L 256

Kommentert [TN9]: These are not presented in loadings plots here, right?

Kommentert [UdW10R9]: No, they are not presented

250 species can correspond signals at 10 mV, although results derived from white wines (unpublished
251 data) suggest that it may be copper, but this result should be further validated in future research.
252 On its side, the signal at 100 mV could be related to the beginning of the anodic curve for ascorbic
253 acid (Kilmartin, Zou, & Waterhouse, 2002; Makhotkina & Kilmartin, 2013). It has to be
254 highlighted that the modeling of initial OCR from voltammetric signals ~~with selection of~~
255 ~~variables~~ omitting voltammetric signals belonging to the second anodic wave (not based on
256 variables selection in PLS) has to be considered with caution. Given the low number of samples
257 and high number of predicting variables, overfitting can be occurring, thus this model only
258 establishes preliminary relationships between voltammetric signals and initial OCR. This
259 hypothesis should be confirmed in further investigations.

260 3.3. Predicting chemical compositional variables from voltammetric signals

261 Table 1 shows the chemical variables that could be satisfactorily modeled from voltammetric
262 signals ($9\% < \text{RMSE} < 12\%$ RMSE between the 9% and the 12% of the range) (29 out of 95).
263 Validated models explain between 23% and 74% (average = 47%) of original variance by full-
264 cross validation, which correspond to moderate-high correlation coefficients ranging from 0.5 to
265 0.9 (average = 0.7). Explained variances by calibration reach values in the range of 48-99% and
266 corresponding to correlation coefficients between 0.7 and 0.9 (average = 0.9). Figure 3 shows the
267 voltammetric signals (in nA of anodic current per increment of mV in the working electrode)
268 included in models and the sign and magnitude of their coefficients following a color code. Figure
269 4 shows some examples of line plots representing the X-loadings corresponding to the first two
270 PLSEs (for the plots of the rest of models see Figure S5 of Supporting information). These
271 representations are useful in the interpretation and for confirming the validity of the predictive
272 models. These plots represent the variables (potentials of the voltammograms) that are important
273 for predicting the variables studied such as the concentration of the compounds.

274 A group of flavonols (quercetin-3-*O*-glucuronide, syringetin-3-*O*-galactoside, isorhamnetin),
275 anthocyanins (petunidin-3-*O*-glucoside, malvidin-3-*O*-glucoside, peonidin-3-*O*-(6-*O*-*p*-
276 coumaroyl) glucoside), flavanols (catechin, epicatechin, epigallocatechin, procyanidin B1 and
277 B2) and important chemical variables such as mean degree of polymerization of tannins and pH

Kommentert [TN11]: No selection of X-variables here, right?

Kommentert [UdW12R11]: Effectively, no selection of variables

278 were satisfactorily modelled (% of explained variance > 50% by full-cross validation, i.e.,
279 correlation coefficients > 0.7). Similarly, validated models for large polymeric pigments (LPP)
280 and free SO₂ could explained 49% of variance in prediction (i.e., correlation coefficients of 0.7)
281 and relatively high in calibration 63% and 92%, respectively.

282 Slightly poorer models with explained variance by full-cross validation higher than 23%, yet with
283 correlation coefficients higher than 0.5, were obtained for quercetin-3-*O*-galactoside, myricetin-
284 3-*O*-glucoside, *c*-cinnamic acid, gallic acid ethyl ester, galocatechin, two anthocyanins,
285 monomeric pigments (MP), small polymeric pigments (SPP), total polyphenol index (TPP),
286 antioxidant capacity-TEAC, absorbances at 420 and 520 nm, and for the measured redox
287 potential. This suggesting that the related results can be presented as hypotheses to be further
288 validated with a larger sample size.

289 In the case of flavonols, leaving aside quercetin, myricetin-3-galactoside and myricetin, relevant
290 derivatives from the quantitative point of view were modelled. In the case of flavanols and
291 anthocyanins, all the most relevant quantitatively were satisfactorily modelled. By contrast, the
292 ability to model cinnamic, hydroxycinnamic acids and their derivatives was very poor, and only
293 two out of 24 components could be satisfactory modelled. Most remarkably, models for predicting
294 compositional data for metals and for absorbance at 620 nm could not be derived from the
295 voltammetric signals.

296 It is interesting to note that models (Figure 3, [Figure 4](#) and [Figure S5 of Supporting Information](#))
297 for flavonols, gallic acid ethyl ester, flavanols, and monomeric anthocyanins, including the overall
298 measure of bleachable anthocyanins (MP), present positive coefficients for potentials belonging
299 to the first anodic wave of voltammograms (mainly 140-600 mV), which is supported by the fact
300 that these compounds are most readily oxidizable molecules of wines and thus involved in most
301 rapid oxidative reactions (Ugliano, 2016). Differently, non-bleachable anthocyanins, named
302 polymeric pigments (both small and large PP), can be predicted mainly from higher potentials,
303 belonging mainly to the second wave of the first derivative of voltammograms (840-1160 mV).
304 Among flavanols, epigallocatechin and galocatechin show positive coefficients for lower
305 potentials (180-250 mV) than the rest of flavanols measured (catechin, epicatechin, procyanidins

306 B1 and B2) (270-520 mV). This is well in accordance with previous reported results, that show
307 that gallo catechins oxidize at the surface of carbon electrodes earlier than other readily oxidizable
308 compounds, such as monomers and dimers of (epi)catechin (Kilmartin, 2016). Remarkably is
309 that non-acylated anthocyanins present similar models positively contributed by positive
310 voltammetric signals at low (160-240 mV) and high (680-800 mV) potentials, while the models for
311 coumaroly anthocyanins, mainly those with higher prediction ability (delphinidin and peonidin-
312 3-*O*-(6-*O*-*p*-coumaroylglucosides)), show positive coefficients mainly in the first anodic wave
313 (180-480 mV), and thus they are more readily oxidizable.

314 In summary, our results suggest that the voltammetric signal in disposable carbon paste electrodes
315 is mainly the result of wine major flavonols, flavanols, anthocyanins, polymeric pigments, pH
316 and free SO₂, being poorly contributed by phenolic acids, metal cations or sulphite adducts.
317 Conversely, it can be also suggested that voltammetric information is highly multidimensional
318 and therefore can be satisfactorily used to predict many relevant chemical compositional data.

319 **Conclusions**

320 The voltammetric signals recorded from wines with disposable carbon paste electrodes are
321 extraordinarily rich in compositional information from a relatively wide range of chemical species
322 and parameters, which are suggested to be satisfactorily extracted using PLS. The best
323 performance in modelling terms was in all cases obtained from the 1st derivative of the
324 voltammograms. The voltammetric signals seem to be mainly influenced by major flavonols,
325 flavanols, anthocyanins, polymeric pigments and free SO₂, all of which could be satisfactorily
326 modelled. Although oxygen consumption rates (OCR) could not be satisfactorily modelled,
327 positive correlations with voltammetric signals and satisfactory models obtained after selection
328 of variables for initial OTR (based on prior knowledge and not on PLS variable selection), allow
329 to draw the hypothesis that OCRs have a potential of ~~could~~ being satisfactorily predicted and thus
330 voltammetry could be also a suitable rapid tool for predicting OCR.

331 The results presented in this work suggeste on firm that disposable carbon paste sensors measuring
332 voltammetric signals and coupled to PLS-modeling have an important potential to be used in
333 wineries for rapid, cheap and easy-to-use approach for wine chemical characterization and

Kommentert [TN13]: Confirm is too string.

Kommentert [UdW14R13]: Ok!

334 oxidation-related control. It is important to emphasiseemphasize that the number of samples is
335 quite low and also that only the best models are selected for presentation in Table 1. Therefore
336 Notwithstanding, the present work is a feasibility study and models must be validated on new
337 data to confirm the results.

338

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348 his advice and discussions on voltammetric data.

349 **Appendix A. Supplementary information**

350 Supplementary information associated with this article can be found online at Supplementary
351 data to this article can be found online at <https://doi.org/xx.xxx/food.chem>

352

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431 **Figure captions**

432 **Figure 1.** First derivative voltammograms for sixteen Spanish red wines.

433 **Figure 2.** First derivative voltammograms of wines with highest and lowest oxygen consumption
434 rates among red wines. Regions marked in green present significant correlations with OCR. In
435 orange voltammetric signals with positive and in blue with negative coefficients in the models
436 predicting OCRs

437 **Figure 3.** Maps with coefficients of variables included in validated PLS-models predicting
438 chemical variables from voltammetric signals for red wines.

439 Figure 4. The X-loadings for the two first PELS components based on the PLS model for a)
440 quercetin-3-O-galactoside, b) quercetin-3-glucoronide, c) catechin, d) epigallocatechin, e)
441 malvidin-3-O-glucoside, and petunidin-3-O-glucoside. The red line represents the first PELS and
442 the blue the second PELS line the second

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Table 1. Variables successfully modeled in the set of red wines (n=16) from voltammetric signals by PLS regression, % of explained variance by full cross validation (and the % of explained variance), the number of PLSs included in each model and the root mean squared error of prediction.

	<i>variable</i>	<i>% explained variance P (number of PLSs) [% explained variance C]</i>	<i>RMSE¹</i>
flavonols	quercetin-3-galactoside	41% (2) [75%]	0.48
	quercetin-3-glucuronide	58% (2) [76%]	0.47
	syringetin-3-galactoside	74% (2) [88%]	0.34
	myricetin-3-glucoside	44% (3) [83%]	0.39
	isorhamnetin	52% (2) [79%]	0.44
acids and derivatives	<i>c</i> -cinnamic acid	48% (1) [57%]	0.63
	gallic acid ethyl ester	38% (2) [66%]	0.56
flavanols	catechin	64% (4) [93%]	0.25
	epicatechin	57% (4) [94%]	0.24
	epigallocatechin	55% (1) [69%]	0.54
	gallocatechin	37% (1) [57%]	0.63
	procyanidin B1	56% (2) [76%]	0.48
	procyanidin B2	63% (1) [80%]	0.43
anthocyanins	petunidin-3- <i>O</i> -glucoside	60% (4) [99%]	0.09
	malvidin-3- <i>O</i> -glucoside	65% (4) [99%]	0.08
	malvidin-3- <i>O</i> -glucoside-8-ethyl-(epi)catechin	43% (4) [99%]	0.11
	malvidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl)glucoside	41% (1) [61%]	0.60
	peonidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl)glucoside	51% (2) [85%]	0.37
polyphenol-related measurements	small polymeric pigments (SPP)	30% (1) [50%]	0.69
	large polymeric pigments (LPP)	49% (1) [63%]	0.59
	monomeric pigments (MP)	23% (3) [88%]	0.51
	mean degree of polymerization (mDP)	53% (1) [88%]	0.17
	total polyphenol index (TPI)	26% (1) [48%]	0.69
	antioxidant capacity-TEAC	29% (2) [65%]	0.57
color	absorbance at 420nm	38% (1) [56%]	0.64
	absorbance at 520nm	38% (2) [72%]	0.51
other parameters	pH	51% (1) [61%]	0.61
	redox potential	28% (2) [67%]	0.56
	free SO ₂	49% (4) [92%]	0.27

¹RMSE is given in z-units for a normal distribution. Given that 99.7% of normal values are between z=-3 and z=3, a RMSE of 0.6 represents around 10% of the range.

Figure 1

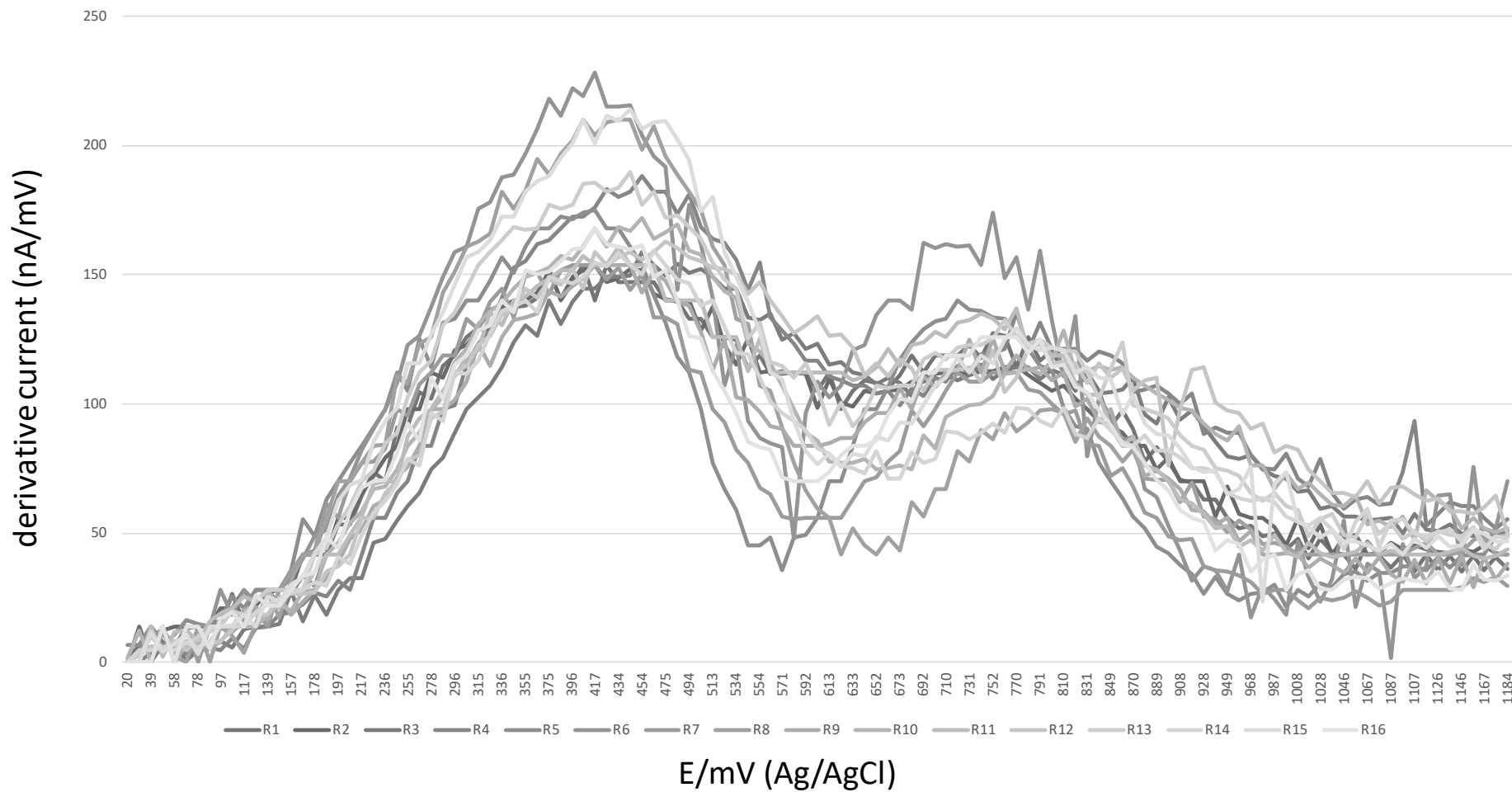


Figure 2

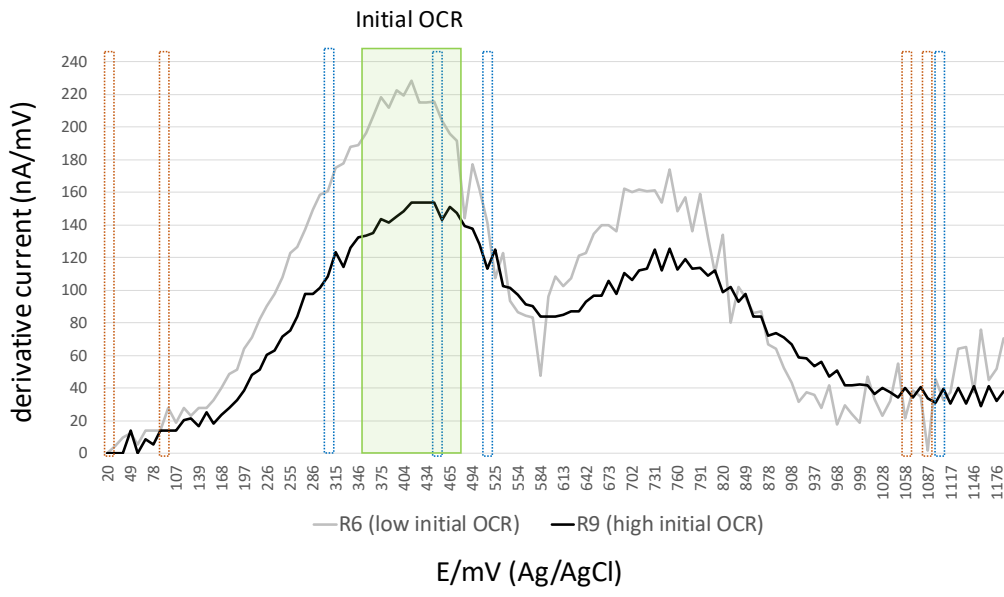
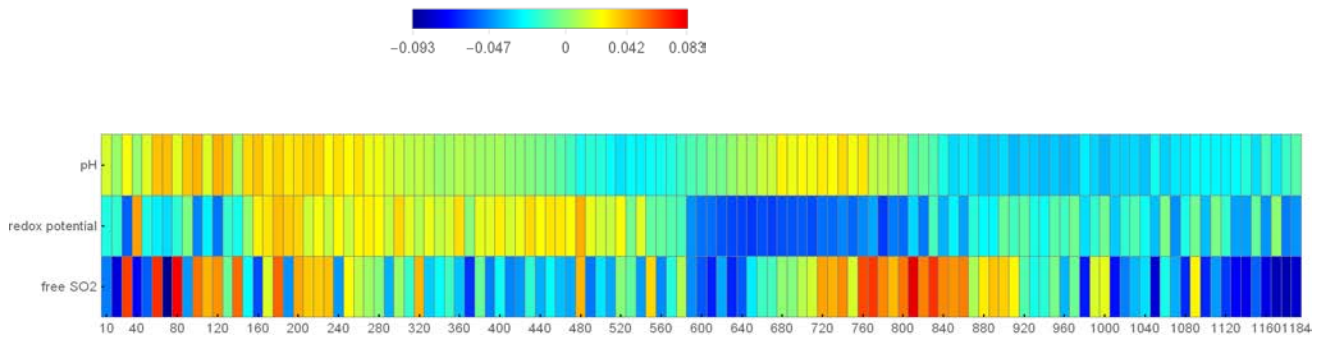
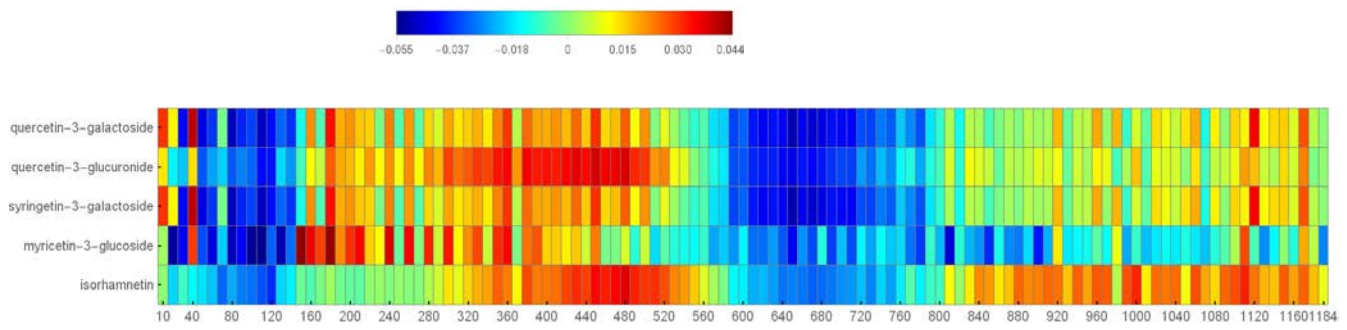


Figure 3

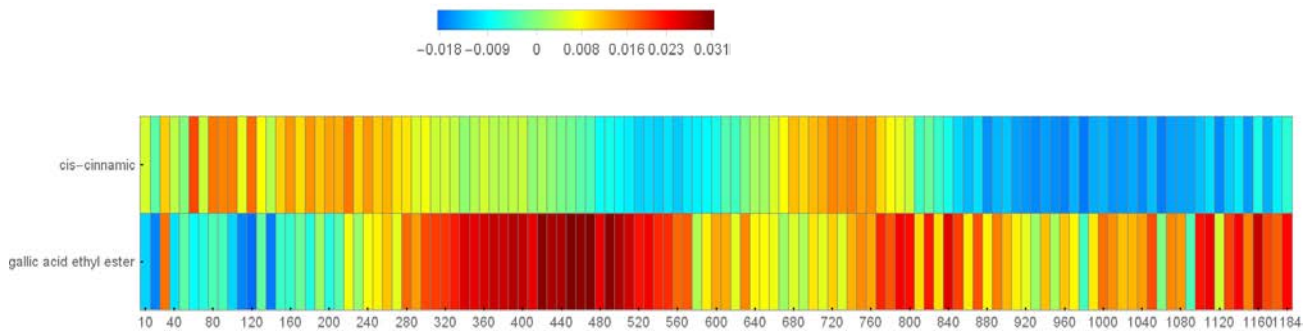
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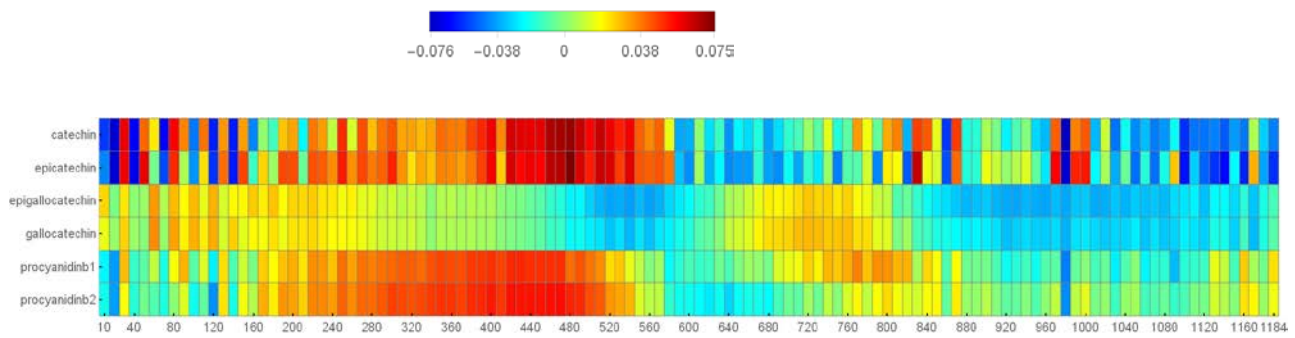
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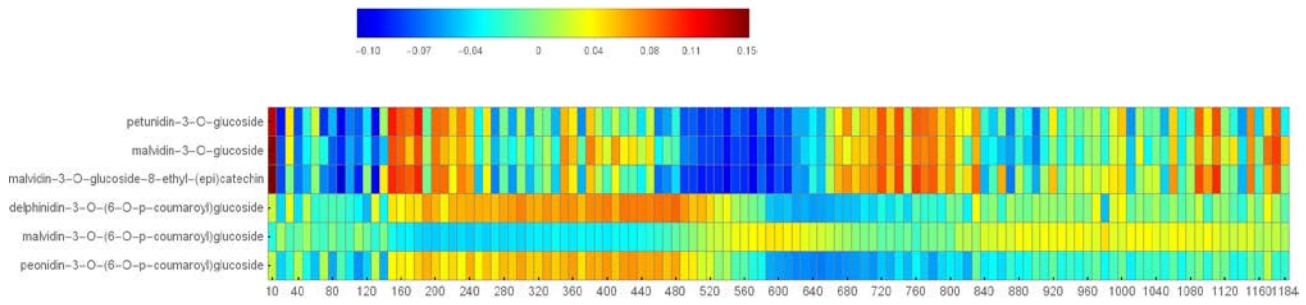
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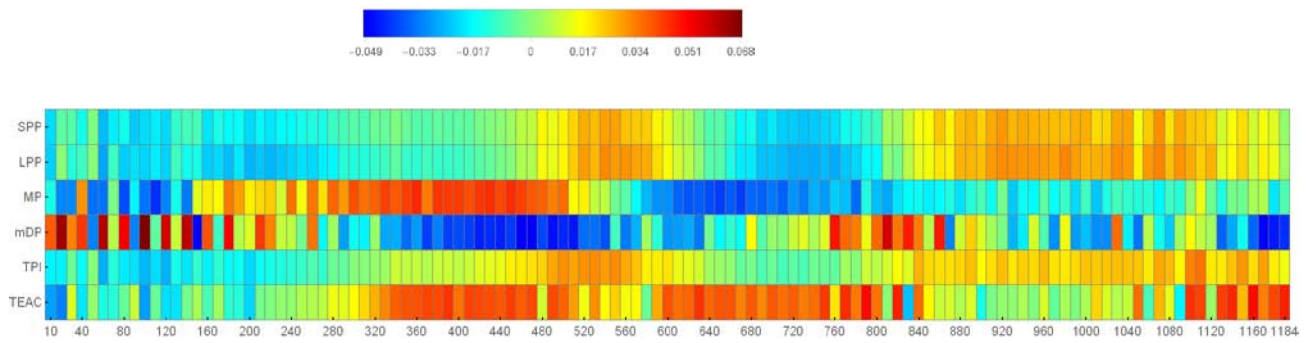
d)



e)



f)



g)

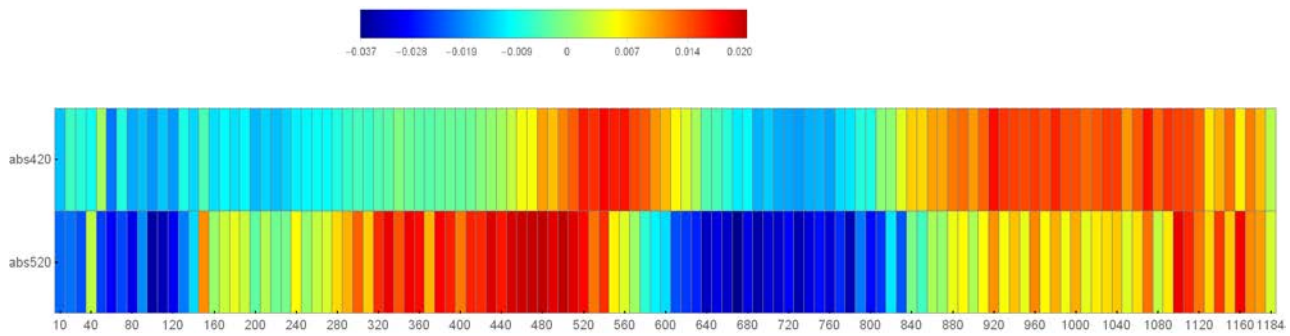
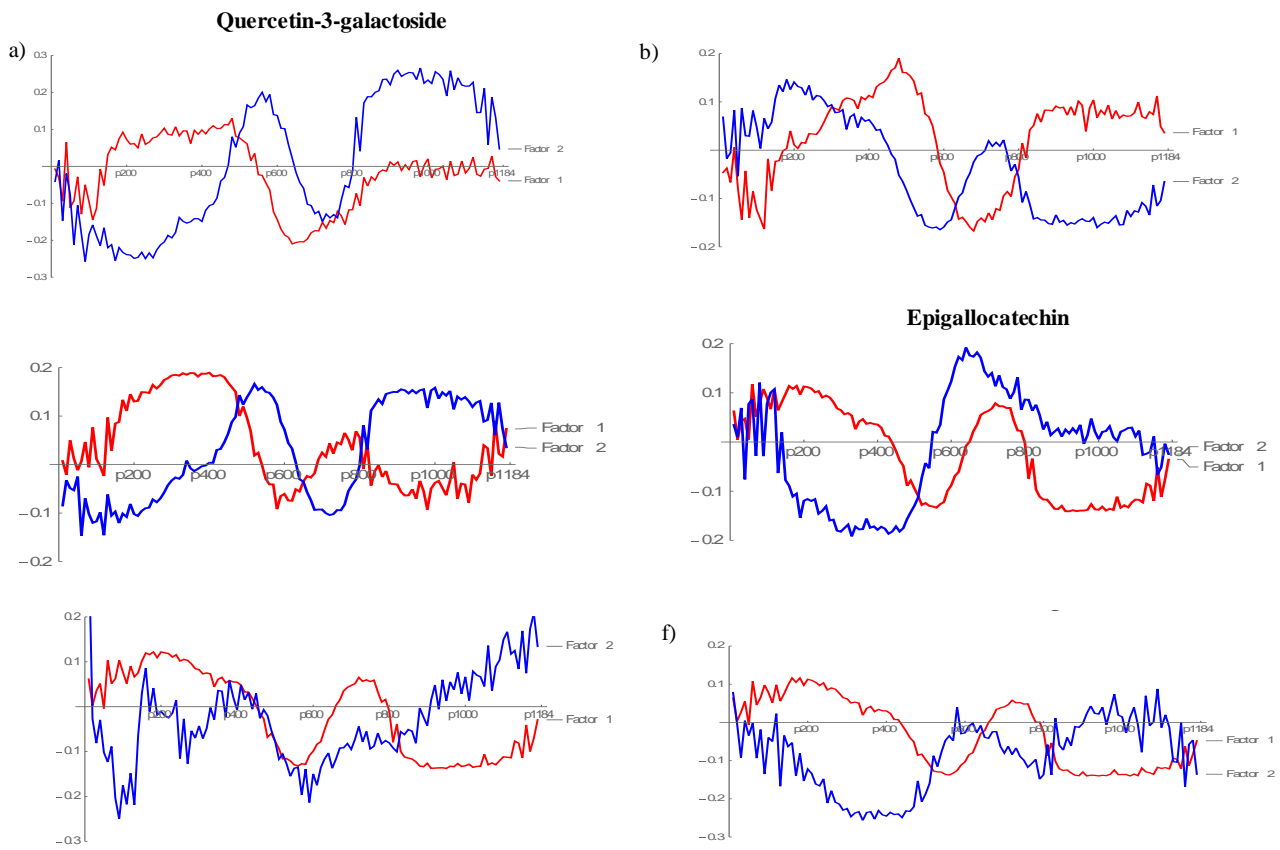


Figure 4



Supplementary Information for

An assessment of voltammetry on disposable screen printed electrodes to predict wine chemical composition and oxygen consumption rates

Chelo Ferreira^{a,d}, María-Pilar Sáenz-Navajas^{a*}, Vanesa Carrascón^a, Tormod Næs^b, Purificación Fernández-Zurbano^c, Vicente Ferreira^a

^aLaboratorio de Análisis del Aroma y Enología (LAAE), Department of Analytical Chemistry, Universidad de Zaragoza, Instituto Agroalimentario de Aragón (IA2) (UNIZAR-CITA), Associate unit to Instituto de las Ciencias de la Vid y del Vino (ICVV) (UR-CSIC-GR), c/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

^bNofima AS, Osloveien 1, P.O. Box 210, N-1431 Ås, Norway

^cInstituto de Ciencias de la Vid y del Vino (ICVV) (CSIC-Gobierno de La Rioja- Universidad de La Rioja), Carretera de Burgos Km. 6, Finca La Grajera, 26007 Logroño, La Rioja, Spain.

^dInstituto Universitario de Matemáticas y Aplicaciones (IUMA-UNIZAR)

*Corresponding author: mpsaenz@icvv.es

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Figure S4. Map with coefficients of variables included in validated PLS-models predicting initial OTR from voltammetric signals.

Figure S5. The X-loadings for the two first PLS components based on the PLS model for a) flavonols, b) acids and derivatives, c) flavanols, d) anthocyanins, e) anthocyanic pigments, and f) other parameters

Table S1. Information of wines employed in the study.

set of wine	code	vintage	grape variety	origin	time in barrel (months)	% ethanol (v/v)	pH	TPI (a.u.)
red wines	R1	2008	Tempranillo	Ribera del Duero	18	14.1	3.9	53.5
	R2	2007	Tempranillo	Rioja	>6	13.5	3.8	55.1
	R3	2008	Garnacha	Campo de Borja	>6	13.5	3.5	61.9
	R4	2010	Garnacha	Campo de Borja	>6	14.5	3.5	86.5
	R5	2012	Tempranillo	Rioja	0	13	3.9	48.2
	R6	2012	Garnacha, Tempranillo	Calatayud	0	14	3.8	62.2
	R7	2012	Tempranillo	Ribera del Duero	6	13.5	3.7	60.8
	R8	2012	Syrah	Vinos de la tierra de Castilla	0	14.5	3.7	69.0
	R9	2010	Tempranillo, Mazuelo, Graciano	Rioja	3	13.5	3.5	52.2
	R10	2011	Garnacha	Campo de Borja	>6	15	3.4	57.9
	R11	2010	Tempranillo	Toro	14	14.5	3.9	66.0
	R12	2008	Garnacha	Campo de Borja	10	15	3.5	72.3
	R13	2009	Syrah, Merlot, Cabernet Sauvignon	Cariñena	>6	14.5	3.6	62.3
	R14	2010	Garnacha	Campo de Borja	>6	15.5	3.4	57.9
	R15	2012	Cabernet Sauvignon, Merlot	Somontano	0	13.5	3.5	60.9
	R16	2012	Tempranillo	Rioja	6	13.5	3.8	53.4

Table S2. Chemical characterization of the 16 red wines studied (data expressed as micrograms per liter, otherwise it is specified). Compounds marked in red were satisfactorily modelled from voltammograms.

Compounds	average	max	min
Flavonols			
quercetin-3-galactoside	1.22	3.69	0.51
quercetin-3-glucoside	1.57	14.58	0.00
quercetin-3-glucuronide	8.86	19.99	3.00
quercetin-3-rutinoside	0.04	0.62	0.00
quercetin	3.05	5.88	1.75
kaempferol-3-glucoside	0.16	1.36	0.00
kaempferol-3-galactoside	0.07	0.31	0.00
kaempferol-3-glucuronide	0.06	0.21	0.00
kaempferol-3-rutinoside	0.30	0.52	0.15
kaempferol	0.96	1.57	0.00
syningetin-3-galactoside	1.47	3.13	0.55
myricetin-3-galactoside	2.90	12.60	1.19
myricetin-3-glucoside	3.45	13.43	1.20
myricetin-3-glucuronide	1.57	1.90	1.35
myricetin-3-rutinoside	1.18	1.21	1.17
myricetin	4.39	7.36	2.48
isorhamnetin -3-glucoside	0.48	4.48	0.00
isorhamnetin -3-galactoside	0.11	0.22	0.00
isorhamnetin -3-glucuronide	0.07	0.14	0.00
isorhamnetin -3-rutinoside	0.14	0.22	0.00
isorhamnetin	4.70	7.67	2.74
Acids and derivatives			
gallic acid	35.14	56.12	22.30
protocatechuic acid	1.10	2.33	0.61
<i>c</i> -caftaric acid	3.13	9.75	0.00
<i>t</i> -caftaric acid	57.79	120.89	21.56
3,4-hydroxyphenylacetic acid	0.31	2.01	0.00
cutaric acid	4.37	6.60	2.72
vanillic acid	0.35	0.54	0.23
caffeic acid	5.79	12.72	1.44
syringic acid	1.06	1.73	0.70
<i>c</i> -coumaric-acid	0.82	0.94	0.00
coumaric acid	1.63	4.26	0.98
<i>c</i> -cinnamic acid	7.73	10.10	5.42
trans-cinnamic acid	17.48	22.10	12.26
protocatechuic acid ethyl ester	0.19	0.47	0.00
caffeic acid ethyl ester	0.79	1.33	0.00
ferulic acid ethyl ester	0.00	0.00	0.00
syringic acid ethyl ester	0.00	0.00	0.00
ellagic acid	24.78	30.58	19.80
gallic acid ethyl ester	2.23	4.06	1.35
coumaric acid ethyl ester	0.52	0.94	0.00
<i>c</i> -aconitic acid	1.99	2.48	1.56
<i>t</i> -aconitic acid	1.45	3.50	0.00
<i>c</i> -ferulic acid	0.36	1.48	0.00
<i>t</i> -ferulic acid	0.34	1.60	0.00
Flavanols			
procyanidin B1	10.75	27.66	3.27
epigallocatechin	6.26	10.28	3.88
catechin	7.48	23.04	3.56
procyanidin B2	5.13	16.44	1.89
epicatechin	5.10	18.88	2.72
epigallocatechin gallate	2.57	3.74	1.73
catechin gallate	0.05	0.40	0.00
epicatechin gallate	0.95	1.26	0.00
procyanidin A2	0.85	1.97	0.00
galocatechin	3.05	4.25	1.33
galocatechin gallate	0.82	2.99	0.00
Anthocyanins			
B-type vitisin of delphinidin-3- <i>O</i> -glucoside	0.05	0.08	0.02
cyanidin-3-glucoside	0.10	0.23	0.05
petunidin-3-glucoside	1.98	9.48	0.03
peonidin-3-glucoside	0.28	0.74	0.03
malvidin-3-glucoside	17.13	75.60	0.16
delphinidin-3- <i>O</i> -(6- <i>O</i> -acetyl) glucoside	0.02	0.02	0.02
vitisin A	0.21	0.59	0.03

Table S2 contd.

Compounds	average	max	min
B-Type vitisin of malvidin-3-oglucoside	0.02	0.02	0.02
petunidin-3- <i>O</i> -(6- <i>O</i> -acetyl) glucoside	0.02	0.03	0.02
malvidin-3- <i>O</i> -glucoside-8-ethyl-(epi)catechin	0.06	0.25	0.02
delphinidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl) glucoside	0.80	5.02	0.02
malvidin-3- <i>O</i> -(6- <i>O</i> -acetyl) glucoside	0.03	0.05	0.02
A-type vitisin of malvidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl)glucoside	0.02	0.02	0.02
petunidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl) glucoside	0.05	0.17	0.02
malvidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl) glucoside	0.03	0.07	0.02
peonidin-3- <i>O</i> -(6- <i>O</i> - <i>p</i> -coumaroyl) glucoside	0.04	0.14	0.02
malvidin-3- <i>O</i> -glucoside-4-vinylphenol	0.03	0.05	0.02
malvidin-3- <i>O</i> -acetylglucoside-4-vinylphenol	0.02	0.02	0.02
Polyphenol-related measurements			
mean degree of polymerization of flavanols (mDP)	1.80	2.08	1.54
small polymeric pigments (SPP)	0.54	0.76	0.26
large polymeric pigments (LPP)	0.42	0.69	0.14
monomeric pigments (MP)	0.42	0.91	0.25
proanthocyanidins (mg/L, expressed as equivalents of catechin)	840	1371	304
protein-precipitable flavanols (mg/L, expressed as equivalents of tannic acid)	1.32	2.26	0.48
antioxidant capacity-TEAC (Mm, expressed as equivalents of Trolox)	40.47	63.50	29.53
antioxidant capacity-Folin (mg/L, expressed as equivalents of gallic acid)	2883	3354	2353
free SO ₂ (mg L ⁻¹)	17.84	36.54	4.53
total SO ₂ total (mg L ⁻¹)	48.30	73.60	14.40
Color			
Abs 420 nm (au)	4.32	5.72	2.68
Abs 520 nm (au)	5.46	7.72	3.72
Abs 620 nm (au)	1.75	4.24	1.11
Metals			
Al	0.14	1.17	0.00
Cu	0.26	0.68	0.17
Fe	2.44	4.07	1.46
Mn	1.15	2.57	0.54
Zn	0.63	1.33	0.22
Redox Potential (mV)	14.50	59.00	-10.00

Table S3. Initial and average oxygen consumption rates for red wines (OCR) expressed as mg O₂/L/day (average of three independent replicates)

code	Initial OCR	Average OCR
R1	1.73±0.56	0.60±0.03
R2	7.70±0.49	0.59±0.03
R3	2.82±0.54	0.58±0.02
R4	1.80±0.07	0.68±0.00
R5	7.89±0.40	0.66±0.02
R6	0.54±0.40	0.65±0.02
R7	1.62±0.65	0.52±0.03
R8	0.89±0.26	0.61±0.02
R9	8.22±0.56	0.40±0.03
R10	6.12±0.49	0.47±0.02
R11	5.73±0.35	0.79±0.03
R12	5.43±0.30	0.72±0.02
R13	2.52±0.62	0.55±0.03
R14	3.45±0.31	0.37±0.01
R15	0.80±0.15	0.54±0.01
R16	2.39±0.51	1.27±0.04

Figure S4. Map with coefficients of variables included in validated PLS-model predicting initial oxygen consumption rate (initial OCR) from voltammetric signals.

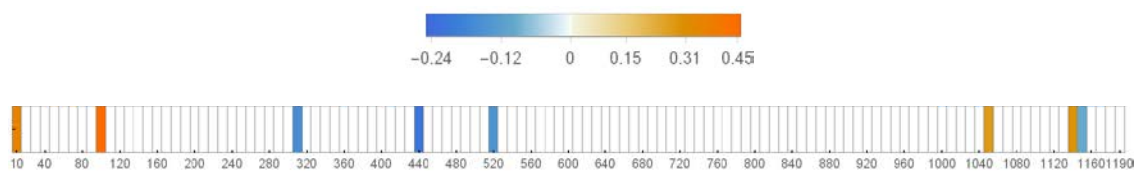
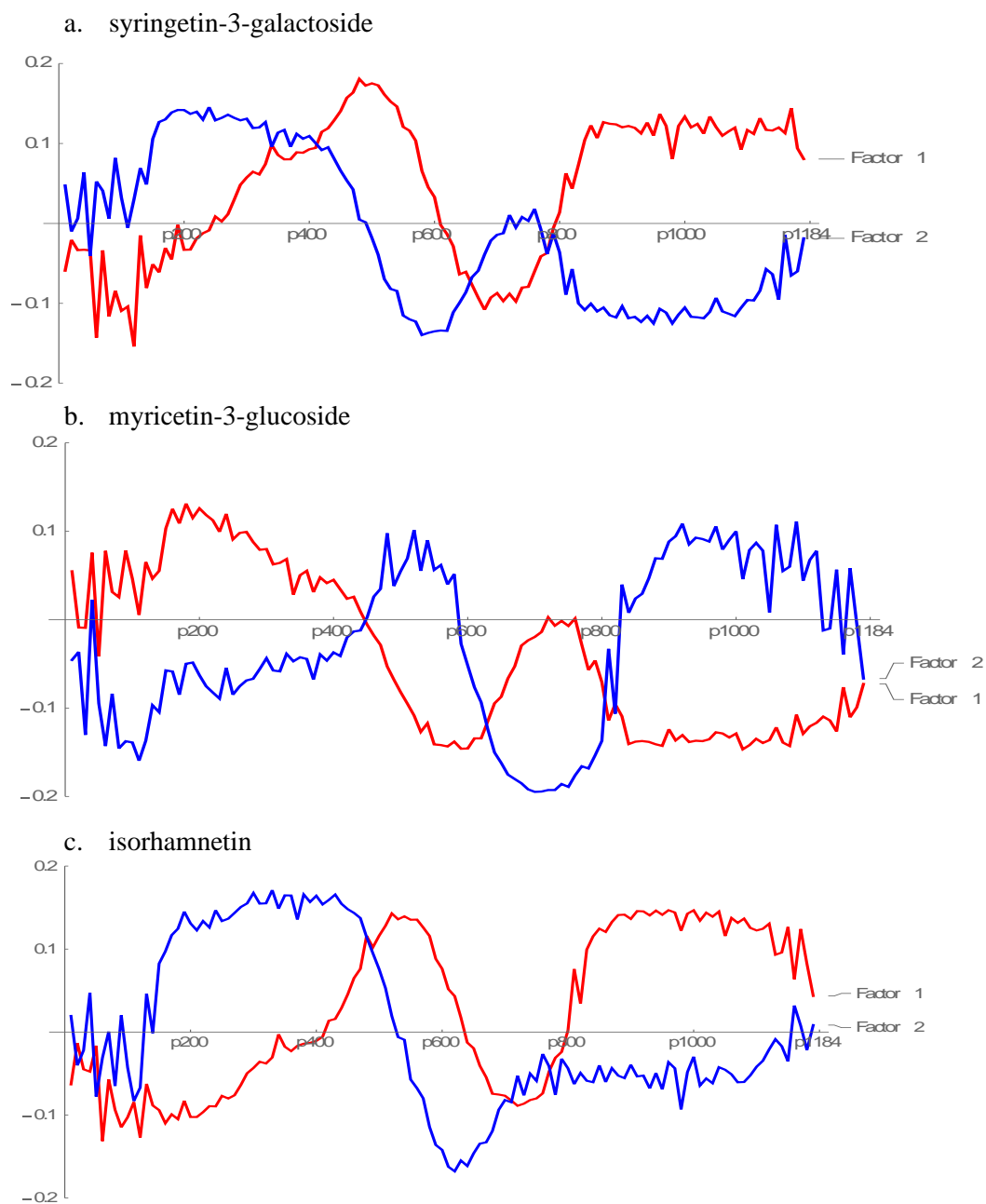


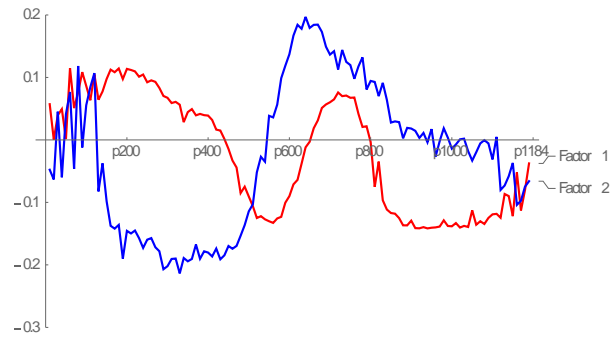
Figure S5.

a) FLAVONOLS

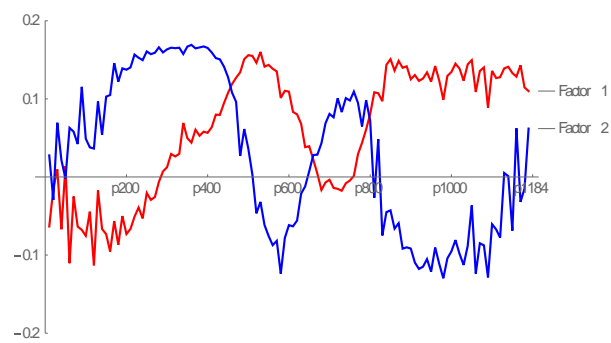


b) ACIDS AND DERIVATIVES

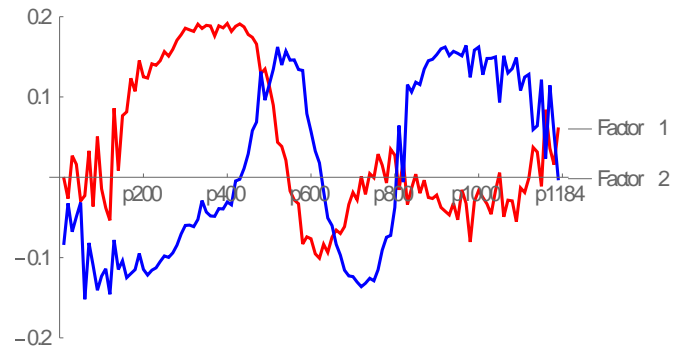
a. c-cinnamic acid



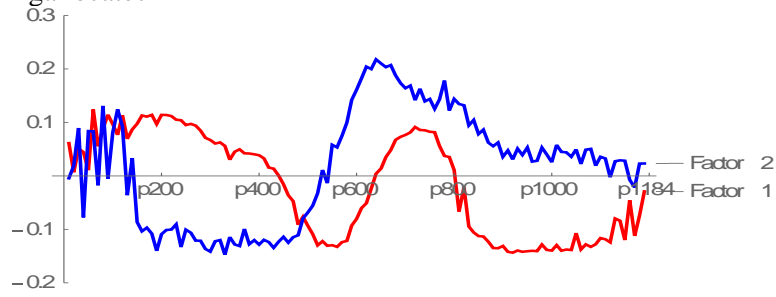
b. gallic acid ethyl ester

**c) FLAVANOLS**

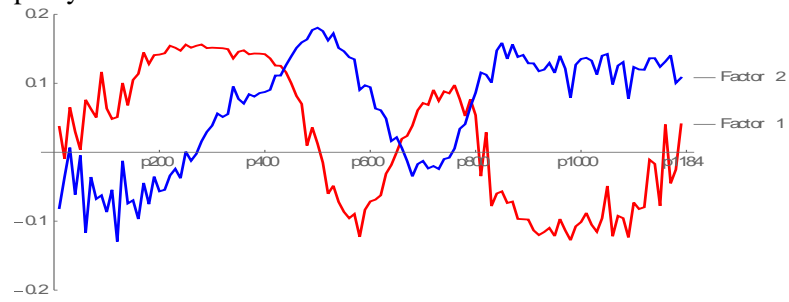
a. epicatechin



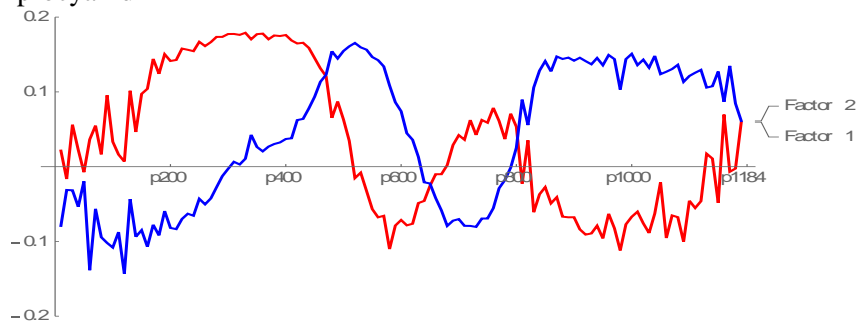
b. gallic catechin



c. procyanidin B1

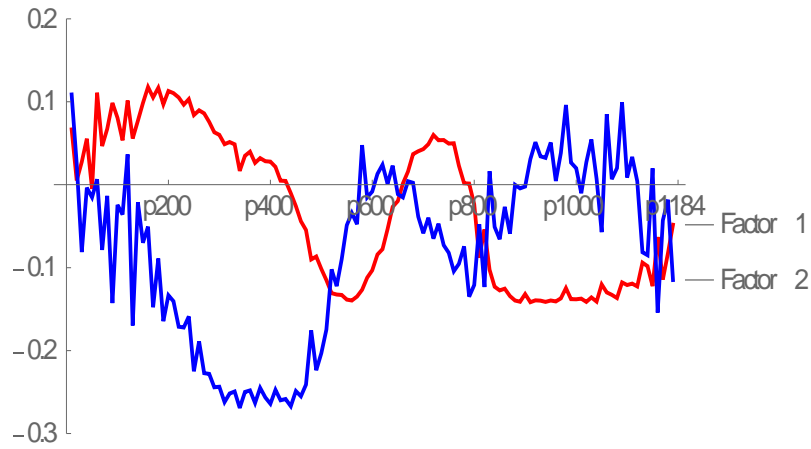


d. procyanidin B2

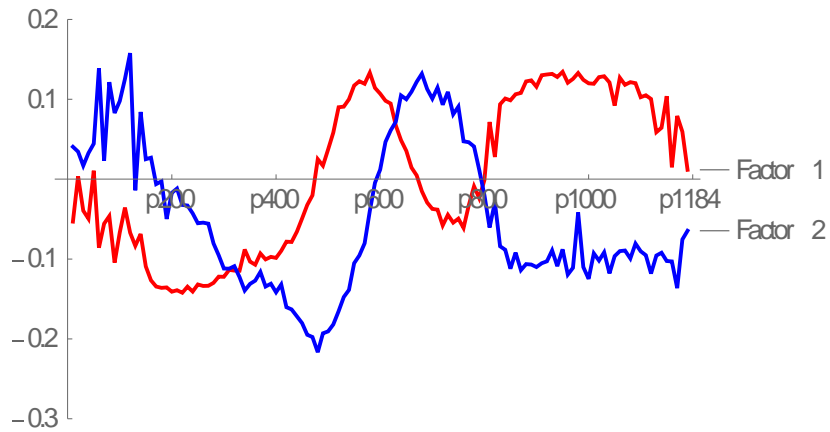


d) ANTHOCYANINS

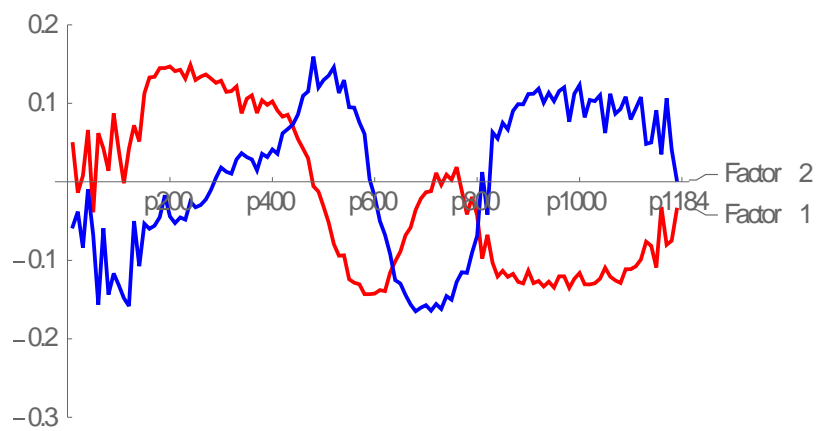
a. malvidin-3-O-glucoside-8-ethyl-(epi)catechin



b. malvidin-3-O-(6-O-acetyl)glucoside

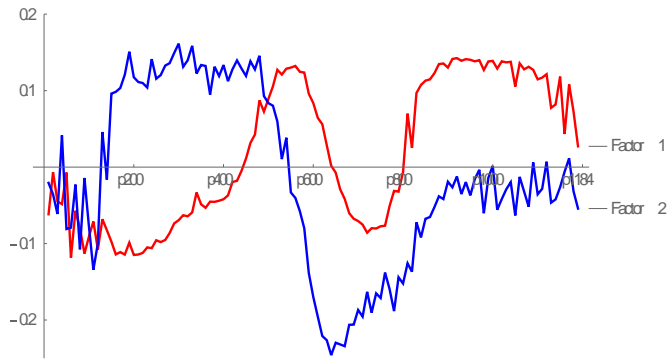


c. peonidin-3-O-(6-O-p-coumaroyl)glucoside

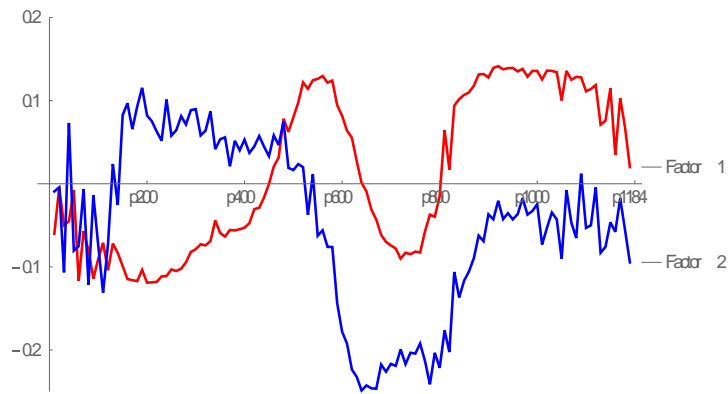


e) ANTHOCYANIC PIGMENTS

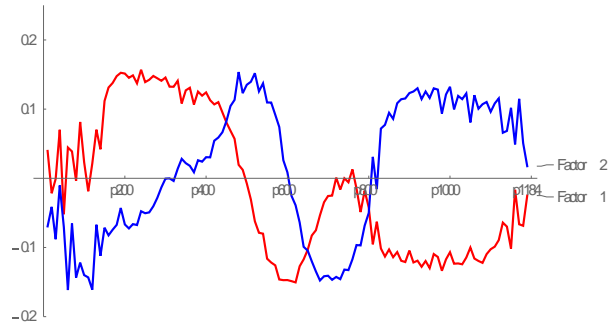
a. SPP



b. LPP

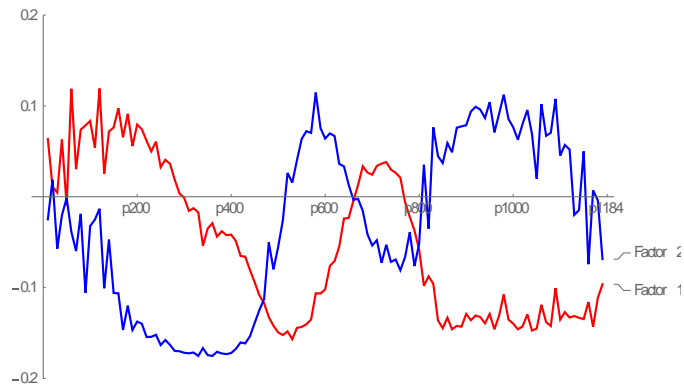


c. MP

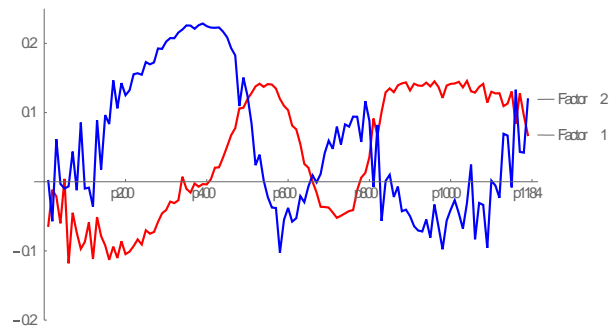


f) OTHER PARAMETERS

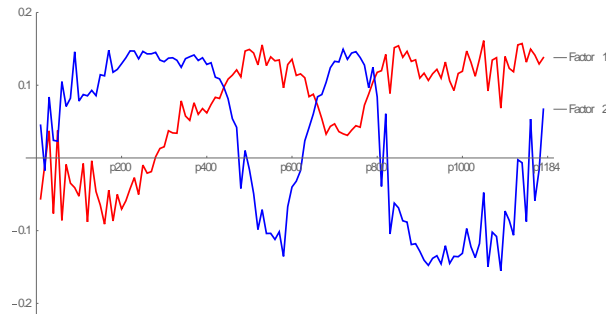
a. mDP



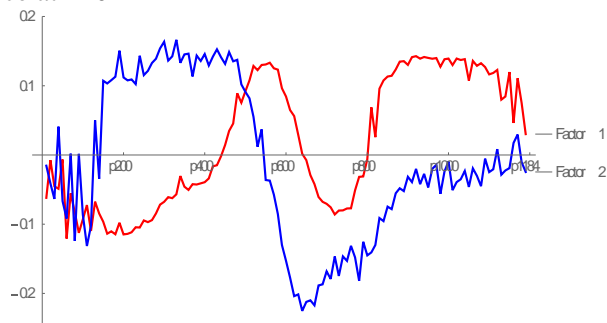
b. TPI



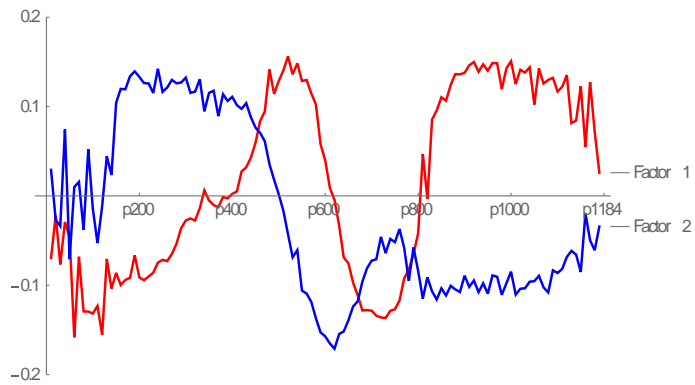
c. TEAC



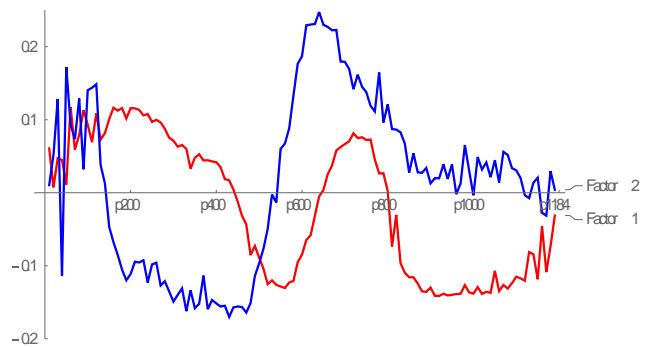
d. absorbance at 420nm



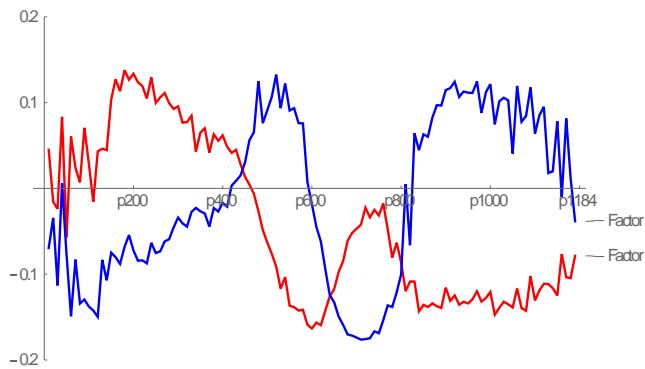
e. absorbance at 520nm



f. pH



g. redox potential



h. free SO₂

