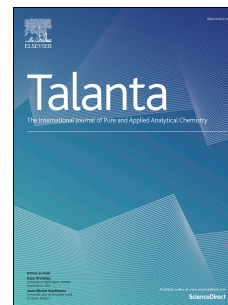


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Development of a voltammetric electronic tongue for the simultaneous determination of synthetic antioxidants in edible olive oils

Lucas Blandon-Naranjo, Rubén Darío Alaniz, María Alicia Zon, Héctor Fernández, Adrian Marcelo Granero, Sebastian Noel Robledo, Gastón Darío Pierini



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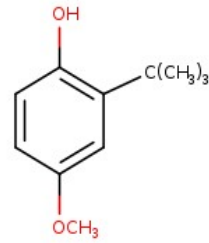
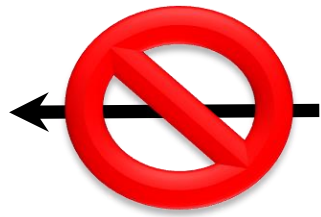
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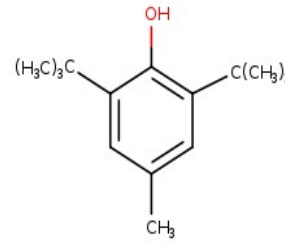
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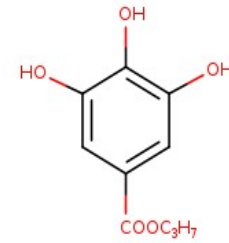
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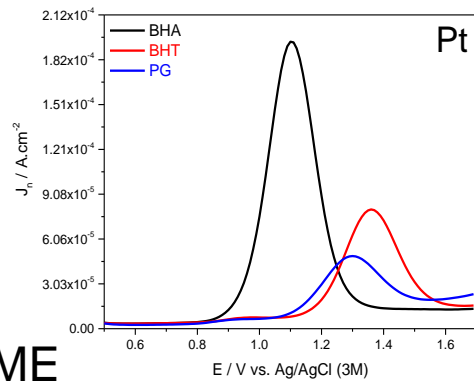
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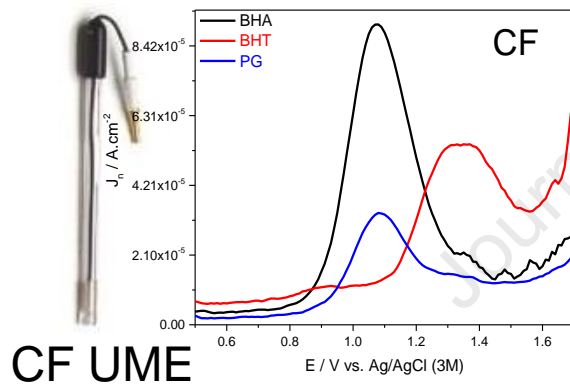
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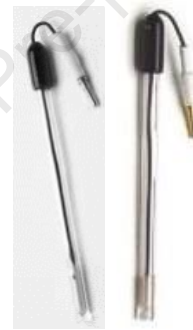
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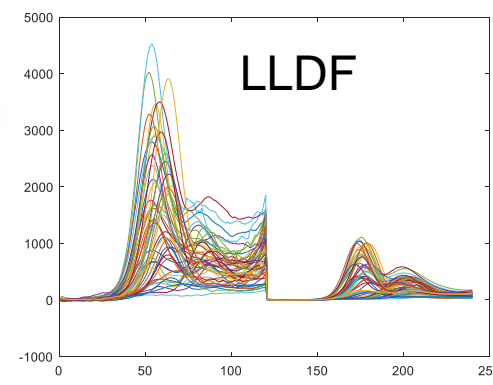
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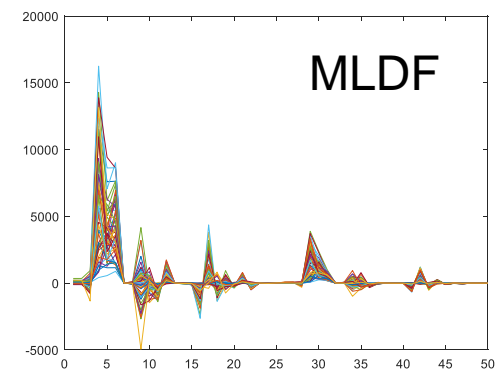
CF



E-tongue

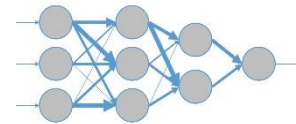


LLDF



MLDF

Artificial Neural Networks (ANN)



Development of a voltammetric electronic tongue for the simultaneous determination of synthetic antioxidants in edible olive oils

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33 Abstract

34

35 A voltammetric electronic tongue (E-tongue) is “a multisensor system, which consists
36 of a number of low-selective sensors and uses advanced mathematical procedures for signal
37 processing based on pattern recognition and/or data multivariate analysis such as artificial
38 neural networks (ANNs), principal component analysis (PCA), among others”. Thus, E-
39 tongues in combination with chemometrics tools result in more accurate and selective
40 analytical methods.

41 In this work, we report results of a simple and reliable electroanalytical method to
42 determine butyl hydroxyanisole (BHA), butyl hydroxytoluene (BHT) and propyl gallate (PG)
43 in edible olive oils (EOO). Therefore, the square wave voltammetry (SWV) was used on
44 platinum and carbon fiber disk ultramicroelectrodes (E-tongue configuration) combined with
45 chemometrics tools to perform these studies.

46 On the other hand, two data fusion strategies were used in order to combine
47 electrochemical data obtained for each working electrode in the E-tongue: low-level data
48 fusion (LLDF) and mid-level data fusion (MLDF). In addition, to reduce the dimensionality
49 of the dataset in MLDF, the discrete wavelet transform (DWT) was used.

50 Finally, to assert the predictive capability of the method for BHA, BHT, and PG
51 determination in real samples, a recovery study for the antioxidants in EOO samples was
52 performed, demonstrating the analytical accuracy of the proposed method. Moreover, from
53 the comparison between the proposed electrochemical method with the AOAC reference
54 method and others found in the literature in terms of the quality of the model (REP %) and
55 the percent recovery assays (%) in different samples, our results were better than other
56 reported previously for the simultaneous determination of BHA, BHT, and PG in real

57 samples. Moreover, the percent recovery assays obtained with the proposed electrochemical
58 method were in good agreement with those obtained by the chromatographic method.

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77 **Keywords:** Electronic tongues; Data fusion strategy; Multivariate calibration; Edible

78 olive oils; Synthetic antioxidants.

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82 **1. Introduction**

83 Olive oils are the extracts obtained from fresh olive fruits using mechanical methods. A
84 large number of phenolic compounds are present in olive oils, being highly appreciated for
85 its nutritional value, its antioxidant properties, and its beneficial role for human health [1].
86 These natural antioxidants play a significant role in retarding the lipid oxidation reactions in
87 food products, and also block the harmful effects of oxygen, and prevent damage to cell
88 membranes produced by free radicals by trapping and neutralizing them [2]. However,
89 natural antioxidants are not enough to fulfill the requirements of the food industry and,
90 synthetic antioxidants are usually added in the manufacturing process in order to guarantee
91 the adequate preservation of the food products, both at the room temperature and when they
92 are subjected to high temperatures. The most frequently synthetic antioxidants used are butyl
93 hydroxyanisole (BHA), butyl hydroxytoluene (BHT) and propyl gallate (PG) [3]. Their
94 chemical structures are shown in Fig. S1 in the Supplementary Material. The analytical
95 determination of synthetic antioxidants in edible vegetable oils is a continuous activity for
96 law enforcement agencies to ensure the safety of oils. Edible vegetable oils are one of the
97 most complex food matrices due the presence of numerous interferences and has been
98 considered the major challenge in the analysis of phenolic antioxidants. Due to toxicological
99 evidence regarding the safety of synthetic antioxidants, their use has been drastically reduced
100 in the past decade [3] and, particularly, the Argentina regulation (Código Alimentario
101 Argentino, 2009) establishes that edible vegetable oils and fats may be added with synthetic
102 antioxidants, with the exclusion of edible olive oils [4].

103 Due to the similar chemical structures of BHA, BHT and PG (Fig. S1 in the
104 Supplementary Material), the most common methods for their determinations are based on
105 separative techniques such as liquid chromatography (LC) with different detection systems

106 such as triple quadrupole mass spectrometry (LC-MS/MS) [5, 6], ultraviolet-visible (LC-
107 UV-Vis) [7]; high performance liquid chromatography (HPLC) in combination with UV-Vis
108 detection (HPLC-UV-Vis) [8-12], diode array detection HPLC-DAD [13-15], gas
109 chromatography (GC) with MS detection (GC-MS) [16-18] and flame ionization detector
110 (GC-FID) [19].

111 On the other hand, electrochemical techniques have gained much attention in the last
112 years due to high degree of accuracy, precision, sensitivity, small size of equipment, low cost
113 and simplicity in sample preparation. However, there are only a few reports regarding on the
114 application of these methods for the quantitation of synthetic antioxidants in oils.

115 Robledo et al. [20] proposed a simple method based on platinum band microelectrodes
116 and square wave voltammetry (SWV) for synthetic antioxidants determination in edible oils.
117 The method used the different acid–base properties of antioxidants in acetonitrile solutions
118 to perform the simultaneous determination of BHA, BHT, PG and tert-butyl hydroquinone
119 (TBHQ). On the other hand, a glassy carbon electrode (GCE) modified with gold
120 nanoparticles (AuNPs/GCE) was used for BHA, BHT and TBHQ determination in edible oil
121 samples [21], where the first-derivative method was used to resolve the overlapped
122 voltammograms. Screen-printed electrodes (SPEs), cetyltrimethylammonium bromide
123 (CTAB), and a peak deconvolution procedure were used for the simultaneous determination
124 of TBHQ, PG and BHA in samples of biodiesel and cosmetic products [22]. Simultaneous
125 determination of TBHQ and BHA, was carried out using a novel nanocomposite based on
126 multi-walled carbon nanotubes (MWCNT) covalently bonded by molecularly imprinted
127 poly(methacrylic acid-hemin) (MIP-MWCNT) and differential pulse voltammetry (DPV) in
128 soybean oils, margarine, mayonnaise and biodiesel [23]. A graphene oxide/ β -cyclodextrin
129 (GO/ β -CD) composite sensor was used for the simultaneous determination of PG and BHA

130 in edible oil samples [24]. Recently, Nunes Angelis et al. [25] proposed a very simple and
131 low cost sensor based on carbon black paste electrode CBPE in the presence of the cationic
132 surfactant (CTAB) for the simultaneous determination of TBHQ and BHA in mayonnaise,
133 margarine and biodiesel samples.

134 All these methods are based on different strategies for the simultaneous determination of
135 synthetic antioxidants such as their acid–base properties, mathematical transformation of the
136 electrochemical signals (deconvolution procedure, first-derivative method) and electrode
137 modifications with nanomaterials. Although in these papers the detection and quantification
138 of antioxidants have been achieved, the electrode modification for the development of
139 selective electrodes involves more difficult steps to carry out the analytical determinations
140 and, usually, its reproducibility is low. On the other hand, the use of unmodified electrodes
141 does not allow the signals adequate separation and, the individual quantification is not
142 possible. Therefore, chemometric tools are a very interesting methodology to solve the
143 overlapped signals (first order advantage) such as in the synthetic antioxidants. Thus, a first
144 report by Galeano Diaz et al. [26] proposed the simultaneous determination of BHA, BHT
145 and PG in different spiked samples of packet soup by the use of DPV in combination with
146 partial least squares (PLS). The recovery percentages obtained were comparable with those
147 obtained by different spectrometric techniques or by the most expensive chromatographic
148 techniques. In addition, the simultaneous determination of BHA, BHT, PG and TBHQ was
149 carried out at a GCE by linear sweep voltammetry (LSV) in combination with PLS. The
150 methodology was successfully applied to determine these synthetic antioxidants in peanut,
151 sesame and salad oils, cakes, biscuits and milk candy [27]. Radial basis function-artificial
152 neural networks (RBF-ANNs) applied to electrochemical data obtained by cyclic
153 voltammetry (CV) at a GCE were used for the simultaneous determination of TBHQ, BHA

154 and PG in buckthorn and linseed oils [28]. This work was the first that used a non-linear
155 statistical method for the quantitation of synthetic antioxidants. The simultaneous
156 determination of BHA, BHT, PG and TBHQ was carried out by DPV in combination with
157 ANNs in biodiesel samples [29]. A platinum ultramicroelectrode (UME) was used as
158 working electrode. For the model construction, a variable selection step through decision
159 trees (DT) was used, that it led to an improved model and, consequently, smaller prediction
160 errors [29]. Very recently, de Souza Schaumlöffel et al. [30] proposed an electrochemical
161 method for the simultaneous determination of BHA, BHT, PG and TBHQ in biodiesel
162 samples using DPV in combination with PLS at a Pt UME as the working electrode [30].

163 According to IUPAC definition voltammetric electronic tongues (E-tongues) are “a
164 multisensor system, which consists of a number of low-selective sensors and uses advanced
165 mathematical procedures for signal processing based on pattern recognition and/or
166 multivariate data analysis—artificial neural networks (ANNs), principal component analysis
167 (PCA), and so forth” [31]. Therefore, E-tongues are a combination of electrochemical
168 techniques with chemometrics tools, in order to obtain more accurate and selective analytical
169 methods. E-tongues have been used in different applications such as pharmaceutical analysis
170 [32], food analysis [33] and, environmental monitoring [34, 35] among others.

171 In this work, we show results of a simple and reliable electroanalytical method to
172 determine BHA, BHT and PG (Fig. S1 in the Supplementary Material) in edible olive oils
173 (EOO). Therefore, we used the SWV on platinum and carbon fiber disk UME’s (E-tongue
174 configuration) combined with chemometrics tools to perform these studies. At the best of our
175 knowledge, this is the first application of E-tongues to determine BHT, BHA and PG in EOO.

176

177

178 **2. Materials and methods**

179

180 **2.1. Reagents and solutions**

181 All reagents were of analytical grade. BHA, BHT and PG were from (Sigma Chemical
182 Co., St. Louis, MO). Tetrabutylammonium perchlorate (TBAP, ≥ 99.0 % Sigma–Aldrich)
183 was used as supporting electrolyte. Acetonitrile (ACN, HPLC grade) was purchased from
184 Sintorgan and kept over 3 Å molecular sieves to minimize the water content in organic
185 solvent to trace levels. Then, it was used without further purification. BHA, BHT and PG
186 stock solutions (10×10^{-3} mol L⁻¹) were prepared in ACN, protected from light and kept in
187 the refrigerator. Working solutions were daily prepared by transferring the proper aliquots of
188 the stock solution to 5.00 mL of ACN + 0.1 mol L⁻¹ TBAP.

189

190 **2.2. Apparatus and software**

191 Voltammetric measurements were performed with a μ Stat 300 Bipotentiostat (Metrohm
192 DropSens) using the manufacturer's electrochemical analysis software. SWV experiments
193 were carried out in a 5 mL electrochemical cell using a Pt disk UME ($\phi = 25$ μ m) and a
194 carbon fiber disk UME ($\phi = 11$ μ m) as working electrodes, a platinum wire and Ag/AgCl
195 (KCl 3 mol L⁻¹) (BAS, RE-5B) as counter and reference electrodes, respectively [20]. All
196 measurements were carried out at a room temperature.

197 A HPLC chromatograph (Waters 2489) with binary pump (Waters 1525), an analytical
198 column (C18, 5 μ m, 250×4.6 mm i.d., PhenoSphere, phenomenex), and a UV/visible detector

199 were used. The flow-rate was 2.0 mL min^{-1} and detection was performed at 280 nm. Other
200 chromatographic parameters were fixed according to the AOAC official method 983.15 [36].

201

202 **2.3. Procedure**

203 Square wave voltammograms were recorded in ACN + 0.1 mol L^{-1} TBAP at Pt disk UME
204 and CF disk UME in the potential range from 0.5 to 1.7 V. The characteristic parameters of
205 SW voltammograms were a square wave amplitude (ΔE_{sw}) of 0.020 V, a staircase step height
206 (ΔE_s) of 0.005 V and a frequency (f) of 20 Hz. Under these conditions, the obtained SW
207 voltammograms contain 120 variables, which corresponds to the recorded current intensities.

208

209 **2.4. Electrochemical characterization of Pt and CF disk UME's**

210 Taking into account that the diameters of Pt and CF UME's are different, it was necessary
211 to estimate its electroactive areas in order to work in terms of current density. Electroactive
212 areas of Pt and CF disks UME's were determined by double potential step
213 chronoamperometry in ACN + 0.1 mol L^{-1} TBAP solution, using the ferrocene/ferrocenium
214 redox couple. This procedure was previously reported by Compton et al. [37]. Thus, the
215 current-times responses were recorded after applying a potential step from 0.0 V (where the
216 faradaic process does not occur) to a potential of 0.7 V (where the electrochemical reaction
217 occurs at the maximum possible rate), using a pulse time of 5 s. The data obtained were
218 analyzed through Shoup and Szabo equations [38]. Figs. S2a and S2b in the Supplementary
219 Material show the cyclic voltammograms recorded in ACN + 0.1 mol L^{-1} TBAP solution +
220 $1 \times 10^{-2} \text{ mol L}^{-1}$ ferrocene at Pt disk UME and CF disk UME, respectively, at a scan rate 0.005

221 V s^{-1} . Both figures show typical sigmoid responses of UME at low scan rates. Figs. S2c and
222 S2d (Supplementary Material) show the corresponding amperometric responses for both
223 electrodes.

224

225 **2.5. Calibration and validation sets**

226 A calibration set was designed according to a fractional factorial design at several levels
227 [39]. It involves a series of three component mixtures at five concentration levels (twenty-
228 five experiments), and a binary mixture of synthetic antioxidants was also used, with a total
229 of fifty-two experiments. A validation set of thirty-six standard solutions was prepared in the
230 concentration range from 1.5 to $9.5 \times 10^{-4} \text{ mol L}^{-1}$ for each synthetic antioxidant in binary
231 and ternary mixtures. These values were chosen taking into account the regional regulation
232 limits for the samples, and varied from 18 to 220 ppm. The sample concentrations for
233 calibration and validation sets are summarized in the Table S1 (Supplementary Material).

234

235 **2.6. Pre-treatment of recorded data and data fusion strategy**

236 As it is well known for quantitative purposes, the electrochemical signals are affected by
237 the baselines of voltammograms [40]. In order to solve this problem, the asymmetric least
238 squares algorithm (AsLS) was used [41].

239 Two data fusion strategies were used in order to combine the electrochemical data
240 obtained for each working electrode in the E-tongues: low-level data fusion (LLDF) and mid-
241 level data fusion (MLDF) [42]. To carry out LLDF, the coupling of datasets was in the

242 direction of the variable, by directly placing the datasets next to the other. Thus, a matrix of
243 52 samples for 240 variables was obtained for the calibration set.

244 To reduce the dimensionality of the dataset in MLDF, the discrete wavelet transform
245 (DWT) was used [43]. Therefore, DWT decomposes the signal in labeled and located
246 contributions for one scale and one position parameter. An additional advantage of this
247 approach is the facility to remove the noise present in signals and the possibility to be used
248 for data compression [44]. DWT have been used in electrochemical data providing a very
249 interesting tool to carry out multivariate calibration models [43, 44]. Thus, a matrix of 52
250 samples with 50 variables was obtained for the calibration set.

251

252 ***2.7. Applications of artificial neuron networks (ANNs)***

253 Multivariate calibration (MC) is the process of learning how to combine data, in order to
254 overcome many problems. MC can lead to a number of several advantages such as noise
255 reduction, non-selective signals can be made selective by use of mathematics (handling
256 interferences), the exploratory aspect, among others [45]. The main advantage of chemometric
257 techniques is their ability to obtain quantitative information from overlapping signals through
258 mathematical procedures, without requiring any prior pretreatment of the sample. In
259 particular, artificial neuron networks (ANNs) are algorithms capable of modeling nonlinear
260 relationships in multivariate calibration. In a simple way, ANNs are constituted by layers of
261 neurons (usually three). The ANNs architecture consisted of an input layer, one hidden, and
262 one output layer. The number of neurons of the input layer was equal to the number of
263 independent variables entered into the model. The number of neurons in the output layer
264 corresponds to the number of output model variables, i.e., concentrations of BHA, BHT and

265 PG, considering one analyte at each time. On the other hand, the number of neurons in the
266 hidden layer was that obtained from the best architecture of ANNs through the following
267 procedure: i) it was created an ANNs with a number N of neurons in the hidden layer. ii) It
268 was defined the type of training and the transfer function. iii) The network was trained with
269 the calibration data set, considering a 70% of learning, a 15% for monitoring, and another
270 15% to test the network. iv) The network was validated using the validation data set
271 (independent set of calibration data, Table S1 in Supplementary Material) and, v) root mean
272 square error (RMSE) values were obtained from points three and four.

273 After obtaining the errors of different architectures, we selected the best amount of the
274 hidden layer neurons, the transfer function, and the training type based on relative errors of
275 predictions REP (%), and RMSE (mol L^{-1}) for the three antioxidants, avoiding the over
276 fitting. Thus, the best network model was obtained using tansig (tangent sigmoid) transfer
277 function in the hidden layer and the purelin linear function for the output layer. The most
278 appropriate algorithm in the training stage was that of Levenberg-Marquardt [46].

279

280 ***2.8. Olive oil samples***

281 The EOO samples were purchased at a local supermarket, with no added synthetic
282 antioxidants, as indicated on the label. 2.0 mL of EOO was dissolved in 8.0 mL of ACN
283 (final volume = 10.0 mL) and homogenized during 2 min in ultrasonic bath. Then, an aliquot
284 of 5.0 mL was added to the electrochemical cell, with the addition of 0.1 mol L^{-1} TBAP as
285 supporting electrolyte up to 10 mL. As can be observed, not extraction stage is necessary in
286 this procedure. Studies performed on EOO samples spiked with synthetic antioxidants in
287 ACN, were carried out following a methodology previously described [20].

288 3. Results and discussions

289

290 3.1. Electrochemical behavior of BHA, BHT and PG

291 The electrochemical behavior of BHA, BHT and PG in ACN + 0.1 mol L⁻¹ TBAP was
292 studied at Pt and CF disk UME's. Fig. 1a displays the SW voltammograms of BHA, BHT
293 and PG at a concentration of 1 x 10⁻³ mol L⁻¹ at Pt disk UME. BHA, BHT and PG show
294 oxidation peaks at 1.10 V, 1.36 V and 1.30 V, respectively. Fig. 1b displays the SW
295 voltammograms of BHA, BHT and PG at CF disk UME under the same conditions as those
296 of Fig. 1a. BHA, BHT and PG show oxidation peaks at 1.08 V, 1.35 V and 1.08 V,
297 respectively. Figs. 1c and 1d show the net current density of SW voltammograms recorded
298 at Pt and CF disk UME's for a mixture of BHA, BHT and PG at a concentration of 1 x 10⁻³
299 mol L⁻¹, respectively.

300

301

Preferred position of Figure 1

302

303 3.2. Analytical curve

304 Fig. S3 (Supplementary Material) displays SW voltammograms and, the respective
305 univariate calibration plots for BHA, BHT and PG at Pt and CF disk UME's at different
306 concentrations. An excellent linear relationship between net peak density current ($J_{p,n}$) and
307 the concentration was obtained in the concentration range from 1 x 10⁻⁴ to 1 x 10⁻³ mol L⁻¹
308 for BHA, BHT and PG at Pt and CF disk UME's. The figures of merit calculated for all the
309 calibration models are shown in Table S2 (Supplementary Material).

310 In spite of the excellent linear relationship between $J_{p,n}$ and concentration found for the
311 three antioxidants (Fig. S3), a chemometric treatment of data was needed to solve the
312 overlapped signals of SW voltammograms recorded for mixtures of the three antioxidants at
313 both Pt and CF disk UME's.

314

315

316 ***3.3. Chemometric studies***

317

318 ***3.3.1. Data pretreatment***

319 The AsLS algorithm was used for the baseline correction. Fig. S4 (Supplementary
320 Material) shows the calibration set of net currents density data obtained at Pt and CF disk
321 UME's, before and after of correction by the baseline. This pretreatment was also used for
322 the validation set and the samples.

323

324 ***3.3.2. Individual models for Pt and CF disk UME's with ANNs***

325 Prior to use the data fusion strategy, we analyze the antioxidant mixtures at both
326 individual disk UME's using ANNs models. Therefore, ANNs architectures were built and,
327 then, the predictive model of the network with an external validation set (Section 2.6) was
328 validated. In this case, 120 parameters obtained from voltammetric responses (corresponding
329 to a Pt or CF disk UME's) were the number of neurons of the input layer. REP value for each
330 analyte was found in the range between 14 % and 45 %. Table 1 displays the linear regression
331 parameters obtained from the dependence between estimated values by ANNs and nominal
332 concentrations. These values were unacceptable, and new strategies need to be carried out
333 for the simultaneous determination of BHA, BHT and PG in EOO.

334

335 **3.3.3. Low-level data fusion model and ANNs (LLDF-ANNs)**

336 Before the vector's concatenation, all data were pretreated according to that explained in
337 a previous section (Section 2.6). After that, a matrix of 52 samples x 240 variables and
338 another matrix of 36 samples x 240 variables were obtained for the validation set,
339 respectively. In this case, 240 variables were the number of neurons of the input layer. Plots
340 of the estimated concentrations versus nominal concentrations for the prediction of the
341 validation set were obtained for BHA, BHT, and PG (results not shown). The linear
342 regression parameters and associated errors obtained from plots of estimated concentrations
343 as a function of nominal concentrations are shown in Table 1. Furthermore, the REP value
344 for each analyte was found in the range between 10 % and 18 %. In spite of these values are
345 acceptable, they still can be improved.

346

347 **3.3.4. Mid-level data fusion model and ANNs (MLDF-ANNs)**

348 Before the vector's concatenation, DWT was applied to reduce the dimensionality of the
349 dataset to 25 variables for each electrode (Section 2.6). After that, a matrix of 52 samples x
350 50 variables and another matrix of 36 samples x 50 variables were obtained for the validation
351 set, respectively. In this case, 50 variables were the number of neurons of the input layer.
352 Plots of the estimated concentrations versus nominal concentrations for the prediction of the
353 validation set were obtained for BHA, BHT, and PG (results not shown). The linear
354 regression parameters and associated errors, obtained from plots of estimated concentrations
355 as a function of nominal concentrations are shown in Table 1. In addition, REP value for each
356 analyte was found in the range between 8 % and 10 % (Table 1).

357

358

Preferred position of Table 1

359

360 Therefore, Table 1 shows the linear regression parameters (obtained vs. expected
361 concentrations for BHA, BHT and PG) for the four models studied: only for CF UME and
362 ANNs, only for Pt UME and ANNs, and for both Pt and CF UME's with LLDF and ANNs
363 (E-Tongue configuration) and Pt and CF UME's with MLDF and ANNs (E-Tongue
364 configuration). As can be observed, the first model (CF UME and ANNs) displays high
365 RMSE (mol L^{-1}) and REP (%) values for BHA, BHT and PG prediction. Pt UME and ANNs
366 show similar results, except for BHA prediction (acceptable values). These results show that
367 CF and Pt disk UME's have different behavior against the response of synthetic antioxidants.
368 E-Tongue configuration displays much better prediction results than the individual UME
369 models. In addition, MLDF-ANNs displays the best prediction parameters. Therefore, this
370 method was chosen as the best to obtain the calibration model.

371

3.4. Application of the electrochemical method to analysis of edible olive oils samples

373 The proposed electrochemical method was then applied to the determination of BHA,
374 BHT, and PG in commercial EOO samples as a quality control method. It was found that the
375 concentration of the synthetic antioxidant, if it would be present in the EOO, was below the
376 detection limit established by the official method in all commercial samples analyzed,
377 according to Argentina's regulations. This analysis was performed by the official method
378 recommended by AOAC 983.15 and the chromatographic response of EOO samples (with
379 and without the addition of BHA, BHT and PG) are shown in Fig. S5 (Supplementary

380 Material). Therefore, untreated EOO samples were spiked with different amounts of BHA,
381 BHT and PG and analyzed in triplicate (Fig. S5, Supplementary Material).

382

383 **3.5. Predictive analysis**

384 Finally, to assert the predictive capability of the method for BHA, BHT and PG
385 determination in real samples, a recovery study for the antioxidants in EOO samples was
386 performed. Table 2 summarizes the results obtained for the quantitation of BHA, BHT and
387 PG in EOO samples by implementing the MLDF-ANNs strategy and by using the AOAC
388 method. In order to appreciate whether the recoveries were different than 100% or not, a
389 hypothesis test was applied, for which an experimental t_{exp} value was estimated by applying
390 the equation 1 (Eq 1) [47].

391

$$392 \quad t_{exp} = \left| 100 - \% \bar{R} \right| \frac{\sqrt{n}}{s_r} \quad (1)$$

393

394 where $\% \bar{R}$ is the mean recovery and s_r is the corresponding standard deviation. If t_{exp} value
395 is higher than the theoretical $t_{(\alpha, \nu)}$ value at level α and $\nu = n-1$ degree of freedom for n samples,
396 the recoveries are statistically different that 100%. For these samples, t_{exp} value for BHA,
397 BHT and, PG were below the critical value $t_{(0.025, 5)} = 2.791$ ($t_{expBHA} = 0.911$, $t_{expBHT} = 0.622$
398 and $t_{expPG} = 0.953$), showing the analytical accuracy of the proposed method.

399 The recovery analysis data obtained demonstrate the suitability of the method for
400 quality control of EOO and that the recoveries obtained with the proposed method were not
401 different that those obtained using the AOAC 983.15 official method.

402

403

Preferred position of Table 2

404

405

3.6. Comparison with other methods

407 Table 3 shows the comparison between the proposed electrochemical method and
408 others electrochemical methods found in literature in terms of the quality of the model (REP
409 %) and the percent recoveries (%) in different samples. As it can be observed, our results are
410 better than others previously published for the simultaneous determination of BHA, BHT and,
411 PG in real samples. Moreover, this is the first report for the simultaneous determination of
412 BHA, BHT and PG, in EEO. Experiments showed by Ni et al. [27] were done in peanut,
413 salad and sesame oils. Thus, the use of E-tongues improves the percent recoveries without
414 not additional experimental cost.

415 In addition, the percent recoveries obtained with the proposed method are similar to
416 those obtained with chromatographic methods in edible oil samples. Recoveries in the 90 –
417 98 % range were reported by HPLC for sunflower, sesame, olive, coconut, castor, peanut and
418 palm kernel oils [11]. Recoveries in the 86 –115% range were reported by GC-MS for corn,
419 olive, sunflower, sesame and peanut oils [16]. Recoveries in the 95 – 105 % range were
420 reported by HPLC for colza, sunflower, peanut and cooking oils [48]. Finally, recoveries in
421 the 82 – 97 % range were reported by GC-FID for sunflower, canola, corn, olive and
422 grapeseed oils [49]. Table S3 (Supplementary Material) summarizes the analytical methods
423 for the synthetic antioxidants determination in edible olive oils. As can be observed, most of
424 them are based on chromatographic techniques. These techniques involve sample
425 pretreatment such as extraction, concentration, methylation steps, etc. On the other hand,

426 chromatography experiments are time consuming (in the best case, at less 10 min for the
427 separation of BHA, BHT and PG). The proposed method has several advantages over the
428 mentioned chromatographic techniques, such as a simpler sample preparation, higher sample
429 throughput, lower solvent consumption and lower cost and time per analysis. On the other
430 hand, the concentration range studied is in very good agreement with the synthetic
431 antioxidants concentration range allowed in many countries worldwide (usually between 100
432 to 200 ppm) [50].

433 The comparison with these chromatographic methods described in literature
434 demonstrates the accuracy of the method proposed, and the great potentiality of E-tongues in
435 the field of food quality control. Thus, this analytical method is suitable for routine
436 qualitative and quantitative analysis of BHA, BHT and PG in EOO.

437

438

439

Preferred position of Table 3

440

441

442 4. Conclusions

443 Results of a simple and reliable electroanalytical method to determine BHA, BHT and
444 PG in edible olive oils using square wave voltammetry on platinum and carbon fiber disk
445 ultramicroelectrodes (electronic tongues configuration) combined with chemometrics tools
446 are reported.

447 Two data fusion strategies were used in order to combine the electrochemical data obtained
448 for each working electrode in the E-tongues: low-level data fusion and mid-level data fusion.

449 In addition, the discrete wavelet transform was used to reduce the dimensionality of the
450 dataset in mid-level data fusion. For low-level data fusion modeled with artificial neural
451 networks, REP values for each analyte were in the range from 10 to 18 %. Despite of these
452 values are acceptable, they still could be improved. Thus, before the vectors concatenation,
453 discrete wavelet transform was applied to reduce the dimensionality. Then, it was
454 implemented mid-level data fusion modeled with artificial neural networks, with REP value
455 for each analyte, which were in the range from 8 to 10 %. Thus, mid-level data fusion
456 modeled with artificial neural networks displayed the best prediction parameters. Therefore,
457 this method was chosen as the best for obtaining the calibration model.

458 Finally, to assert the predictive capability of the method for BHA, BHT and PG
459 determination in real samples, a recovery study for the antioxidants in edible olive oil samples
460 was performed, demonstrating the analytical accuracy of the proposed method. In addition,
461 from the comparison between the proposed electrochemical method and others found in
462 literature in terms of the quality of the model (REP %) and the percent recoveries (%) in
463 different samples, our results were better than others reported for the simultaneous
464 determination of BHA, BHT and PG in real samples. Moreover, this is the first report for the
465 simultaneous determination of BHA, BHT and PG in edible olive oils, with improvements
466 in the recovery assays obtained without additional experimental cost. Additionally, the
467 recovery percentages obtained with the proposed method were similar to those obtained with
468 chromatographic methods in oil samples.

469

470

471

472

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474

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483

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642

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643 **FIGURE CAPTIONS**

644

645 **Figure 1.** Square wave voltammograms recorded in ACN + 0.1 mol L⁻¹ TBAP containing
646 pure solutions of BHA (black line), BHT (red line) and PG (blue line) at a) Pt disk UME and
647 b) CF disk UME, and mixtures of BHA, BHT and, PG at c) Pt disk UME and d) CF disk
648 UME. BHA, BHT and PG concentrations were 1 x 10⁻³ mol L⁻¹, respectively. Dotted line
649 represent the background currents. Square wave conditions were display in section 2.3.

650

Table 1. Linear regression parameters obtained from the comparison line for obtained vs. expected concentration for BHA, BHT and PG with external validation test set for different calibration models. RMSEP and REP values are also reported.

	CF-ANNs			Pt-ANNs			LLDF-ANNs			MLDF-ANNs		
	BHA	BHT	PG	BHA	BHT	PG	BHA	BHT	PG	BHA	BHT	PG
Slope / A L mol⁻¹ cm⁻²	0.86	0.58	0.54	0.97	0.57	0.93	1.00	0.97	0.96	1.00	0.98	1.00
Intercept / A cm⁻²	8.1x10 ⁻⁵	9.9x10 ⁻⁵	0.00012	5.6x10 ⁻⁵	0.00014	3x10 ⁻⁵	-1.5x10 ⁻⁵	1.4x10 ⁻⁵	-1.4x10 ⁻⁵	-1.6x10 ⁻⁵	1.3x10 ⁻⁵	-6.2x10 ⁻⁵
r	0.8613	0.7994	0.7482	0.9728	0.7418	0.8365	0.9926	0.9880	0.9865	0.9931	0.9894	0.9935
RMSEP / mol L⁻¹	1.67x10 ⁻⁴	2.12x10 ⁻⁴	2.36x10 ⁻⁴	8.44x10 ⁻⁵	2.21x10 ⁻⁴	1.85x10 ⁻⁴	4.40x10 ⁻⁵	5.24x10 ⁻⁵	5.11x10 ⁻⁵	3.93x10 ⁻⁵	4.65x10 ⁻⁵	3.81x10 ⁻⁵
REP / %	28.50	38.73	43.14	14.41	40.41	33.84	10.32	14.34	17.44	8.32	10.30	8.64

Table 2. Predictive results obtained for BHA, BHT and PG concentrations in EOOs samples using the MLDF-ANNs strategy with E-tongue and the reference method AOAC 983.15.

Sample	Reference method AOAC 983.15.									Proposed method					
	Nominal concentration (mol L ⁻¹)			Found concentration (mol L ⁻¹)			Recovery (%)			Found concentration (mol L ⁻¹)			Recovery (%)		
	BHA	BHT	PG	BHA	BHT	PG	BHA	BHT	PG	BHA	BHT	PG	BHA	BHT	PG
M1*	-	-	-	n.d.	n.d.	n.d.	-	-	-	n.d.	n.d.	n.d.	-	-	-
M2	1.10 x 10 ⁻⁴	9.08 x 10 ⁻⁴	-	1.24 x 10 ⁻⁴	9.59 x 10 ⁻⁴	-	112.7	105.6	-	1.05 x 10 ⁻⁴	9.71 x 10 ⁻⁴	-	95.5	106.9	-
M3	1.10 x 10 ⁻⁴	-	9.40 x 10 ⁻⁴	9.44 x 10 ⁻⁵	-	7.95 x 10 ⁻⁴	89.5	-	84.6	1.02 x 10 ⁻⁴	-	8.65 x 10 ⁻⁴	92.7	-	92.0
M4	-	9.08 x 10 ⁻⁴	9.40 x 10 ⁻⁴	-	9.09 x 10 ⁻⁴	9.47 x 10 ⁻⁴	-	100.1	100.7	-	9.8 x 10 ⁻⁴	9.96 x 10 ⁻⁴	-	107.9	105.9
M5	1.10 x 10 ⁻⁴	4.54 x 10 ⁻⁴	4.70 x 10 ⁻⁴	1.04 x 10 ⁻⁴	4.87 x 10 ⁻⁴	4.85 x 10 ⁻⁴	94.5	107.3	103.2	1.13 x 10 ⁻⁴	4.95 x 10 ⁻⁴	4.32 x 10 ⁻⁴	102.7	109.0	91.9
M6	4.10 x 10 ⁻⁴	1.10 x 10 ⁻⁴	9.40 x 10 ⁻⁴	4.59 x 10 ⁻⁴	1.01 x 10 ⁻⁴	9.61 x 10 ⁻⁴	111.9	91.8	102.2	4.02 x 10 ⁻⁴	1.04 x 10 ⁻⁴	9.69 x 10 ⁻⁴	98.0	94.5	103.1
M7	9.40 x 10 ⁻⁴	1.10 x 10 ⁻⁴	4.70 x 10 ⁻⁴	1.01x10 ⁻³	1.20 x 10 ⁻⁴	4.69 x 10 ⁻⁴	107.4	109.1	99.8	9.62 x 10 ⁻⁴	1.02 x 10 ⁻⁴	4.35 x 10 ⁻⁴	102.3	92.7	92.5
% \bar{R}¹							103.2	102.8	98.1				98.2	102.2	97.1

¹ % \bar{R} mean recovery in %. M1*, is an edible olive oil without the addition of BHA, BHT and PG.
n.d.: not detected.

Table 3. Comparison between the electrochemical method proposed here and other electrochemical methods found in the literature.

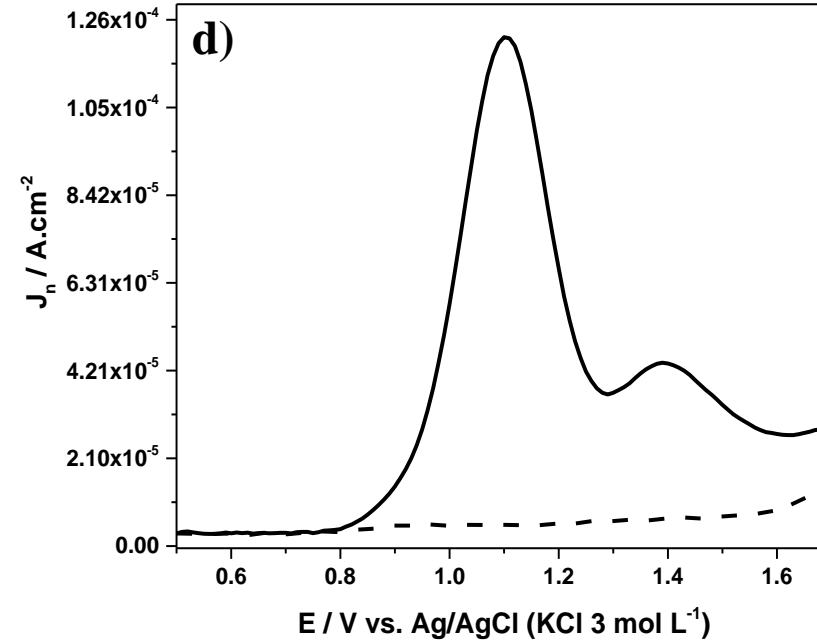
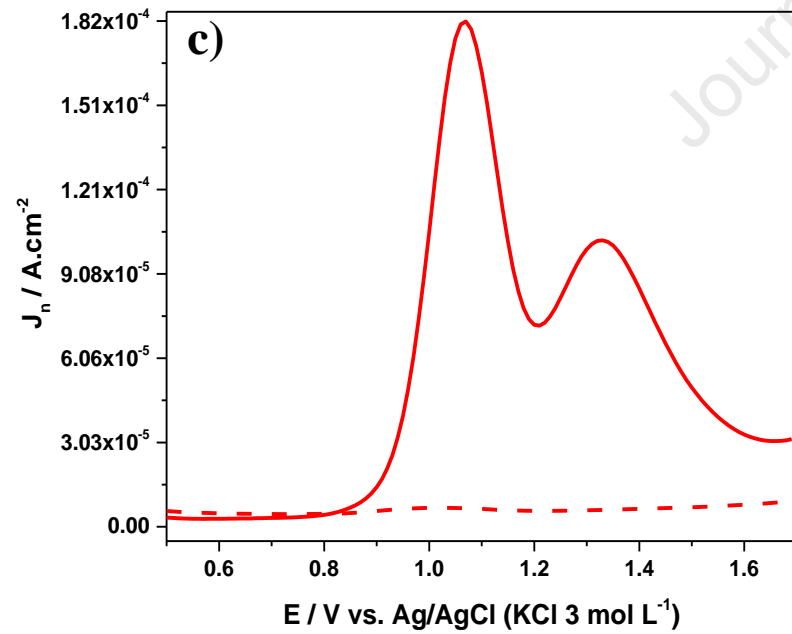
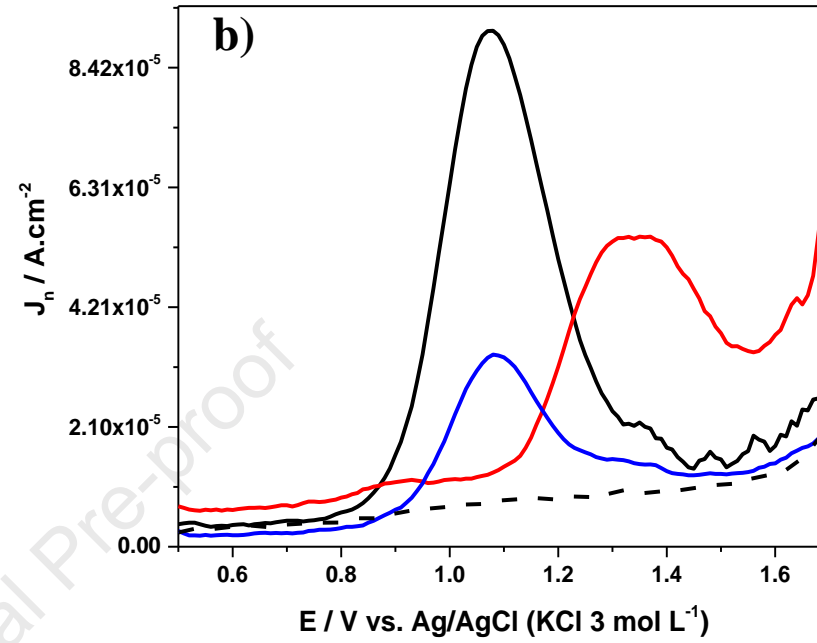
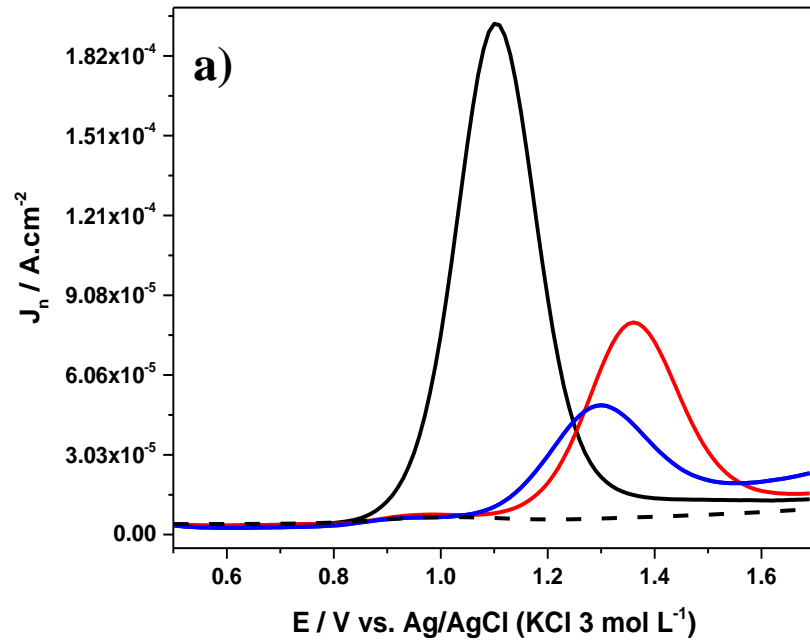
Method	Electrode	REP(%) ¹			Sample	Recovery assays (%) ²			Reference
		BHA	BHT	PG		BHA	BHT	PG	
DPV-PLS	GCE	n.r. ³	n.r. ³	n.r. ³	Packet soup	77 - 92	78 - n.r.	91 - 101	[26]
LSV-PLS	GCE	8.16	9.84	9.89	Vegetable oil and solid food	87 - 131	71 - 108	85 - 118	[27]
DPV-DT- ANN	Pt-UME	13.6	17.0	15.7	Biodiesel	88 - 104	83 - 115	76 - 107	[29]
DPV-PLS	Pt-UME	15	8	15	Biodiesel	84 - 100	92 - 104	83 - 93	[30]
SWV- MLDF- ANN	CF-UME and Pt- UME	8.32	10.30	8.64	Edible olive oil	95 - 103	93 - 109	92 - 106	This work

¹ For the validation set.

² Recoveries of BHA, BHT and, PG in real samples.

³ not reported.

Figure 1
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- E-Tongues were used for the determination of BHA, BHT and PG in EOO samples.
- Square wave voltammetry was used to perform the development of the method.
- Mid-level data fusion (MLDF) to reduce the dimensionality of the dataset was used.
- The method is very suitable to determine BHA, BHT and PG in EOO samples.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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