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Application of a potentiometric electronic tongue for assessing phenolic and volatile profiles of Arbequina extra virgin olive oils

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ABSTRACT

The capability of determining the phenolic and volatile profiles of olive oils is of major relevance since these compounds are known to greatly influence the gustatory and olfactory positive attributes of olive oils. An electronic tongue with multiple linear regression models was used to evaluate both profiles based on olive oils potentiometric data generated during a single assay. The proposed electronic tongue-chemometric procedure enabled the quantification of flavonoids, phenolic acids and phenol alcohols of Arbequina extra-virgin olive oils with a similar accuracy of UPLC-MS ($0.93 \pm 0.03 \leq R^2 \leq 0.98 \pm 0.08$ for the repeated K-fold cross-validation procedure). Also, it was verified that the potentiometric device should not be applied to evaluate volatile compounds in solution ($0.80 \pm 0.14 \leq R^2 \leq 0.94 \pm 0.05$ for the repeated K-fold cross-validation procedure), showing a lower accuracy than HS-SPME-GS-MS. The overall satisfactory results showed that electronic tongue could be used as a practical sensing instrument to generate a chemical profile of the compounds known to influence the positive sensory attributes of olive oils.

1. Introduction

Olive oil is a food product with recognized healthy and nutritional properties, mainly due to their composition in phenolic compounds such as flavonoids, phenolic acids and phenol alcohols (Apetrei, Gutierez, Rodriguez-Mendez, & de Saja, 2007). These chemical compounds are not only responsible for the olive oil antioxidant capacity but also by several gustatory positive sensations, including bitterness and pungency. In addition, the volatile compounds usually found in olive oil are responsible for the positive olfactory attributes (Fortini, Migliorini, Cherubini, Cecchi, & Calamai, 2017; Kalua et al., 2007). The overall organoleptic quality assessment of olive oil is based upon the perception of flavour, which is the combined effect of odour (perceived via ortho-nasal and retronasal routes), taste and chemical responses (pungency) (Barbieri, Bendini, Valli, & Toschi, 2015).

For the sensory evaluation, a trained panel is required as part of the legal control classification of the olive oils according to the European Commission regulation (EC, 2013), although being recognized as a time-consuming, costly and subjectivity procedure (Apetrei et al., 2010). Alternatively, voltammetric or potentiometric electronic tongues (E-tongues) together with chemometric tools have been successfully applied as low-cost, fast and reliable taste sensor devices to directly evaluate positive (e.g., bitter, green and/or fruity intensity degrees) (Apetrei et al., 2007; Apetrei, 2012; Apetrei et al., 2010; Rodríguez-Méndez, Apetrei, & de Saja, 2008; Veloso, Dias, Rodrigues, Pereira, & Peres, 2016; Slim et al., 2017) and negative sensory attributes of olive oils (e.g., rancid, winey-vinegary, musty or fusty) (Veloso et al., 2018), providing practical and valuable additional information for trained sensory panels. Voltammetric E-tongues combined with partial least square (PLS1 and PLS2) models were previously successfully applied to assess, in a single assay, the bitterness index of EVOO as well as to quantify the contents of total phenols and phenolic compounds in EVOO, which are directly related to positive sensory attributes (Apetrei & Apetrei, 2013; Apetrei, 2012; Apetrei et al., 2010, 2007; Enache, Amine, Brett, & Oliveira-Brett, 2013; Rodríguez-Méndez et al., 2008). Indeed, the voltammetric E-tongues allowed achieving a similar quantitative accuracy compared to the standard spectrophotometric and liquid chromatography techniques. However, to our best knowledge, potentiometric E-tongues have not yet been used for quantifying EVOO's phenolic contents, although their capability for

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monitoring the contents of quality physicochemical data and oxidative stability during EVOO storage has been previously demonstrated (Rodrigues, Dias, Veloso, Pereira, & Peres, 2016). Moreover, no attempt has been made to evaluate the possibility of using E-tongue devices (potentiometric or voltammetric), as an alternative to standard gas chromatography techniques, for the indirect assessment of the contents of volatile compounds (e.g., alcohols, aldehydes, hydrocarbons, esters and terpenes), which are responsible for olfactory positive sensations usually perceived in olive oils. Thus, the aim of the present study was to apply a labmade E-tongue for assessing phenolic and volatile compounds of Arbequina EVOO, produced in different regions of Spain and Brazil, which are known to be related to the sensory profile of olive oils. The E-tongue comprised multiple lipid polymeric sensor membranes with cross-sensibility towards chemical species that mimic positive and negative sensory sensations usually perceived in olive oils. Finally, the potentiometric E-tongue performance was checked against experimental total phenols contents determined by UV–Vis spectrophotometry, phenolic and volatile profiles determined using liquid chromatography with time-of-flight mass spectrometry detector (UPLC-TOF-MS) and gas chromatography with mass spectrometry detector coupled with headspace solid-phase microextraction technique (HS-SPME-GC-MS), respectively.

2. Materials and methods

2.1. Chemicals

All chemicals were analytical reagent grade or higher purity. Bidistilled deionized water was obtained from a Milli-Q purification system (Millipore, Bedford, MA). The internal standard 4-methyl-2-pentanol was provided by Sigma (Sigma-Aldrich, St. Louis, MO). The labmade E-tongue had lipid polymeric membranes prepared with plasticizers (bis(1-butylpentyl) adipate, dibutyl sebacate, 2-nitrophenyl octylether, tris(2-ethylhexyl)phosphate and dioctyl phenylphosphonate) and additives (octadecylamine, oleyl alcohol, methyltrioctylammonium chloride and oleic acid), obtained from Fluka with high purity (≥97%). A polyvinyl chloride with high molecular was used to support the polymer.

2.2. Samples

A total of eleven Arbequina EVOO (n = 3 bottles for each olive oil) were studied, being 9 produced in Spain (samples OO1 to OO9) and the other 2 produced in Brazil (samples OO10 and OO11). The olives were collected at the early stage of harvest; the harvest date was: late October to mid-November of 2014 for Spanish samples and mid-March to early Abril of 2015 for Brazilian samples. The oil was extracted within 24 h, under a two-phase extraction system. The oils were adequately packaged for preserving from light and high temperatures and sent to CSIC laboratories (Granada, Spain) to perform the analysis. The samples were transported in adequately conditions for Polytechnic Institute of Bragança (Portugal) to perform the volatile and E-tongue analysis. All samples were analyzed according to the regulation established by the European Union regulation n° 2568/91 for extra virgin olive oil, as was showed previously (Borges et al., 2017a). Furthermore, to confirm the classification as EVOO a sensory analysis was performed (*i.e.*, perception of defect, fruity, bitter and pungent sensations) by the Official Panel of Laboratorio Agroalimentario de Granada (Atarfe, Granada, Spain) according to European Regulation. The samples showed values for fruit sensation, bitterness and pungency ranging between 4.4 and 6.5, 1.8–3.3 and 2.3–3.7, respectively, and none of the oils presented any sensory defect, which confirmed their EVOO classification. The sensory analysis pointed out that, in general, the olive oils were very fragrant oils with aromas reminiscent of almonds, green and ripe, very floral (aromatic herbs) leaving a trace of the aroma of healthy and fresh olive fruit, for which the green sensation predominates over the ripe one. In the mouth all olive oils had a sweet note that, depending on the state of the fruit, stayed with the ripe notes, bitter (not very marked) and pungent sensations, rising with the green attribute. The retronasal sensation was, generally, of fruits with green nuances, with marked almond green (alloza, apple) and ripe (almond) attributes.

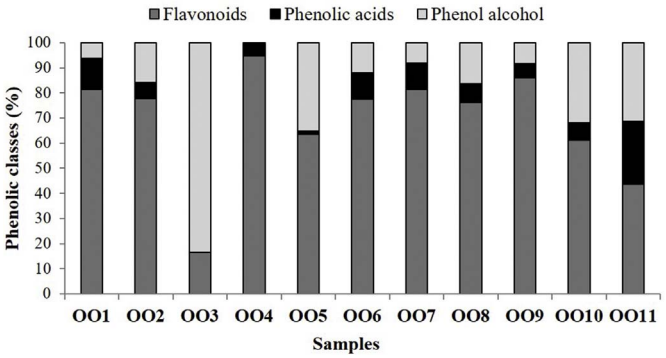

Fig. 1. Amount (%) of the phenolic classes of cv Arbequina EVOOs obtained from different regions of Spain (samples OO1 to OO9) and Brazil (samples OO10 and OO11).

2.3. Phenolic compounds determination

Total phenol content was assessed by the Folin-Ciocalteau method, as described by Borges, Pereira, Cabrera–Vique, and Seiquer (2017b). The final results were expressed as mg of caffeic acid equivalents per kg of olive oil (mg CAE/kg). The determination of the individual phenolic fraction of samples was performed after an extraction with methanol/water (80:20) according to the International Olive Oil Council (IOC, 2009). The extracts were analyzed by UPLC-TOF-MS following the method validated by Rivas, Sanchez-Ortiz, Jimenez, García-Moyano, and Lorenzo (2013) and described by Borges, López, Pereira, Cabrera–Vique, and Seiquer (2017c). Briefly, the UPLC system consisted of a AcQuity UPLC equipped with a binary pump system (Waters, Milford, MA, USA) using a AcQuity UPLC BEH C18 column (1.7 mm, 2.1 mm × 100 mm inner diameter). The system was coupled to a Micromass/Waters LCTPremier XE benchtop orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer equipped with an ESI interface. A calibration curve using a solution of sodium formate (containing 0.05 of formic acid and 5 mM of sodium hydroxide in isopropanol/H_2O 9:1, v/v) was used for quantification and accurate mass data of molecular ions were processed with MassLynxs (Waters).

2.4. Volatile headspace solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS) conditions

For the HS-SPME, a fibre of 2 cm coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS; 50/30 μm) from Supelco (Bellefonte, USA) was used. The olive oil sample was weight (4.6 g) placed in 50 mL vials to avoid any contact of samples with fibre and to provide efficient extraction. Then, 4-methyl-2-pentanol was added as internal standard (100 ppm in methanol; 10 μl) and the vials were sealed with a polypropylene cap with silicon septum. The volatiles were released at an extraction temperature of 59 °C, using a water bath and vigorously stirred with a stir bar (350 rpm) during 5 min. Afterwards, the DVB/CAR/PDMS fibre was exposed during 43 min and immediately inserted into the injection port of the GC system for thermal desorption and reconditioning (10 min at 280 °C). All the samples extractions were carried out in triplicate. The chromatographic analysis was performed on a Shimadzu GC-2010 Plus equipped with a Shimadzu GCMS-QP2010 SE detector (Malheiro et al., 2017, 2013; Pinho et al., 2008). A TRB-5MS (30 m × 0.25 mm × 0.25 μm) column (Teknokroma, Spain) was used. The injector was set at 220 °C and the manual injections were made in splitless mode with a ratio of 1/40 and

Table 1
Volatile compounds contents (μg × kg^{-1} of olive oil) found by HS-SPME-GC-MS in Spanish (samples OO1 to OO9) and Brazilian (samples OO10 and OO11) Arbequina olive oils (mean ± SD).

	OO1	OO2	OO3	OO4	OO5	OO6	OO 7	OO8	OO9	OO10	OO11
Alcohols											
1-heptanol	–	–	–	0.77 ± 0.77	–	–	–	–	–	–	–
1-octanol	–	0.47 ± 0.18	1.38 ± 0.11[c]	0.66 ± 0.24	0.40 ± 0.04	1.48 ± 0.45	0.76 ± 0.06	–	1.37 ± 0.18	0.54 ± 0.05	0.67 ± 0.04
1-nonanol	–	0.28 ± 0.28	0.43 ± 0.08	0.49 ± 0.49[b]	0.15 ± 0.14	0.57 ± 0.12	0.32 ± 0.02	–	0.97 ± 0.25	–	–
E − 2-hexen-1-ol	–	–	–	–	–	–	–	–	–	–	44.0 ± 0.41
phenylethyl alcohol	–	1.99 ± 1.98	3.22 ± 0.21	4.76 ± 2.29	4.65 ± 1.67	3.32 ± 0.06	–	1.76 ± 0.16	4.46 ± 0.73	–	8.72 ± 0.39
Aldehydes											
E − 2-hexenal	55.5 ± 10.6	165 ± 30	37.1 ± 2.8	149 ± 3	222 ± 80	163 ± 4	288 ± 2	48.0 ± 4.4	209 ± 16	188 ± 0.7	380 ± 5
oxohex-2-enal	37.8 ± 0.8	–	–	–	–	–	–	–	–	–	–
nonanal	1.61 ± 0.92	2.90 ± 0.70	6.86 ± 0.58	2.63 ± 0.66	3.33 ± 0.52	7.59 ± 2.62	5.48 ± 0.02	1.69 ± 0.21	6.23 ± 0.99	3.26 ± 0.41	6.46 ± 0.32
octanal	–	–	2.80 ± 0.15	–	–	–	–	–	–	–	–
Hydrocarbons											
3- ethyl-1,5-octadiene	24.2 ± 4.0	15.5 ± 8.0	8.5 ± 0.1	9.9 ± 4.3	22.8 ± 1.8	10.4 ± 1.3	–	–	16.4 ± 4.5	–	–
nonane	–	–	–	–	–	–	3.74 ± 0.09	–	–	–	–
heptane	–	–	–	–	–	–	21.1 ± 0.35	–	–	–	–
Esters											
Z-3 hexenyl acetate	107 ± 10	21.3 ± 6.0	95.1 ± 4.3	6.75 ± 6.51	53.2 ± 19.9	48.4 ± 3.8	57.7 ± 0.1	250 ± 10	68.8 ± 23.6	–	–
hexyl acetate	17.4 ± 1.2	8.82 ± 0.15	21.6 ± 1.1	7.70 ± 0.44	16.0 ± 8.5	16.0 ± 1.1	–	14.0 ± 0.3	26.5 ± 1.4	8.85 ± 0.34	9.78 ± 0.21
E − 2 hexenyl acetate	–	–	–	–	–	–	–	9.67 ± 0.89	–	–	–
Methyl ester benzoate	–	0.81 ± 0.70	–	–	1.26 ± 1.20	–	–	–	2.11 ± 0.18	4.32 ± 0.56	–
Terpenes											
β-ocimene	–	1.20 ± 1.21	0.99 ± 0.07	1.16 ± 0.35	1.62 ± 0.22	2.84 ± 0.32	–	–	6.10 ± 1.30	3.07 ± 0.23	24.2 ± 0.81
copaene	0.75 ± 0.12	–	1.07 ± 0.15	–	–	0.26 ± 0.26	–	–	–	–	–
farnesene	–	0.53 ± 0.53	0.38 ± 0.11	1.02 ± 0.48	0.78 ± 0.07	1.32 ± 0.19	0.49 ± 0.02	–	1.31 ± 0.56	0.97 ± 0.11	5.29 ± 0.38
Phenols											
Guaiacol	–	–	–	3.42 ± 3.40	–	–	–	–	–	–	–

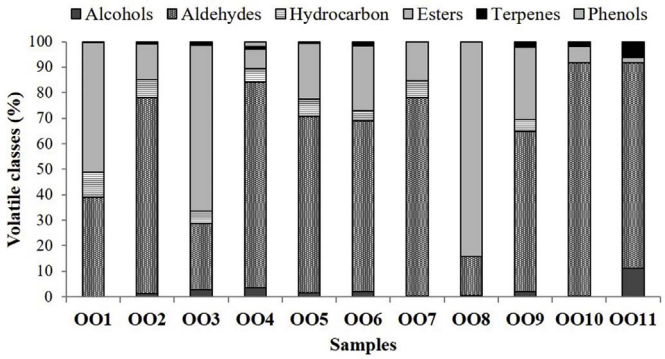

Fig. 2. Amount (%) of the volatile classes of cv Arbequina EVOOs obtained from different regions of Spain (samples OO1 to OO9) and Brazil (samples OO10 and OO11).

the split valve was opened after 1 min. The mobile phase consisted in helium (Praxair, Portugal) at constant flow of 1 mL/min. The oven temperatures were the following: 40 °C/1 min; 2 °C/min until 220 °C; 220 °C during 30 min. The ionization source was maintained at 250 °C with ionization energy of 70 eV, and with an ionization current of 0.1 kV. All mass spectra were acquired by electron ionization. The ionization was left off during the first 2 min. The MS spectra fragments were compared with those obtained from a database (NIST 11), and further compared to the GC retention index. Furthermore, retention indices were obtained using commercial n-alkanes C_7-C_{30} (Sigma-Aldrich, St. Louis, USA) by direct splitless liquid injection (1 μL) while all further conditions of GC and MS, as settled for the volatile analysis. The identification was also performed, considering for tentative of identification at least 95% of match spectra and for identification at least 98% in accordance to Cecchi and Alfei (2013). The semi-quantification purposes were carried out in relation to the internal standard method, i.e.; the area of each compound was divided by the area of the internal standard. All the contents are show as μg of internal standard × Kg^{-1} of olive oil.

2.5. E-tongue analysis

The samples were extracted using a hydroethanolic solution (ethanol–water: 20:80 v/v) and randomly analyzed with a labmade potentiometric E-tongue, as previously described (Dias et al., 2014). In each assay, 5 g of olive oil were mixed with 50 mL of hydroethanolic solution during 5–10 min at 500 rpm (vortex stirrer LBX V05, lbx instruments). Then, the mixture was left at ambient temperature during 60 min, being removed 40 mL of the supernatant solution, which was immediately analyzed with the E-tongue. The device included two print-screen potentiometric arrays containing 40 sensors (diameter: 3.6 mm; thickness: 0.3 mm) obtained from the combination of 4 lipid additives (octadecylamine, oleyl alcohol, methyltrioctylammonium chloride and oleic acid; ≈3%); 5 plasticizers (bis (1-butylpentyl) adipate, dibutyl sebacate, 2-nitrophenyl-octylether, tris(2-ethylhexyl) phosphate and dioctyl phenylphosphonate; ≈65%) and high molecular weight polyvinyl chloride (PVC; ≈32%) (Dias et al., 2014). These lipid polymeric membranes were used due to the satisfactory signal stability over time (%RSD < 5%, for 5 min signal record), intra- and inter-day repeatability (0.5% < %RSD < 15%) and the capability to provide qualitative and quantitative responses towards taste attributes (sweet, acid, bitter, salty and umami) (Dias et al., 2009; Marx et al., 2017) as well as to olive oils' positive and negative sensory sensations (Slim et al., 2017; Veloso et al., 2018). Each sensor is identified with a letter S (for sensor) followed by a code for the sensor array (1: or 2) and the number of the membrane (1–20, corresponding to different combinations of plasticizer and additive used). The electrochemical analysis took 5 min, enabling to record several electrochemical scans and being the last one used assuming that it corresponded to a pseudo-equilibrium state. Electrochemical assays were performed in duplicate for each olive oil sample, being a third assay carried out if the coefficients of variation of the potentiometric signals generated by the E-tongue sensors were greater than 20% (Rodrigues et al., 2016). To minimize the risk of overoptimistic results, for data split (training and internal-validation sets) and modelling purposes, only one electrochemical "average" signal profile per sample was used, avoiding that results from duplicate assays of the same olive oil sample could be included into both training and validation sets.

2.6. Statistical analysis

In this study, Multiple linear regression (MLR) models were established to estimate and/or predict the contents of phenolic and volatile compounds of olive oils, which were detected in the majority of the olive oil samples analyzed by conventional chromatography techniques, using the potentiometric E-tongue signal profile. These models had the most representative and non-collinear sub-sets of sensor signal profiles that were selected, in each case, by applying the simulated annealing (SA) meta-heuristic algorithm. This algorithm has proven to be a powerful variable selection algorithm, for both qualitative (Dias, Rodrigues, Veloso, Pereira, & Peres, 2016; Dias et al., 2014; Slim et al., 2017; Souayah et al., 2017; Veloso et al., 2018, 2016) and quantitative (Rodrigues et al., 2016) evaluation of olive oil using potentiometric taste sensor devices. The quality criterions involved the maximization of the coefficient of determination (R^2) and the minimization of the root-mean-square error (RMSE) for the lowest number of sensors with non-collinear potentiometric signals responses, based on the results achieved for the leave-one-out (LOO) cross-validation (CV) procedure (Cadima, Cerdeira, & Minhoto, 2004; Cadima, Cerdeira, Silva, & Minhoto, 2012; Cortez, 2014). The repeated K-fold-CV procedure was also applied (which is a suitable CV variant when the dataset does not allow the establishment of a representative external data sub-set) for comparison purposes with the LOO-CV technique results, and to infer about possible overfitting issues that could occur for the latter CV variant. In each run, the data was randomly divided into K folds (set equal to 4 in this study), being K-1 folds used, at each time, for training purposes (to establish the best E-tongue-MLR-SA model) and the data of the remaining fold used for test purposes (internal validation). This process was repeated until all folds were used for internal validation. The procedure was then randomly repeated (10 times in this work) leading to the formation of other data folds containing different sets of olive oil samples. When the quality of the linear regression justified, the possibility of using the selected E-tongue-MLR-SA models (for both LOO-CV and repeated K-fold-CV procedures) as complementary tools for the quantification of the phenolic and/or volatile composition of Arbequina EVOO from Spain and Brazil, was further checked, as suggested by Roig and Thomas (2003a, 2003b). The checking technique involved the establishment of the 95% intervals of confidence (IC) for the slope and intercept values of the single linear regression (LR) obtained by plotting the chemical contents predicted by the E-tongue-MLR-SA models versus the respective experimental data determined by chromatographic techniques. The proposed E-tongue based approach could be foreseen as a satisfactory tool if the 95% IC contained the theoretic values of "zero" and "one" for the intercept and slope values, respectively (Roig & Thomas, 2003a, 2003b). All statistical analysis were performed using the Subselect (Cadima et al., 2004, 2012) and MASS (Venables & Ripley, 2002) packages of the open source statistical program R (version 2.15.1), at a 5% significance level.

3. Results

3.1. Phenolic profile

As reported and discussed by Borges et al. (2017b, 2017c), it was possible to quantify the concentration of the total phenols content (74–335 mg

Table 2
Predictive capability of the E-tongue-MLR-SA models established to quantify the concentration of the major volatile and phenolic compounds detected in the 11 Arbequina olive oils evaluated, 9 from Spain and 2 from Brazil (n = 33: 11 olive oils × 3 independent samples).

Chemical compound		Concentration range (μg × kg^{-1} of olive oil)[a]	E-tongue-MLR-SA models[b]				
			No of sensors[c]	Determination coefficient (R^2)		Root-mean-square errors (*RMSE*, μg × kg^{-1} of olive oil)	
				LOO-CV[d]	Repeated *K*-fold-CV[e]	LOO-CV[d]	Repeated *K*-fold-CV[e]
Phenolics							
Total phenols		[74, 335] × 10^3	13[f]	0.967	0954 ± 0028	17.6 × 10^3	(17.7 ± 5.4) × 10^3
Flavonoids	Apigenin	[14, 453]	14[g]	0.981	0.962 ± 0.019	25.9	28.6 ± 5.9
	Luteolin	[84, 1615]	13[h]	0.969	0.930 ± 0.031	109.0	126.0 ± 26.6
	Naringenin	[15, 143]	15[i]	0.982	0.958 ± 0.035	6.2	7.2 ± 2.4
Phenolic acids	p-Coumaric acid	[0, 239]	14[j]	0.995	0.974 ± 0.05	6.3	8.6 ± 6.6
	Vanillic acid	[0, 133]	13[k]	0.992	0.982 ± 0.014	6.8	8.5 ± 3.1
Phenol alcohols	Hydroxytyrosol	[3, 1620]	12[l]	0.988	0.983 ± 0.017	70.1	73.9 ± 21.7
Volatile compounds							
Alcohols	1-octanol	[0, 2]	13[z]	0.932	0.881 ± 0.071	0.192	0.20 ± 0.10
	Phenylethyl alcohol	[0, 9]	10[y]	0.903	0.795 ± 0.140	1.19	1.3 ± 0.5
	Total	[0, 54]	13[q]	0.993	0.860 ± 0.218	1.80	1.9 ± 0.6
Aldehydes	E − 2-hexenal	[45, 386]	13[x]	0.947	0.909 ± 0.072	33.7	31.7 ± 15.9
	Nonanal	[0.6, 10]	13[w]	0.895	0.818 ± 0.118	1.0	1.1 ± 0.4
	Total	[45, 392]	8[p]	0.943	0.897 ± 0.079	29.4	34.4 ± 9.7
Hydrocarbons	3- ethyl-1,5-octadiene	[0, 27]	10[v]	0.934	0.871 ± 0.103	3.4	3.6 ± 1.2
	Total	[0, 27]	10[o]	0.929	0.865 ± 0.105	3.6	3.7 ± 1.3
Esters	Z-3 hexenyl acetate	[0, 262]	14[u]	0.980	0.935 ± 0.068	10.6	15.8 ± 4.3
	Hexyl acetate	[0, 28]	11[r]	0.914	0.857 ± 0.110	3.1	3.2 ± 1.5
	Total	[7, 286]	12[m]	0.976	0.941 ± 0.050	16.6	17.6 ± 3.4
Terpenes	β-ocimene	[0, 25]	14[t]	0.993	0.941 ± 0.075	0.8	0.9 ± 0.5
	Farnesene	[0, 6]	10[s]	0.975	0.862 ± 0.172	0.3	0.3 ± 0.2
	Total	[0, 31]	12[n]	0.990	0.905 ± 0.136	1.2	1.4 ± 0.6

[a] Experimental concentration range levels found in the Arbequina olive oil (Borges et al., 2017c, 2017b).
[b] Multivariate linear regression (MLR) model based on sub-sets of potentiometric sensors, established using the simulated annealing (SA) algorithm, selected among the 40 possible signal profiles obtained with the electronic tongue (E-tongue) during the analysis of the olive oil hydroethanolic extracts.
[c] Number of signals included in the E-tongue-MLR-SA model, selected from the 40 electrochemical signals recorded by E-tongue during analysis of each olive oil hydroethanolic extract.
[d] LOO-CV: leave-one-out cross validation procedure.
[e] Repeated *K*-fold-CV: cross-validation procedure with 4 folds, ensuring that at least 25% of the original data are used for internal validation, and 10 repetitions.
[f] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:2, S1:8, S1:9, S1:11, S1:12, S1:13, S1:14, S1:20, S2:2, S2:5, S2:7 and S2:15.
[g] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:2, S1:4, S1:7, S1:8, S1:11, S1:13, S1:14, S1:20, S2:1, S2:5, S2:9, S2:17, S2:18 and S2:20.
[h] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:2, S1:3, S1:4, S1:6, S1:12, S2:1, S2:2, S2:8, S2:9, S2:11, S2:14, S2:15 and S2:18.
[i] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:6, S1:7, S1:8, S1:10, S1:11, S1:14, S1:16, S1:17, S1:18, S2:2, S2:8, S2:9, S2:13 and S2:14.
[j] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:4, S1:7, S1:12, S1:16, S1:17, S1:20, S2:2, S2:4, S2:9, S2:10, S2:17, S2:18 and S2:20.
[k] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:3, S1:7, S1:10, S1:11, S1:15, S1:20, S2:1, S2:2, S2:6, S2:7, S2:14, S2:17 and S2:19.
[l] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:4, S1:5, S1:9, S1:13, S1:15, S1:19, S1:20, S2:2, S2:3, S2:4, S:7 and S2:17.
[m] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:2, S1:3, S1:6, S1:9, S1:10, S1:11, S1:20, S2:5, S2:13, S2:15 and S2:19.
[n] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:2, S1:6, S1:16, S1:19, S2:2, S2:3, S2:5, S2:10, S2:12, S2:15 and S2:17.
[o] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:3, S1:8, S1:13, S1:15, S1:19, S1:20, S2:2, S2:5 and S2:11.
[p] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:2, S1:12, S1:19, S1:20, S2:2, S2:6, S2:14 and S2:20.
[q] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:4, S1:9, S1:10, S1:12, S1:14, S1:15, S1:17, S2:3, S2:5, S2:10, S2:14, S2:16 and S2:19.
[r] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:2, S1:3, S1:5, S1:7, S1:8, S1:9, S1:20, S2:2, S2:5, S2:6 and S2:12.
[s] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:6, S1:9, S1:11, S1:17, S2:3, S2:5, S2:10, S2:16, S2:19 and S2:20.
[t] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:2, S1:6, S1:7, S1:10, S1:16, S2:2, S2:3, S2:5, S2:8, S2:10, S2:12, S2:14 and S2:15.
[u] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:5, S1:9, S1:12, S1:15, S1:17, S2:1, S2:4, S2:8, S2:9, S2:11, S2:13, S2:17, S2:18 and S2:19.
[v] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:6, S1:9, S1:12, S1:15, S2:2, S2:5, S2:8, S2:10, S2:18 and S2:19.
[w] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:4, S1:8, S1:13, S1:14, S1:15, S1:16, S2:5, S2:8, S2:9, S2:10, S2:11, S2:17 and S2:19.
[x] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:5, S1:7, S1:8, S1:13, S1:14, S2:1, S2:5, S2:10, S2:15, S2:17, S2:18 and S2:20.
[y] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:6, S1:8, S1:10, S1:18, S1:19, S1:20, S2:5, S2:8, S2:11 and S2:13.
[z] E-tongue sensor signals included in the E-tongue-MLR-SA model: S1:1, S1:2, S1:3, S1:5, S1:6, S1:8, S1:12, S1:18, S1:20, S2:4, S2:7, S2:15 and S2:19.

CAE × Kg^{-1}), 3 flavonoids (apigenin, 14–453 μg × Kg^{-1}; luteolin, 84–1615 μg × Kg^{-1}; and naringenin, 15–143 μg × Kg^{-1}), 2 phenolic acids (p-coumaric acid, 0–239 μg × Kg^{-1}; and vanillic acid, 0–133 μg × Kg^{-1}) and 1 phenol alcohol (hydroxytyrosol, 3–1620 μg × Kg^{-1}). The extensive dynamic concentration ranges pointed out that, although only 11 olive oils were evaluated, their phenolic contents varied significantly. Fig. 1, shows the relative proportion of the three phenolic classes found in the evaluated Arbequina EVOO. The results variability pointed out the quite different phenolic composition profiles of the Arbequina olive oil samples according to the production region, which may contribute to different sensory sensations. These results show the need of fast and cost-effective assessment using portable and in-situ measuring devices.

3.2. Volatile profile

Nineteen volatile compounds were identified in the EVOO samples (Table 1), being grouped according to six chemical classes: alcohols, aldehydes, hydrocarbons, esters, terpenes and phenols, which relative proportions are shown in Fig. 2. In general, the highest concentrations values were obtained for aldehydes and esters, mainly from the LOX pathway, with E − 2-hexenal (48–380 μg × Kg^{-1}) and Z-3-hexenyl acetate (9–250 μg × Kg^{-1}) having higher levels. The highest concentrations of these individual compounds are linked to desirable odour descriptors such as green, green astringent, bitter, apple-like, banana-like and fruity (Aparicio & Morales, 1998; García-González, Romero, &

Table 3
Parameters of the single linear regression established between the values of concentration levels predicted by E-tongue-MLR-AS models (LOO-CV and repeated *K*-fold-CV) and the respective phenolics experimental concentration values quantified by the conventional chromatographic technique (UPLC-MS): coefficient of determination (R^2); slopes, intercept values and respective confidence intervals (CI) at 95%.

Phenolic compounds		LOO-CV[a]					Repeated K-fold-CV[b]				
		R^2	Slope	Slope CI[c]	Intercept	Intercept CI[d]	R^2	Slope	Slope CI[c]	Intercept	Intercept CI[d]
Total phenols		0.967	0.980	[0.885, 1.076]	3.26	[-15.57, 22.08]	0.926	0.978	[0.948, 1.008]	3.88	[-2.07, 9.84]
Flavonoids	Apigenin	0.981	0.951	[0.881, 1.020]	4.51	[-13.90, 22.92]	0.951	0.953	[0.929, 0.977]	4.30	[-1.93, 10.53]
	Luteolin	0.969	0.962	[0.872, 1.052]	13.50	[-72.04, 99.04]	0.914	0.962	[0.930, 0.994]	12.44	[-18.04, 42.93]
	Naringenin	0.982	0.942	[0.876, 1.008]	1.00	[-2.79, 4.79]	0.946	0.949	[0.924, 0.973]	0.66	[-0.74, 2.07]
Phenolic acids	p-Coumaric acid	0.995	0.979	[0.942, 1.016]	0.17	[-3.21, 3.55]	0.967	0.971	[0.951, 0.990]	0.41	[-1.37, 2.20]
	Vanillic acid	0.992	0.970	[0.924, 1.016]	0.08	[-3.14, 3.31]	0.971	0.958	[0.940, 0.976]	0.09	[-1.17, 1.35]
Phenol alcohols	Hydroxytyrosol	0.988	0.960	[0.906, 1.014]	5.72	[-26.00, 37.43]	0.971	0.962	[0.944, 0.981]	5.39	[-5.25, 16.03]

[a] LOO-CV (leave-one-out cross-validation).
[b] Repeated *K*-fold-CV (4 folds × 10 repeats).
[c] 95% slope confidence interval.
[d] 95% intercept confidence interval.

Aparicio, 2010; Luna & Aparicio, 2002; Morales, Luna, & Aparicio, 2005). Moreover, the predominance of these individual volatile compounds agree with previous studies that showed them as more remarkable in Arbequina olive oils from Spain and Tunisia (García-González et al., 2010; Reboredo-Rodríguez et al., 2015). Particularly, E−2-hexenal seems to be one of the main contributors of the aroma in olive oils from different cultivars due to the low odour threshold of this compound (Luna, Morales, & Aparicio, 2006; Pérez et al., 2016). In the Brazilian olive oil 11, which showed high vales of E−2-hexenal, the alcohol E−2-hexen-1-ol was also quantified (Table 1). A similar behaviour was observed in Arbequina oils from Chile and Italia which showed mainly E−2-hexenal and others alcohols such as hexanol and ethanol as major volatile of olive oils (García-González et al., 2010; Procida, Cichelli, Lagazio, & Conte, 2016). The E−2-hexen-1-ol has been linked to undesirable attributes described such as grassy (Aparicio & Morales, 1998), in spite of the fact that E−2-hexen-1-ol is a stable compound that came from the LOX pathway and depend on the level of the specific enzymes such as hydroperixide lyase and alcohol dehydrogenase (Procida et al., 2016).

3.3. Assessment of olive oil phenolic and volatile profiles using a potentiometric E-tongue-MLR-SA approach

The predictive performances of the selected E-tongue-MLR-SA models (based on sub-sets of 8–15 sensors) are reported in Table 2, as well as detailed information (number and type of sensors included in the MLR models) concerning the predictors used for assessing chemical compound. The modelling procedure was only carried out for a particular chemical compound if it was quantified in the olive oils collected in at least half of the olive oils under study. So, an E-tongue-MLR-SA model was established for all the phenolic compounds (apigenin, luteolin, naringenin, p-coumaric acid, vanillic acid and hydroxytyrosol) and total phenols content but only for 2 alcohols (1-octanol and phenylethyl alcohol), 2 aldehydes (E−2-hexenal and nonanal), 1 hydrocarbon (3- ethyl-1,5-octadiene), 2 esters (Z-3 hexenyl acetate and hexyl acetate) and 2 terpenes (β-ocimene and farnesene).

Regarding the assessment of the phenolic contents the overall R^2 and RMSE values obtained for LOO-CV ($0.967 \leq R^2 \leq 0.995$ and $6.2 \leq \text{RMSE} \leq 109.0\ \mu g \times Kg^{-1}$ of olive oil) and repeated K-fold-CV ($0.930 \pm 0.031 \leq R^2 \leq 0.983 \pm 0.017$ and $7.2 \pm 2.4 \leq \text{RMSE} \leq 126.0 \pm 26.6\ \mu g \times Kg^{-1}$ of olive oil) showed the practical possibility of applying the proposed E-tongue-chemometric approach as a successful tool for the quantification of total phenolics, flavonoids, phenolic acids and phenol alcohols found in Arbequina EVOO, which are related to the positive olive oil gustatory sensations. These results showed that the potentiometric E-tongue was able to quantify the olive oil polyphenols or total polyphenolic contents and other phenolic families with similar or greater accuracy when compared to the results obtained in studies using voltammetric E-tongues or combined electrochemical devices, as fusing voltammetric E-tongues and E-noses. For instance, voltammetric E-tongues allowed a satisfactory quantification of the total polyphenols (Apetrei & Apetrei, 2013; Apetrei et al., 2010, 2007; Rodríguez-Méndez et al., 2008) and, in combination with an E-nose of total polyphenols, flavonoids, phenolic acids and other phenolic fractions (Apetrei et al., 2010), extracted from EVOO ($0.773 \leq R^2 \leq 0.977$ and $0.1 \leq \text{RMSE} \leq 111.0\ \mu g \times Kg^{-1}$ of olive oil; for full cross-validation, *i.e.*, LOO-CV).

The predictive E-tongue-MLR-SA capability for quantifying the total phenols and individual phenolic contents of olive oil (Roig & Thomas, 2003a, 2003b) was also evaluated. In accordance, for the two CV variants, the parameters (slope and intercept values) of the single linear regression models established between the contents predicted by the E-tongue-MLR-SA and the total phenols content, determined by Folin-Ciocalteau method, and flavonoids, phenolic acids and phenol alcohols contents determined by chromatography, were determined. Table 3 presents these parameters including the determination coefficients (R^2), the slope and intercept values and the respective 95% confidence intervals, for LOO-CV and repeated K-fold-CV. The results showed that, at 5% significance level, the slope and intercept values were statistically equal to the expected theoretic values, since the confidence intervals contain the values one and zero, respectively. Moreover, the satisfactory R^2 values obtained also confirmed the predictive overall quantitative performance of the E-tongue based models ($R^2 \geq 0.914$). Thus, it could be concluded that the E-tongue together with the MLR-SA modelling could satisfactory assess the phenolic contents of olive oil, when compared with the results obtained by chromatographic conventional technique. The quality of the regression results for the two CV variants (LOO-CV and repeated K-fold-CV) can be further verified from Fig. 3. This figure allows the visualization of the satisfactory single linear regression obtained between the selected phenolic compounds and total phenols contents predicted by the E-tongue-MLR-SA, for LOO-CV or repeated K-fold-CV, and those obtained by the reference methods (Folin-Ciocalteau and chromatographic methods). It should also be remarked that, in general, the dynamic phenolic concentration intervals clearly show the formation of at least two data groups, which can be tentatively attributed to the different geographical origins of the EVOO evaluated (*i.e.*, Spain and Brazil).

On the other hand, and from the results shown in Table 2, the proposed E-tongue-MLR-SA approach, based on the potentiometric data recorded during the analysis of the olive oil's hydroethanolic extracts, showed a less promising potential for the evaluation of the volatile profiles of Arbequina EVOO (LOO-CV: $0.895 \leq R^2 \leq 0.993$ and $0.2 \leq \text{RMSE} \leq 33.7\ \mu g \times Kg^{-1}$ of olive oil; repeated K-fold-CV: $0.818 \pm 0.118 \leq R^2 \leq 0.941 \pm 0.075$ and $0.2 \pm 0.1 \leq \text{RMSE} \leq 34.4 \pm 9.7\ \mu g \times Kg^{-1}$ of olive oil). In fact, a

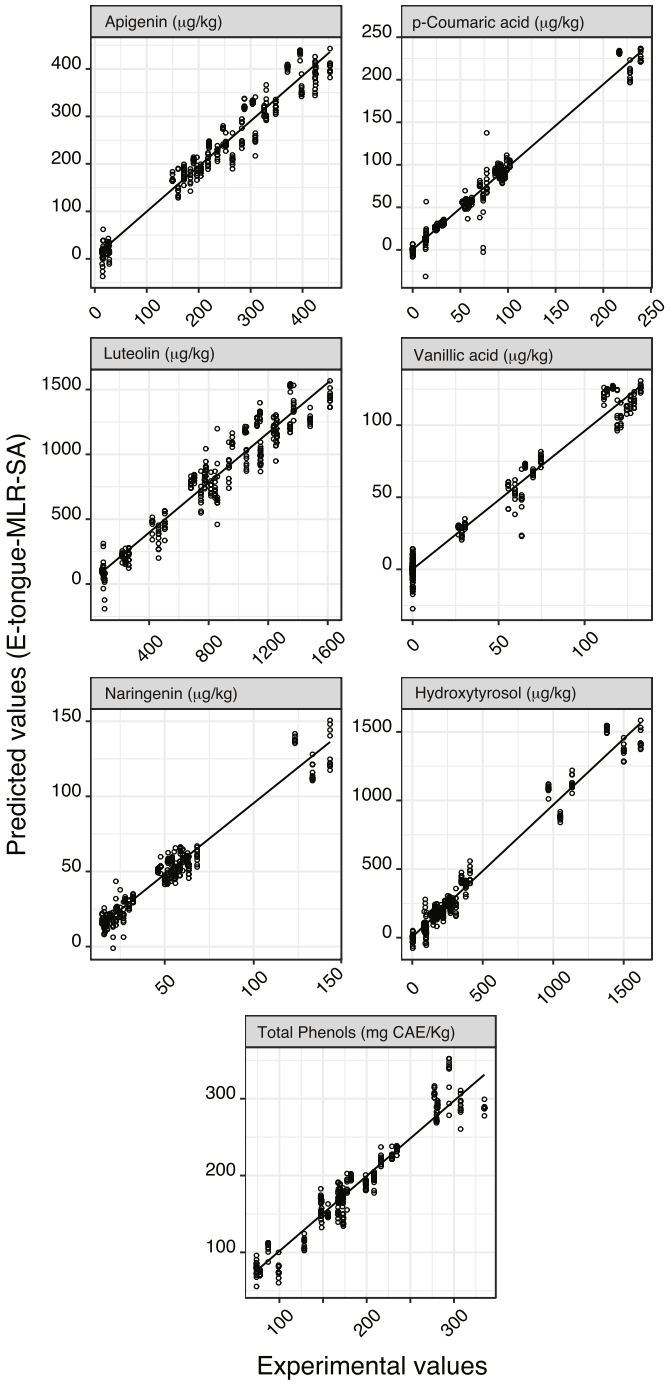

Fig. 3. Phenolics contents of Spanish and Brazilian cv Arbequina EVOOs: comparison of E-tongue-MLR-SA prediction performance (repeated K-fold-CV procedure) versus the experimental values determined by Folin-Ciocalteau method (total phenols content) or by UPLC-TOF-MS (flavonoids, phenolic acids and phenol alcohols).

linear trend could only be cautiously assumed regarding the prediction of total content of alcohols, aldehydes, esters or terpenes, showing that the E-tongue could not be used as an alternative tool to the chromatographic analysis. This less satisfactory performance could be partially explained since, contrary to the assessment of the phenolic compounds, which contents are directly related to the concentration found in the liquid extracts, the volatile levels are indirectly evaluated through the analysis of the same liquid extract, which may not be an accurate representation of the olive oil volatile fractions.

4. Conclusions

The study allowed verifying the successful combination of a potentiometric electronic tongue with multiple linear regression models for assessing the contents of phenolic compounds found in olive oil, which are responsible for positive gustatory sensations. The work showed that the potentiometric profiles of olive oil hydroethanolic extracts could give quantitative information of the total phenols contents as well as the individual phenolic contents, flavonoids, phenolic acids and phenol alcohol found in cv Arbequina olive oil. Moreover, the accuracy of the lab-made potentiometric device was similar to that achieved with UPLC-TOF-MS as well as to those previously reported for voltammetric electronic tongues. It was also shown that potentiometric device could not be satisfactorily used to indirectly assess the levels of olive oil volatile compounds. Even so, considering the low-cost, the analysis time and the simplicity of the electrochemical-chemometric procedure, together with the versatility of evaluating in a single run the levels of total and individual phenolic compounds, the proposed approach can be envisaged as a helpful analytical tool for olive oil analysis.

Conflicts of interest

The authors declare no competing financial interest.

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