



Application of a lab-made electronic nose for extra virgin olive oils commercial classification according to the perceived fruitiness intensity

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ABSTRACT

An electronic nose, comprising nine metal oxide sensors, has been built aiming to classify olive oils according to the fruity intensity commercial grade (riply fruity or light, medium and intense greenly fruity), following the European regulated complementary terminology. The lab-made sensor device was capable to differentiate standard aqueous solutions (acetic acid, cis-3-hexenyl, cis-3-hexen-1-ol, hexanal, 1-hexenol and nonanal) that mimicked positive sensations (e.g., fatty, floral, fruit, grass, green and green leaves attributes) and negative attributes (e.g., sour and vinegary defects), as well as to semi-quantitatively classify them according to the concentration ranges (0.05–2.25 mg/kg). For that, unsupervised (principal component analysis) and supervised (linear discriminant analysis: sensitivity of 92% for leave-one-out cross validation) classification multivariate models were established based on nine or six gas sensors, respectively. It was also showed that the built E-nose allowed differentiating/discriminating (sensitivity of 81% for leave-one-out cross validation) extra virgin olive oils according to the perceived intensity of fruitiness as ripely fruity, light, medium or intense greenly fruity. In conclusion, the gas sensor device could be used as a practical preliminary non-destructive tool for guaranteeing the correctness of olive oil fruitiness intensity labelling.

1. Introduction

Olive oil is a seasoning edible food product that, contrary to vegetable oils, has typical colour and a variety of different flavours arising from the traditional mechanical oil extraction from olives, without the use of organic solvents and not requiring any de-acidification, bleaching and deodorization process [1,2]. Olive oil richness in bioactive compounds (e.g., phenolic compounds and tocopherols), which are related to several nutritional and health positive effects, together with the worldwide appreciated flavour [1–3], positively contributes to enhance the consumers' preference when buying a vegetable oil. According to the European Union (EC) regulations and the International Olive Council (IOC) recommendations, olive oils trade grade (i.e., extra virgin, virgin and lampante olive oils; EVOO, VOO and LOO, respectively) depends on the physicochemical levels (free acidity, peroxide value, extinction

coefficients at 232 and 268 nm) and sensory attributes (fruity positive intensity, off-flavour perception and intensity) [4,5]. According to the EC regulations, EVOO and VOO can be further labelled using a complementary terminology: ripely fruity (oil with a set of olfactory sensations characteristic of ripe olives) or greenly fruity (oil possessing a set of olfactory sensations characteristic of green olives) [4]. Greenly fruity olive oils can be further labelled according to the perceived intensity of positive attributes (in a scale from 0 to 10, corresponding to absence of attribute or maximum level perceived) as intense (median intensity > 6) medium ($3 \leq$ median intensity ≤ 6) and light/mild (median intensity < 3). This optional terminology for labelling purposes is in-line with the increasing demands of olive oil consumers regarding information and guarantees on oil characteristics [2]. In this context, since besides the objective physicochemical analysis, the olive oil classification also depends on the sensory analysis, which although performed by trained

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panellists, comprises an intrinsic human subjectivity degree, being an expensive and time-consuming task [6–8]. To partially overcome some limitations related to the olive oil sensory analysis, different analytical strategies have been proposed. Recently, Veloso et al. [9] showed that a potentiometric electronic tongue, with lipid polymeric membranes, could be satisfactorily used as a taste sensor device to classify EVOO according to the intensity perception of fruitiness, bitterness and pungency attributes, as intense, medium or light oils. Although the proposed approach was user-friendly, fast, portable sensor device, with the possibility of *in-situ* use, the procedure was invasive requiring a destructive sample pre-treatment step (i.e., a hydro-ethanolic extraction) due to the difficulty of carrying out electrochemical assays in non-conductive viscous liquids like olive oil [10]. Non-invasive/non-destructive analytical techniques that do not require any oil pre-treatment, were proposed aiming to classify olive oils based on the fruity intensity. Near and mid infrared spectroscopy were successfully used by Sinelli et al. [7] as rapid tools to classify EVOO according to the fruity attribute intensity, without requiring any sample pre-treatment. On the other hand, proton transfer reaction-time of flight-mass spectrometry was used by Taiti and Marone [1] as a non-invasive analytical tool, based on the fast detection of volatile compounds, for olive oil analysis, allowing a rather well discrimination of EVOO with different fruity intensity levels. Alternatively, electronic noses (E-nose), comprising for example metal oxide sensors (MOS) or surface acoustic waves (SAW) sensors, have been applied for non-invasive olive oil analysis. The use of E-noses has been reported for monitoring the oxidation stage and quality decay of olive oils during storage; discriminating olive oils according to quality grade, olive cultivar or geographical origin; assessing sensory defects in oils; detecting olive oil adulterations; identifying olive oil blended with hazelnut, peanut, corn or sunflower oil; detecting the undeclared blending of EVOO with soft-refined oils; and, monitoring olive oil processing [11–27]. To the authors' best knowledge, no E-nose has been specifically applied to classify EVOO according to the fruity intensity perception. Thus, in this study, a lab-made E-nose-MOS portable device was designed and built for that purpose and its performance evaluated based on unsupervised and supervised pattern recognition multivariate statistical tools. The capability of the lab-made device to differentiate standard solutions of chemical compounds that mimic sensory sensations usually perceived during the olive oil evaluation by panellists was also evaluated.

2. Materials and methods

2.1. Standard solutions of volatile chemical compounds that mimic olfactory attributes perceived in olive oils

Aqueous standard solutions (concentrations ranging from 0.5 to 2.0 mg/kg) of volatile chemical compounds that mimic sensory positive and negative attributes, which can be perceived by trained panellists during the olive oils evaluation were used to evaluate the E-nose performance. Deionized water was used for preparing the solutions. Table 1 lists the chemical compounds analysed (chemical formula, chemical family and concentration range studied), which included nonanal (purity of 95%, from Acros Organics), hexanal (purity \geq 98%, from Sigma-Aldrich), cis-3-hexenyl acetate (purity \geq 98%, from Sigma-Aldrich), cis-3-hexen-1-ol (purity \geq 98%, from Sigma-Aldrich), acetic acid (purity of 96%, from Panreac) and 1-hexenol (purity of 98%, from Acros Organics). The sensory sensations listed in Table 1, related to each of the above-mentioned compounds, as well as the tested concentration ranges, were selected based on literature data [6,11,16,28–32].

2.2. Olive oils samples

Olive oils from 8 different commercial brands (2 independent samples/bottles from each brand) were evaluated. All oils were industrially extracted in two-phase olive mills from olives harvested in olive groves

Table 1

Volatile chemical compounds (standard aqueous solutions: 0.05–2.25 mg/kg, depending on the compound) related to olfactory sensations (positive and negative attributes) usually perceived in olive oils: name, chemical structure, chemical family and main olfactory mimicked attributes.

Chemical compound	Chemical formula	Chemical family	Concentration range (mg/kg)	Descriptor related to olfactory attributes
Acetic acid	C ₂ H ₄ O ₂	Carboxylic acid	0.15–0.60	Sour/vinegar off-flavours
cis-3-hexen-1-ol	C ₆ H ₁₂ O	Alcohol	0.5 to 2.0	Banana/green
cis-3-hexenyl acetate	C ₈ H ₁₄ O ₂	Acetate ester	0.5 to 2.0	Fruity/green leaves
Hexanal	C ₆ H ₁₂ O	Alkyl aldehyde	0.125 to 2.25	Apple/grass/green
1-Hexenol	C ₆ H ₁₂ O	Alcohol	0.5 to 2.0	Fruity/banana off-flavour
Nonanal	C ₉ H ₁₈ O	Aldehyde	0.05 to 0.14	Fatty/floral/grass

located in Trás-os-Montes region (northeast of Portugal). According to the label, all oils had a high quality grade, being all of them classified as EVOO, following the international regulations [4,5]. Moreover, the referred olive oils were also commercially labelled according to the olfactory perceived sensations, two brands as EVOO ripely fruity (oil with a set of olfactory sensations characteristic of ripe olives) and the other six brands as EVOO greenly fruity (oil possessing a set of olfactory sensations characteristic of green olives) [4]. This latter oils group was further split into 3 levels (2 brands per level) according to the perceived intensity of the fruity sensation as EVOO greenly fruity intense (median intensity > 6), EVOO greenly fruity medium (3 \leq median intensity \leq 6) and EVOO greenly fruity light/mild (median intensity < 3). The commercial complementary grade terminology indicated in the oils' labels was based on sensory analysis data and was confirmed by the sensory panel of the School of Agriculture of the Polytechnic Institute of Bragança, Portugal [33].

2.3. E-nose analysis

2.3.1. Lab-made device

The E-nose used in this study was designed and built (Fig. 1) by the research team, as an all-in-one olfactory multi-sensor device. The device integrated multiple systems, namely a heated sampling unit and a heated multi-sensor detection array. To ensure a constant temperature at the sampling system (\sim 28 °C) and at the detection unit (\sim 35 °C), two commercial silicone rubber heating blankets (100 \times 120 mm with a Ni–Cr/FeCrAl heating elements, from Vinson, China) were used. To provide an efficient, fast and complete delivering of the homogenous headspace gas phase of the sampling unit, which contained the representative volatile fraction of a specific sample, to the detection chamber, a diaphragm vacuum air pump (model SC3502PM, from SKOOCOM, China) was included in the device. The vacuum pump also allowed performing the all-in-one system cleaning, between samples analysis. The detection system includes nine MOS (Table 2), which electrical properties change according to the adsorption phenomena that occurs on the sensors surface when in contact with volatile compounds. The same or similar MOS have been previously used due to their capability to detect different aroma compounds of olive fruits [34] and vegetable oils [17,22,35,36]. The MOS sensors are porous layers heated by a filament that undergoes a redox reaction when it comes in contact with a reducing or oxidizing volatile compound, changing the electrical resistance across the circuit proportionally to the compound concentration. The specific sensor responses (electrical resistance in ohms) are then recorded using an Agilent data acquisition unit (model 34970A),

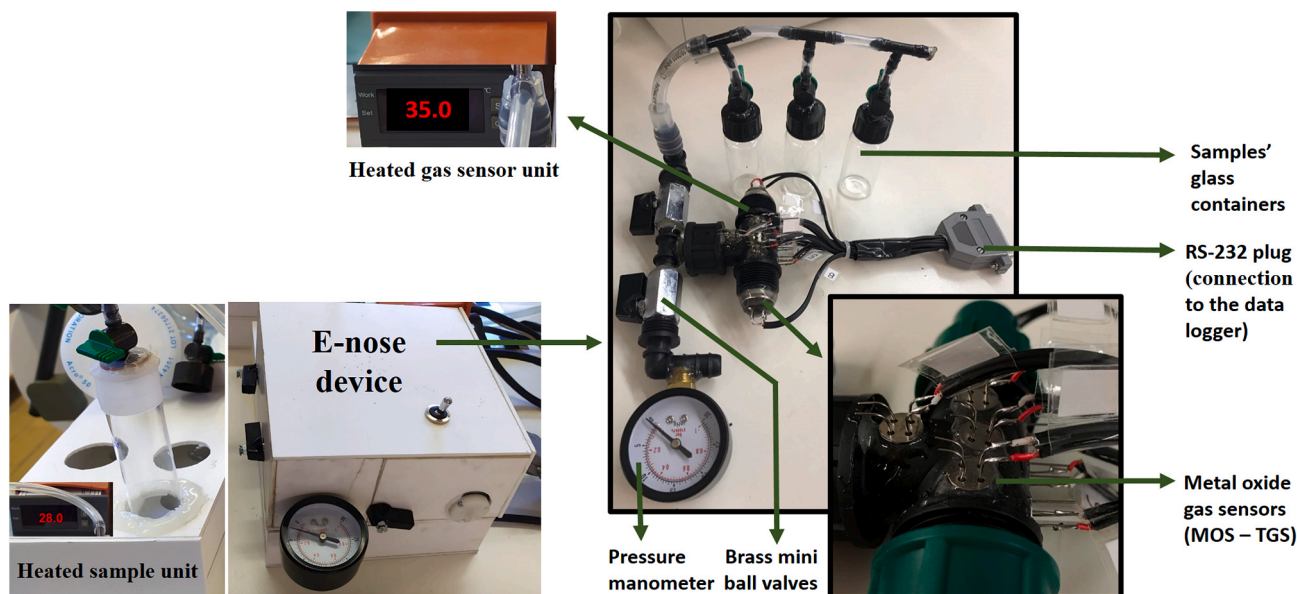


Fig. 1. E-nose-MOS lab-made device comprising: sample heated unit, gas sensor heated unit and data logger interface.

Table 2
Metal oxide gas sensors (MOS) included on the lab-made E-nose device.

Sensor code	Commercial sensor code	Target gases
S1	TGS 2600 B00	General air contaminants
S2	TGS 2602	General air contaminants
S3	TGS 2610 C00	Butane, liquid petroleum gases
S4	TGS 2611 C00	Methane, natural gas
S5	TGS 2610 D00	Butane, liquid petroleum gases (carbon filter)
S6	TGS 2611 E00	Methane, natural gas (carbon filter)
S7	TGS 2612	Methane, propane, iso-butane
S8	TGS 826 A00	Ammonia
S9	TGS 823 C12 N	Organic solvent vapours

controlled by an Agilent BenchLink Data Logger software, allowing transforming the signal into a digital value, which is computed generating unique resistance volatile fingerprint corresponding to each sample being evaluated. The MOS are connected to the data logger by a RS-232 plug serial communication.

2.3.2. Sample conditioning and analysis

At the first use, the sensitive materials comprised on the TGS.MOS, which operating temperature is above 200 °C, were activated during 48 h. In all subsequent uses, the activation was not required, being needed to pre-heated the sampling's and sensors' units (~30 min). Samples (0.5 mL) were then put into a glass vial (25 mL) and placed in the sampling chamber during 13 min (to allow obtaining a headspace with a volatile fraction representative of the sample) at 28 °C (temperature recommended by the International Olive Council for olive oils sensory analysis) [5]. Although several gas sample pre-concentration procedures exist, the static headspace technique was chosen due to its simplicity and rapid acquisition of a representative sample of the oil's volatile fraction, allowing an easy on-line and in-situ implementation, being widely implemented with both lab-made and commercial E-noses [30,35,36]. At the same time, the E-nose system was cleaned during 13 min using air flow (pumped under vacuum) or nitrogen flow (UN 1066, Linde 089 cyl 02/15) for the standard solutions or olive oils analysis, respectively, enabling reaching a stable signal baseline, indicative of a cleaned environment. The sample's gas headspace was delivered, through suction, to the sensors unit (closed chamber) with the help of the vacuum pump, being allowed to interact with the MOS array during 2.5 min.

During this analysis time-period, the resistance signals of each of the 9 MOS were recorded at each 4 s.

2.3.3. Data acquisition, feature extraction and signal treatment

As previously mentioned, data signals (resistance in ohm) from each of the 9 MOS were acquired by a data logger (Agilent 34970A) and then recorded by the Agilent BenchLink Data Logger software, installed in a PC. The signal recorded is generated at the sensors' surfaces being plotted versus the analysis time using the abovementioned software. So, for each analysis and sensor, a total of 37–38 resistance values are recorded (signals acquired during 2.5 min at a 4 s time-interval). Therefore, different feature extraction methods were considered aiming to establish a representative E-nose fingerprint of each standard solution or olive oil sample's volatile fraction. Different feature extraction parameters were used in this study, as proposed by Gila et al. [34]:

- (i) Last response point (LP): more stable resistance signal value within the analysis time-interval;
- (ii) Integral of the response curve (INT): area below the signals' curve, numerically calculated using the Simpson's integration rule;
- (iii) Maximum response point (MAX): maximum resistance value recorded within the analysis time-interval;
- (iv) Minimum response point (MIN): minimum resistance value recorded within the analysis time-interval;
- (v) Sum of the response curve (SUM): sum of all the resistance signal values recorded within the analysis time-interval;
- (vi) Average of the response curve (MEAN): sum of the values of all the resistance signals recorded divided by the number of points gathered; and,
- (vii) Standard deviation (SD) of the response curve.

2.4. Statistical analysis

Single linear regression was applied to verify the existence of a linear correlation between the sensors resistance signals and the concentration of the aqueous standard solutions of volatile chemical compounds that mimic different positive and negative sensory attributes usually perceived in olive oils. The Pearson correlation coefficient (R -Pearson) was determined to evaluate the linearity level. Unsupervised and supervised pattern recognition multivariate techniques were used to

evaluate the classification performance of the lab-made E-nose-MOS device for both standard solutions and olive oil samples. Thus, principal component analysis (PCA) and linear discriminant analysis (LDA) were applied. For the latter the simulated annealing (SA) algorithm, which is a meta-heuristic variable selection algorithm, was implemented to identify the best subsets of non-redundant sensors that allowed achieving the best classification performance. For internal validation purposes, the leave-one-out cross-validation (LOO-CV) procedure was used and the quality of the results were evaluated taking into account the sensitivity (i.e., the percentage of corrected classified samples) as well as through 2D and 3D plots. The statistical analysis was performed using the Sub-select [37] and MASS [38] packages of the open-source statistical program R (RStudio version 1.2.5033), at a 5% significance level.

3. Results and discussion

3.1. E-nose-MOS response towards aqueous standard solutions of volatile chemical compounds that mimic olfactory attributes perceived in olive oils

The E-nose-MOS responses towards standard solutions of six selected volatile chemical compounds (cis-3-hexenyl acetate - fruity/green leaves; cis-3-hexen-1-ol - banana/green sensations; 1-hexenol - fruity/banana; hexanal - apple/grass/green; nonanal - fatty/floral/grass; and, acetic acid - sour/vinegar) were acquired. As aforementioned, seven feature extraction parameters were considered (LP, INT, MAX, MIN, SUM, MEAN and SD). The preliminary unsupervised pattern recognition analysis (*data not shown*) pointed out that the LP, MIN and MEAN feature approaches were those that allowed a better classification performance of the E-nose-MOS device, being the results achieved with the LP slightly better. Thus, LP response signals were used in this study. Different resistance ranges (LP data varying from 176 to 66460 Ω) were recorded by the nine MOS, which signal greatly depended on the chemical compound under study and respective concentration. In general, the resistance signal decreased when the concentration increased (higher

Table 3

E-nose-MOS signal responses (LP feature parameter) towards aqueous standard solutions of volatile chemical compounds related to different positive/negative olfactory sensations (R-Pearson correlation coefficient and slope of the linear regression between the resistance signals versus the concentration, as well as the minimum-maximum signal interval range).

Sensor	Linear regression	Aqueous standard solutions of selected volatile chemical compounds (related sensory sensations)					
		Acetic acid (sour/vinegar)	cis-3-hexen-1-ol (banana/green)	cis-3-hexenyl acetate (fruity/green leaves)	Hexanal (apple/grass/green)	1-hexenol (fruity/banana)	Nonanal (fatty/floral/grass)
S1 (TGS 2600 B00)	R-Pearson	-0.8650	-	-0.9976	-0.9673	-0.9861	-0.9550
	Slope (Ω kg/mg)	-4060	-	-585	-2020	-839	-34084
	[min, max] (Ω)	[7958, 13174]	[6423, 8832]	[5064, 7222]	[2633, 7756]	[5666, 7608]	[6852, 11553]
S2 (TGS 2602)	R-Pearson	-0.9220	-0.9848	-0.9907	-0.9551	-0.9823	-0.9158
	Slope (Ω kg/mg)	-3763	-231	-253	-246	-243	-13805
	[min, max] (Ω)	[730, 3032]	[713, 1172]	[496, 798]	[176, 722]	[755, 1168]	[565, 2334]
S3 (TGS 2610 C00)	R-Pearson	-0.8074	-	-0.9866	-0.9676	-0.9990	-0.9708
	Slope (Ω kg/mg)	-3174	-	-1809	-2448	-681	-22514
	[min, max] (Ω)	[13658, 16813]	[10980, 13353]	[9520, 12214]	[7560, 13319]	[10476, 12930]	[13206, 16104]
S4 (TGS 2611 C00)	R-Pearson	-	-0.9532	-0.9984	-0.9527	-0.8605	-0.9413
	Slope (Ω kg/mg)	-	-171	-3254	-3929	-834	-18923
	[min, max] (Ω)	[23705, 28052]	[18656, 22628]	[15477, 20291]	[12102, 21017]	[17413, 21779]	[22948, 26606]
S5 (TGS 2610 D00)	R-Pearson	-	-	-	-0.9988	-	-
	Slope (Ω kg/mg)	-	-	-	-5384	-	-
	[min, max] (Ω)	[34998, 49575]	[28812, 36866]	[26726, 35987]	[27870, 46859]	[28170, 36140]	[34797, 48487]
S6 (TGS 2611 E00)	R-Pearson	-	-	+0.8381	-	+0.9072	-
	Slope (Ω kg/mg)	-	-	+2107	-	+1899	-
	[min, max] (Ω)	[16042, 21662]	[11970, 18288]	[11789, 18075]	[14549, 20243]	[12377, 18048]	[15840, 21241]
S7 (TGS 2612)	R-Pearson	-	-	-	-0.9260	-	-
	Slope (Ω kg/mg)	-	-	-	-6033	-	-
	[min, max] (Ω)	[38562, 66460]	[30610, 44884]	[30107, 46536]	[34771, 65153]	[30188, 46926]	[38252, 65891]
S8 (TGS 826 A00)	R-Pearson	-0.9517	-0.9862	-0.9202	-0.9545	-0.9854	-0.9832
	Slope (Ω kg/mg)	-15765	-1309	-1052	-1674	-1310	-80135
	[min, max] (Ω)	[4976, 14754]	[4588, 6998]	[3113, 4998]	[1157, 4838]	[4251, 6380]	[3920, 12767]
S9 (TGS 823 C12 N)	R-Pearson	-0.9360	-0.9327	-0.8853	-0.9518	-0.9644	-0.9518
	Slope (Ω kg/mg)	-22794	-2474	-2128	-2774	-2568	-137234
	[min, max] (Ω)	[10625, 26903]	[8508, 13866]	[4861, 9345]	[1800, 8136]	[6298, 11059]	[8011, 22201]

concentrations were related to higher reactivity leading to a lower resistance value), as can be inferred by the negative sign of the correlation coefficient and slope values (Table 3). The nine MOS showed a resistance response in the presence of the six volatile compounds under study and, for one or more of the volatiles it was possible to establish a linear decreasing regression ($-0.9990 \leq R\text{-Pearson} \leq -0.8074$) between the recorded resistance (LP) signals and each compound concentration (Table 3), with the exception of sensor S6, for which a linear positive trend was observed for some of the standard compounds ($+0.8381 \leq R\text{-Pearson} \leq +0.9072$). These findings allowed foreseeing a possible (semi) quantitative application of the E-nose-MOS device towards the detection of olive oils' positive/negative olfactory-related sensations. Globally, sensor S2 showed the highest reactivity towards the six compounds evaluated (lower resistance signal values), followed by S8, S1 and S9. Lastly, the intra-day and inter-day signal (LP) repeatability was evaluated for all sensors, by analysing three times in one day and three times in three consecutive days, the same standard solution of each volatile compound (being chosen the solution with the 2nd highest concentration for each standard: acetic acid, 0.15 mg/kg; cis-3-hexen-1-ol, 1.0 mg/kg; cis-3-hexenyl acetate, 1.0 mg/kg; 1-hexanal, 0.75 mg/kg; 1-hexenol, 1.0 mg/kg; and, nonanal, 0.08 mg/kg). The relative standard deviations varied between 0.4 and 6.0% for the intra-day assays and from 2.3 to 15.1% for the inter-day assays, showing a satisfactory resistance signal repeatability.

The capability of the lab-made E-nose-MOS device to differentiate the six standard solutions of volatile compounds, which included alcohols, esters, aldehydes and carboxylic acids (Table 1), and are related to known olfactory sensations of olive oils, was further evaluated. The resistance signal profiles recorded by the nine MOS allowed the unsupervised differentiation of the standard solutions studied, although a slight data overplotting was observed, namely for the two volatile alcohols, as can be visualized from Fig. 2a. The 3D plot showed the overall performance of the established E-nose-MOS-PCA model, which first 3 principal components (PC) explained 98% of the data variance. To further check the E-nose-MOS performance a supervised LDA was applied. The E-nose-MOS-LDA-SA model (three discriminant functions,

LD, explaining 100% of the data variability) was based on the resistance signal data (LP) of six non-redundant sensors (S2, S4, S5, S6, S8 and S9) selected using the SA algorithm. The classification linear multivariate model correctly classified all the original data samples (sensitivity of 100% for the original data groups, Fig. 2b) and showed a satisfactory predictive performance with a sensitivity of 92% (one hexanal and one nonanal standard solutions misclassified), for the LOO-CV. The unsupervised and supervised satisfactory performances clearly pointed out the potential use of the lab-made E-nose-MOS as a practical and powerful olfactory sensor tool for olive oils evaluation, which could be used by sensory panel as a complementary analytical tool. Finally, to strengthen this hypothesis, it was also evaluated the capability of the E-nose-MOS to differentiate different concentration ranges of the studied standard solutions. Fig. 3 shows that the E-nose-MOS could be used as a semi-quantitative tool to assess the concentration level of the standard solutions studied, based on the PCA unsupervised classification, confirming the prospective use of the device as an olfactory analytical tool.

3.2. Classification of olive oils according to the sensory intensity perception based on the E-nose-MOS signal profiles

As previously mentioned, EVOO can be labelled using a complementary terminology that takes into account the sensory intensity perception of ripe and green sensations based on the evaluation performed by trained panellists. In this sense, EVOO are commercially available as EVOO ripely fruity, EVOO greenly fruity light, medium or intense, aiming to fulfil the increasing complex demands of the worldwide olive oil consumer, who seeks new sensory experiences, emotions and feeling (Clodoveo et al., 2020). However, the scarcity of official sensory panels, the limited number of samples that can be evaluated in a daily basis and the human subjectivity intrinsically linked to the sensory analysis, makes urgent the development of complementary non-invasive sensory analytical tools, which turns out to be a challenging task. Therefore, the lab-made E-nose-MOS device was applied to verify its capability in classifying EVOO according to the abovementioned complementary labelling terminology. An E-nose-MOS-PCA model, based on

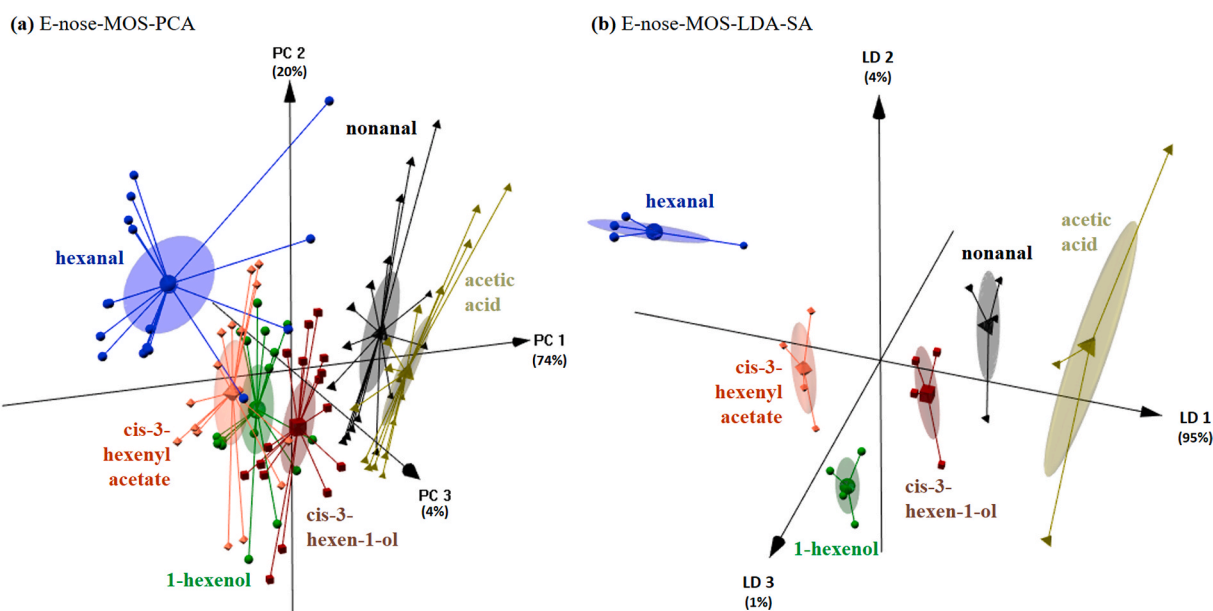


Fig. 2. E-nose-MOS response towards aqueous standard solutions (acetic acid, cis-3-hexen-1-ol, cis-3-hexenyl acetate, 1-hexenol, hexanal and nonanal), with different concentrations (0.05–2.25 mg/kg) that mimic positive and negative sensory attributes (sour/vinegar off-flavour, banana/green, fruity/green leaves, fruity/banana off-flavour, apple/grass/green and fatty/floral/grass sensations, respectively) usually perceived in olive oils: (a) PCA unsupervised differentiation based on the last response resistance signals acquired by the nine MOS (S1 to S9); and, (b) LDA-SA supervised discrimination (original grouped data) based on the on the last response resistance signals acquired by six non-redundant MOS (S2, S4, S5, S6, S8 and S9), selected by the SA algorithm. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

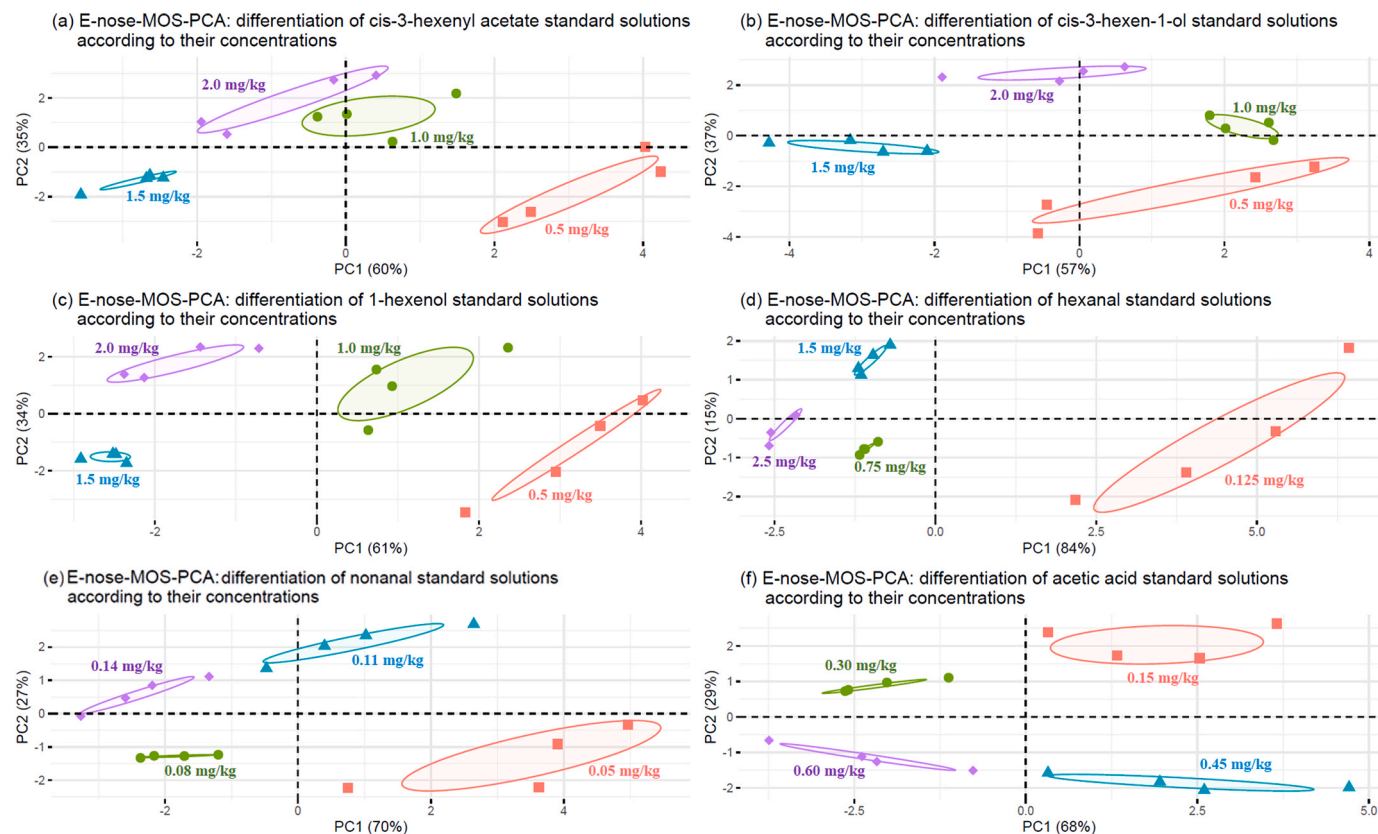


Fig. 3. E-nose-MOS semi-quantitative unsupervised PCA classification of standard solutions according to the concentration range studied, based on the last response resistance signals acquired by the nine MOS (S1 to S9): (a) cis-3-hexenyl acetate aqueous solutions (0.5–2.0 mg/kg) that mimic fruity/green leaves sensations; (b) cis-3-hexen-1-ol aqueous solutions (0.5–2.0 mg/kg) that mimic banana/green sensations; (c) 1-hexenol aqueous solutions (0.5–2.0 mg/kg) that mimic fruity/banana off-flavours; (d) hexanal aqueous solutions (0.125–2.25 mg/kg) that mimic apple/grass/green sensations; (e) nonanal aqueous solutions (0.05–0.14 mg/kg) that mimic fatty/floral/grass sensations; and, (f) acetic acid aqueous solutions (0.15–0.60 mg/kg) that mimic sour/vinegar off-flavours. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

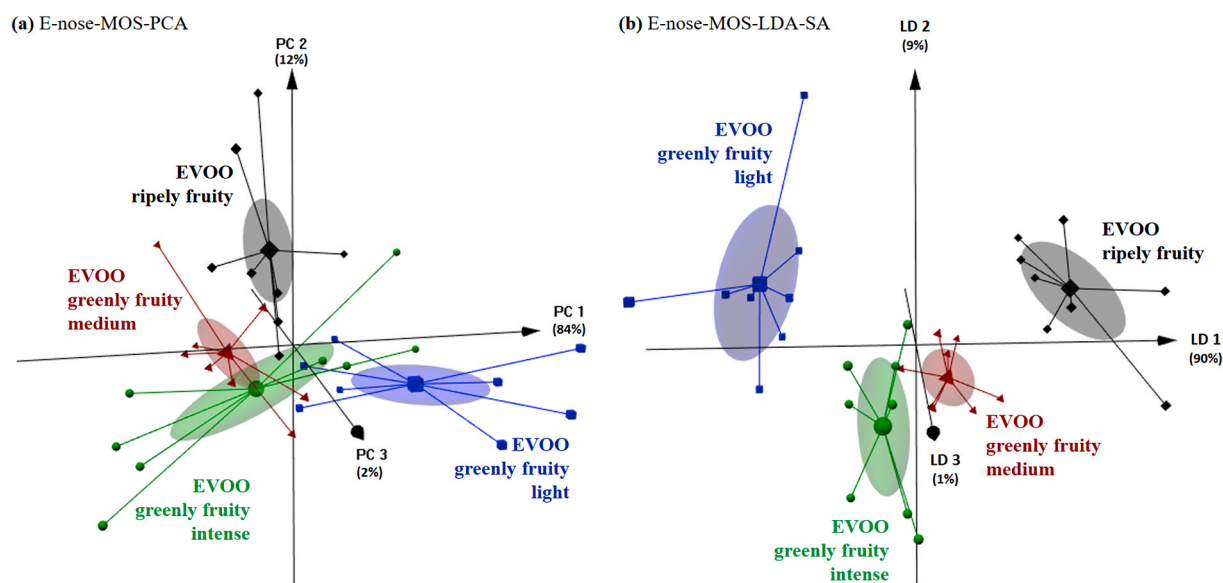


Fig. 4. E-nose-MOS response during the analysis of commercial EVOO labelled using complementary terminology based on the sensory sensations perceived (EVOO ripely fruity: oil with a set of olfactory sensations characteristic of ripe olives; EVOO greenly fruity light, medium or intense: oils possessing a set of olfactory sensations characteristic of green olives with a light, medium or intense fruity intensity) (Annexes II and IX in Commission Regulation (EEC) N° 2568/91 from 11th July and amendments): (a) PCA unsupervised differentiation based on the last response resistance signals acquired by the nine MOS (S1 to S9); and, (b) LDA-SA supervised discrimination (original grouped data) based on the last response resistance signals acquired by eight non-redundant MOS (S1, S2, S4, S5, S6, S7, S8 and S9), selected by the SA algorithm. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the nine MOS, was first established, showing that the resistance signal profiles, recorded during the non-invasive oil analysis of the volatile fraction, allowed the unsupervised split of eight commercial EVOO according to the sensory intensity perception (Fig. 4a). The results showed that ripely fruity oils and greenly fruity light oils were the better differentiated, being an overplotting observed between greenly fruity medium and intense oils. The satisfactory classification performance was also confirmed through a supervised approach. So, an E-nose-MOS-LDA-SA model (based on the signals recorded by eight sensors, S1, S2 and S4 to S9) was capable to correctly discriminate 97% (original data groups, Fig. 4b) and 81% (LOO-CV procedure) of the studied oils. The results showed that all ripely fruity oils were correctly classified, occurring the misclassifications among the greenly fruity medium and intense oils. It should be remarked, that the E-nose-MOS was used to analyse oils from different brands and extracted from different olive cultivars, which could contribute to the observed misclassification rate, since the olfactory sensor device would also give a signal response to other olfactory sensations, specific of each oil. Globally, the predictive classification was slightly inferior compared with the performance previously reported by Veloso et al. [9] for a lab-made potentiometric E-tongue, comprising lipid polymeric sensor membranes. However, this latter sensor-based device is an invasive-destructive technique, requiring a preliminary ethanolic-aqueous extraction of each olive oil under analysis. In this context, and taking into account the non-invasive nature of the E-nose-MOS analysis, the proposed strategy could be an accurate complementary sensory tool, allowing to minimize the number of oils that must be tested by a sensory panel.

4. Conclusions

The sensory attributes and methodology to label extra virgin olive oils according to the sensations perceived and related intensities (riply fruity or greenly fruity light, medium and intense oils) are fixed by European regulations. The use of this complementary sensory grade terminology requires the availability of trained sensory panels, which is a major concern for olive oil producers. Olive oil official panellists are scarce and the analysis is expensive and time-consuming and so, hardly meet the commercialization needs. The present study proposed a fast and non-invasive approach for extra virgin olive oils sensory grade classification, based on a lab-made electronic nose comprising metal oxide sensors. The olfactory sensor device was capable to recognize different chemical volatile compounds that are responsible for typical positive and negative sensory attributes of olive oils as well as to satisfactorily discriminate oils according to the main olfactory sensation perceived and its intensity. The olive oil analysis was non-invasive and required a small sample volume, being able to provide a result within a short time-period (~15 min). Although the successful preliminary results reported, further studies would be needed in the future in order to enhance the spectrum of oils studied and to reinforce the validation methodologies applied. In conclusion, the future implementation of the proposed methodology as a non-invasive routine olfactory device for the sensory grade labelling of olive oils could be of utmost commercial interest for olive oil producers.

Credit author statement

Guilherme G. Teixeira: Software; Formal analysis; Investigation; Writing - Original Draft; Writing - Review & Editing. **Luís G. Dias:** Resources; Software; Funding acquisition; Writing - Review & Editing. **Nuno Rodrigues:** Resources; Writing - Review & Editing. **Ítala M.G. Marx:** Investigation; Writing - Review & Editing. **Ana C.A. Veloso:** Formal analysis; Funding acquisition; Writing - Review & Editing. **José A. Pereira:** Resources; Funding acquisition; Writing - Review & Editing. **António M. Peres:** Methodology; Formal analysis; Funding acquisition; Writing - Review & Editing.

Compliance with ethics requirements

Conflict of interest

The authors declare that they have no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent

Not applicable.

Declaration of competing interest

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.

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