



Application of a lab-made voltammetric electronic tongue to identify musty and vinegary defects in olive oils

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Abstract

The olive oil sector is undergoing a technological transformation promoted by high international competitiveness. This transformation must be aligned with the concepts of industry 4.0 that are already well defined and implemented in other sectors. The integration of advanced sensorics in the process phase in which the quality of the manufactured product is inspected is key to responding in the shortest possible time to deviations in the desired quality. In this work, the results of the experimentation carried out with an e-tongue voltammetric sensor are presented to evaluate its potential in the detection of two of the organoleptic defects that appear more frequently in olive oil (musty and vinegary). This sensor has been built in the research group's laboratory and is made up of three metals in the measurement probe (nickel, silver and copper). Three classification algorithms (Support Vector Machines, Naïve Bayes and Classification Trees) were used and musty-type defect was identified with a success rate of 72%, while the vinegary-type defect was detected with a success rate of 84%.

Keywords Electronic tongue · Olive oil quality · Machine learning · Olive Oil production process · Process analytical technology · Chemometrics

Introduction

The Mediterranean diet based on the consumption of cereals, fruits, legumes, vegetables and of course, Extra Virgin Olive Oil (EVOO) contributes very actively to the increase in life expectancy as well as an improvement in the quality of life (Tosti et al., 2018). The nutritional and health properties of olive oil constitute the healthiest fat. All this makes its cultivation today one of the most interesting in the agricultural industry. In addition, the world consumption of olive oil was around 3.2 millions of tons, which represents an increase of 5.8% compared to previous season according to the International Olive Council institution (IOC, 2022). The same report shows that the accumulated increase in consumption in the last two decades has been 91.1%.

There are different institutions such as IOC that regulate the qualities of olive oils defining which parameters are required to evaluate in order to minimize the risk of fraudulent practices like mislabelling or to enable health claims (e.g. sensory attributes such as fruitiness intensity sensation and absence/presence of organoleptic defects). The EU No 61/2011 and EU No 1348/2013 European regulatory standards describe aforementioned definitions. The certified means of sensory characterization of oils and subsequent categorization are known as tasting panels. They only make use of the olfactory-gustatory sensory response. The experts make use of the receptors: nasal and buccal cavity. Specifically, for olfactory sensitivity the human being relies on the nasal cavity. However, taste sensitivity involves the tongue (sour, salty, bitter and sweet) and the oral cavity that perceives tactile qualities such as, for example, sharpness, astringency or metallic. It is important to remark that these tasting panels are carried out outside the oil mills in certified laboratories, once the oil is stored in tanks. So, nowadays they allow labelling the quality of the produced oil, but nothing can be done for improving its quality. This later requires the measurement, in real time, of different aspects and different stages of the Olive Oil elaboration process

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and their quality according to the parameters established by IOC. Hence, optimizing the production of quality oil entails integrating non-invasive sensors (e.g. electronic noses and electronic tongues) into the production process.

The use of non-invasive sensors is widespread in agrifood, for example, different nanosensors have been developed and tested to detect vanillin (Roostae and Sheikhshoae, 2022), nitrites (Yang et al. 2022), carmoisine (Bijad et al., 2018) or mancozeb (Buledi et al., 2022). The feasibility of electronic noses and electronic tongues in agrifood is guaranteed as illustrate (Leake, 2006; Tan and Xu, 2020) which present some applications examples.

In olive oil field, there are several e-tongue based applications for the classification of olive oils according to the quantity of polyphenols (Apetrei and Apetrei, 2013; Rodríguez-Méndez et al., 2008), olive fruit variety (Dias et al., 2014), olive oil shelf-life and trend during storage (Rodrigues et al., 2016), geographical origin of olive cultivar (Haddi et al., 2013; Souayah et al., 2017; Tahri et al., 2018), phenolic and volatile profiles (Borges et al., 2018; Prata et al. 2018) among other applications. All these works support the use of electronic tongue in olive oil. Unfortunately, as far as the authors know, none of them use it to be able to identify defects regulated by the IOC institution.

The goal of this work is to study the feasibility of applying a voltammetric electronic tongue on olive oil samples to determine organoleptic features such as level and type of defect. In concrete, the proposed e-tongue identifies the most common defects in olive oils, which are musty and vinegar. Musty-humid-earthly defect is a characteristic flavour of oils obtained from fruit in which large numbers of fungi and yeasts have developed as a result of its being stored in humid conditions for several days or of oil obtained from olives that have been collected with earth or mud on them and which have not been washed. The winey-vinegary is a characteristic flavour of certain oils reminiscent of wine or vinegar.

This work has been structured as follows. The [materials and methods](#) section contains information on the experimental setup, the characteristics of the samples used and the methodology followed for the extraction of features and classification. Section 3 describes the results of proposed classification methods. This section ends with a discussion about the results and with a comparison of them against other techniques. Finally, Sect. 4 presents the conclusions.

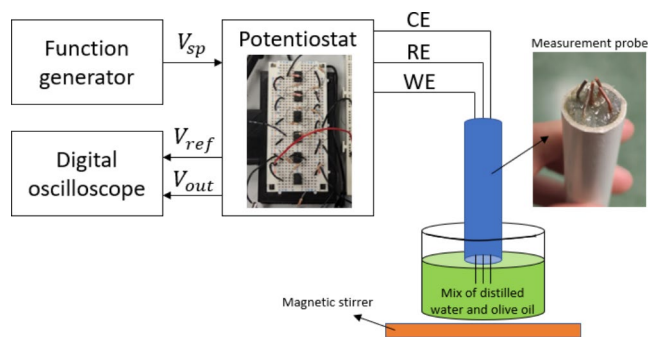


Fig. 1 Setup configured to carry out measurements according to the voltammetry technique where RE is the reference electrode, WE is the working electrode and CE is the counter electrode. V_{sp} is the analog voltage that the potentiostat must apply between the reference and working electrode, V_{ref} is the voltage applied to the sample and V_{out} is the voltage proportional to the current flowing through the working electrode

Materials and methods

Experimental setup

The measurement technology that has been used for experimentation with olive oil samples is the voltammetry technique. This technique is based on the application of a controlled voltage at the electrode-solution interface of a working electrode, so that the current flowing through this same electrode is measured. This current will vary with time depending on the waveform of the applied voltage and the reactions that take place in the electroactive species of the solution (Chesney 1996).

The setup for performing the voltammetric measurements consists of: a Tektronix TDS 2012B digital oscilloscope, an Aim-TTi TGA1241 function generator and a potentiostat that measures the electronic current, which circulates between the electrodes immersed in the solution formed by distilled water and olive oil (Fig. 1). The potentiostat design was made following the guidelines proposed in (Ramón et al. 2019; Shi et al., 2008; Yunus et al., 2011) research works. During the measurement process, the dilutions were mixed using a LBX Instruments brand magnetic stirrer, model S03D.

The measuring probe was made of PVC tube and filled with epoxy resin. Metallic filaments with a length equal to 10 cm and a section equal to 1 mm were placed inside it as electrodes. Copper was used as counter electrode and reference electrode and copper, silver and nickel were used as working electrodes, with purities equal to 99.98%, 99.99% and 99.99% respectively.

Fig. 2 Histograms showing the distribution of the intensity of the defect for the experimental olive oil samples. On the scale of values, the value 0 indicates that the defect is not present and 5 that the defect is very marked

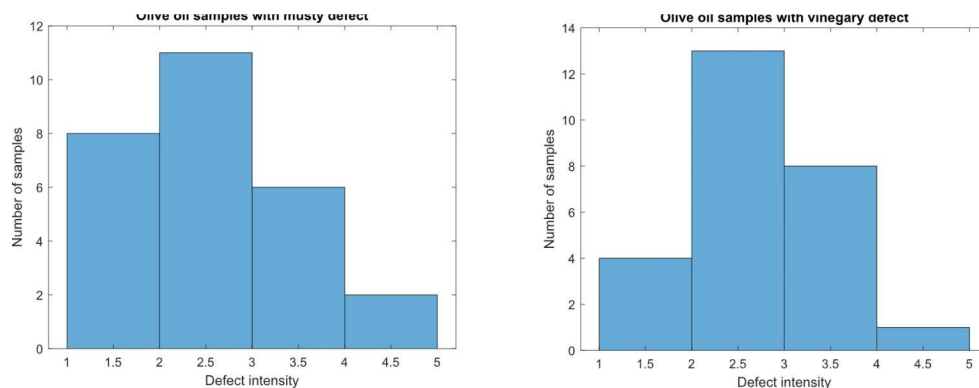
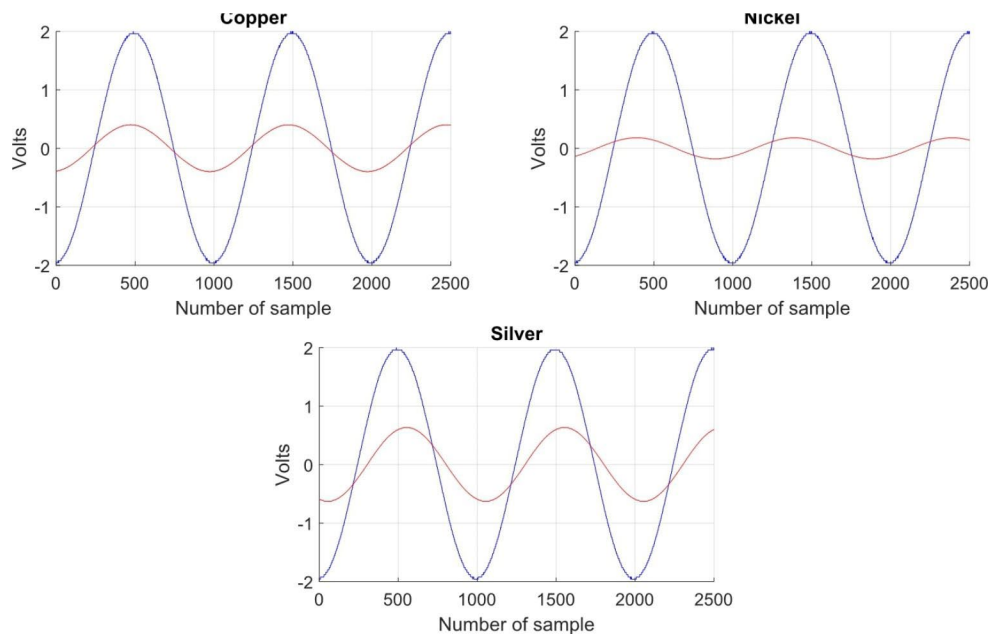


Fig. 3 Example of signals acquired for an olive oil sample and for each of the three metals used. The blue and red signals correspond to the reference and measured analog voltage respectively



Experimental olive oil samples

The olive oil samples used for the experimentation were obtained from olives of the *Picual* variety. These olives were harvested during the 2020/2021 season from different producers in the province of Jaén (Spain). The samples were organoleptically analyzed by the accredited Citoliva laboratory (www.citoliva.es), according to the international method described by the IOC in the document “Sensory analysis of olive oil: method for the organoleptic assessment of virgin olive oil” (COI/T.20/Doc. No 15/Rev. 10 2018). The method was carried out by a group of 8–10 expert tasters called panelists. As commented above, the process consists of smelling and tasting the oil and issuing an assessment according to the positive and negative sensations transmitted by the tested oil.

In total, 104 olive oil samples were analyzed, of which 51 did not present any defect, 26 presented a vinegary type defect and 27 presented a musty type defect. Not all defective samples showed the same defect intensity. On a scale

from 1 to 5, the averages of the intensity of the defects found were 2.7 ± 0.7 and 2.5 ± 0.8 for the vinegary and musty types, respectively. Figure 2 shows the distribution of the results obtained after the organoleptic determinations.

Data acquisition and feature extraction

The olive oil samples were mixed with distilled water in order to increase their electrical conductivity (Grossi et al., 2014, 2013). Water is not miscible with olive oil but is capable of extracting from it some minor polar components (sugar, phenolic compounds, short chain free fatty acid) (Boselli et al., 2007) and these minor components could be related to the organoleptic characteristics of the oil (Baccouri et al., 2020). In our case, each sample was prepared with 80 g of distilled water and 10 g of olive oil, using a precision analytical balance model AS 220.R2 PLUS.

To carry out the measurement, the probe was introduced into the dilution while the magnetic stirrer homogenized the sample rotating at 250 rpm. Next, a sinusoidal signal of 10

Khz and 4 Vpp was configured using the signal generator equipment (V_{sp}) and finally, the analog signal received by each of the three working electrodes was acquired: copper (V_{out}^{Cu}), silver (V_{out}^{Ag}) and nickel (V_{out}^{Ni}). This acquisition was made using a digital oscilloscope and the coupled noise was filtered using an average of 64 measurements.

Figure 3 shows the above-mentioned working signals. The procedure was carried out once for each sample. Analysing obtained signals for each electrode and sample two main properties have been selected as main characteristics: attenuation and the phase shift of the acquired signal. Hence, each sample is characterized by a vector with six characteristics, two per electrode, being them: attenuation (Vpp) and the phase shift of the acquired (Phase). Hereinafter these characteristics will be referred to as CuVpp, CuPhase, NiVpp, NiPhase, AgVpp and AgPhase.

Classification algorithms

From the vectors of characteristics associated with each olive oil sample, three classification algorithms were tested in order to evaluate the possibility of detecting in a rapid and non-invasive way the presence of organoleptic defects from the e-tongue response. The selected classifiers were the Vector Support Machine algorithm (SVM), decision trees and Naïve Bayes (NB). These classifiers have been successfully tested on characteristics extracted from olive oils from other non-invasive sensors (Martínez Gila et al., 2021; Ordukaya and Karlik 2017).

The Naïve Bayes classifier (Friedman et al., 1997) is a probabilistic classification method and is based on obtaining the probability of belonging to each class. In our problem, three classes are defined: oils without defect, oils with mouldy defect and oils with vinegary defect. Since the extracted characteristics from the e-tongue sensor are continuous variables and are normally distributed, the distribution of each class can be represented as a Gaussian probability density function in terms of its mean μ_c and standard deviation σ_c . In this way the probability of belonging of each sample to each class will be given by Eq. 1 and Eq. 2.

$$p(v_{n,sxf}|c) = g(v_{n,sxf}; \mu_c, \sigma_c), \text{ where} \tag{1}$$

$$g(v_{n,sxf}; \mu_c, \sigma_c) = \frac{1}{\sigma_c \sqrt{2\pi}} e^{-\frac{(v-\mu_c)^2}{2\sigma_c^2}} \tag{2}$$

where $g(v_{n,sxf}; \mu_c, \sigma_c)$ is the Gaussian probability density function. In addition, three kernel density estimators (Pérez et al., 2009) were evaluated: Gaussian, box, Epanechnikov, and triangle.

Real class	Predicted class by the model		
	Evaluated class	Other classes	Other classes
Evaluated class	TP	FN	
Other classes	FP	TN	

Fig. 4 Confusion matrix obtained for each evaluated class. TP is the number of true positives, FN is the number of false negatives, FP is the number of false positives, and TN is the number of true negatives

Decision trees (Loh, 2011) are supervised classification algorithms that use predictor variables (characteristics extracted from the response of the e-tongue) to build a tree topology. In each node of the tree a condition is evaluated and the result of the evaluation allows to evolve through a branch of the tree until the class is found at the end of each branch. Two split criteria were evaluated in order to build the classification: Gini’s diversity index (Caso and Gil, 1988) and maximum deviance reduction respectively (Breiman et al., n.d.). Finally, different number of splits were evaluated (from 1 to 63) in order to control the depth of the tree.

The last classifier was Support Vector Machines (SVM) (Cortes et al. 1995). The main idea is to find the hyperspace where our considered classes could be optimally separated. This approach is based on a decision boundary which can be described as a hyper-plane that is expressed in terms of a linear combination of functions parameterized by support vectors that give the best separating hyper-plane using a kernel function (Eq. 3 and Eq. 4).

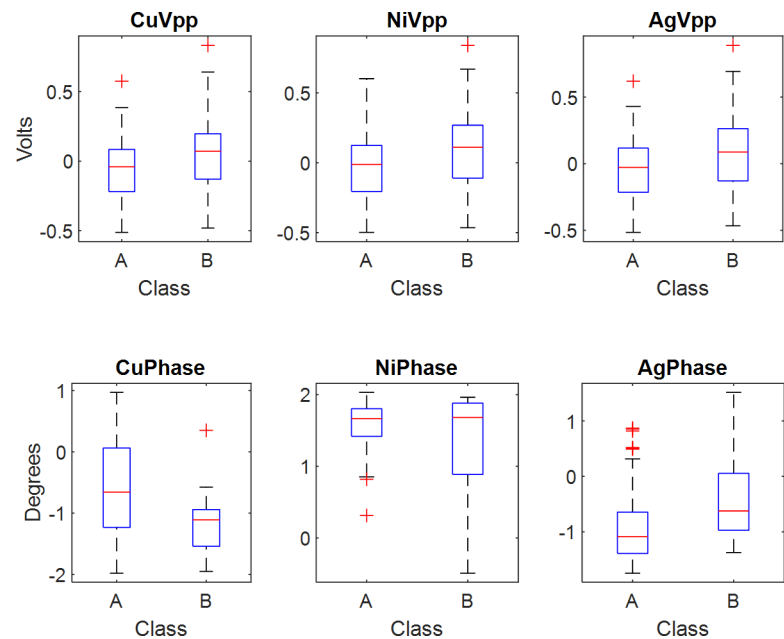
$$\min_{\gamma, C} \frac{1}{2} \gamma^2 + C \sum_{i=1}^N \xi_i \tag{3}$$

$$\text{subject to } \gamma (x_i^T \cdot w_0) \geq 1 - \xi_i \forall i \tag{4}$$

The methodology used to evaluate the performance of the aforementioned classifiers was 5-fold cross-validation. It consists of dividing the data randomly into 5 groups of approximately the same size, 4 groups are used to train the model and one of the groups is used as validation. This process is repeated 5 times using a different group as validation in each iteration. The process generates k estimates of the error, the average of which is used as the final estimate. The results will be evaluated based on a confusion matrix, as shown in Fig. 4.

The performance of the classification models was assessed in terms of true positive (TP) rate, false positive (FP) rate, precision, recall, F-measure, Matthews correlation coefficient (MCC), receiver operating characteristic (ROC) curve and precision-recall curve (PRC). The TP rate is the percentage of observations that have been assigned to an evaluated class when they truly belong to that class; the higher this value is, the better the result. The FP rate is

Fig. 5 Distribution of the characteristics extracted from the response of the electronic tongue for the different metals contained in the measurement probe, where classes A and B represent no defective and musty olive oils respectively



the percentage of observations that have been assigned to a certain class when they do not truly belong to that class; the lower this value is, the better the result. The precision is the ratio of correctly predicted positive observations to the total number of predicted positive observations (Eq. 5); the recall is the ratio of correctly predicted positive observations to all the observations in the evaluated class (Eq. 6). The F-Measure is the weighted average of the precision and recall (Eq. 7). The MCC is a measure of the classification quality. It returns a value between -1 and 1 , where 1 represents a perfect prediction (Eq. 8).

$$Precision = \frac{TP}{TP + FP} \quad (5)$$

$$Recall = \frac{TP}{TP + FN} \quad (6)$$

$$F - Measure = \frac{2 \times (Recall \times Precision)}{Recall + Precision} \quad (7)$$

$$MCC = \frac{TP \times TN - FP \times FN}{\sqrt{(TP + FP) \times (TP + FN) \times (TN + FP) \times (TN + FN)}} \quad (8)$$

RESULTS AND DISCUSSION

The machine learning process was performed with the array of features extracted from the e-tongue response, according to [Materials and Methods](#) section. As commented above, these features were analysed by the tree different algorithm (Decision Trees, Naïve Bayes, Support Vector Machine)

and two different binary classification methods were independently evaluated.

For the first binary classification method, two classes were defined: class A and class B. The olive oil samples that were assigned to class A were those that did not present any defect during the sensory analysis phase carried out by the experts. On the other hand, to class B oils classified as defective were assigned, in which the majority defect was the sensation of mould.

For the second binary classification method, a new category was defined, class C. To this class the olive oil samples with a vinegary defect were assigned.

Following sub-sections presents the results of both binary classification methods, their limitations and a comparison of those results against the obtained in other research works where use other technology.

Results for the Binary classification I

Firstly, the ANOVA test was applied to evaluate the differences between the characteristics extracted from the oils of each of the two classes (Class A and Class B). The results of ANOVA test denote that the characteristic with the highest discriminatory power was CuPhase with an F statistic of 6.48 and p-value of 0.01, followed by NiVpp (6,36–0,01), CuVpp (3,79–0,05), AgPhase (2,83–0,09), NiPhase (1,68–0,19) and AgVpp (0,35–0,55). Figure 5 shows the distribution of the characteristics extracted from the e-tongue signals obtained with the different metals used in the measurement probe. While CuPhase groups classes better, it can be observed that the mean of the distribution is approximately the same for the two classes compared.

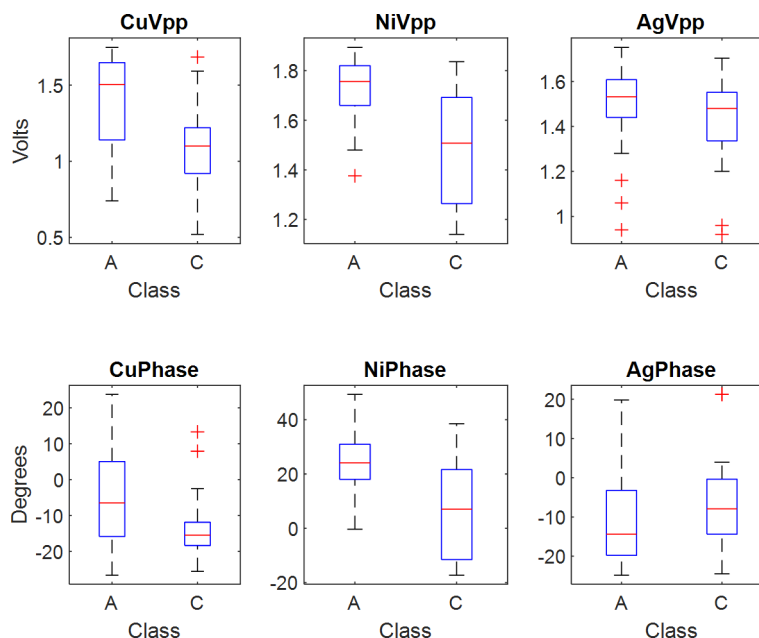
Table 1 Classification results for the Binary Classification I

SVM							
Features	Class	TP	FP	Precision	Recall	F-measure	MCC
CuPhase	A	42	22	0,66	1,00	0,79	-
	B	0	0	0,00	0,00	-	-
	Average			0,33	0,50	-	-
CuPhase + NiVpp	A	41	19	0,68	0,98	0,80	0,22
	B	3	1	0,75	0,14	0,23	0,16
	Average			0,72	0,56	0,52	0,19
CuPhase + NiVpp + CuVpp	A	41	19	0,68	0,98	0,80	0,22
	B	3	1	0,75	0,14	0,23	0,16
	Average			0,72	0,56	0,52	0,19
CuPhase + NiVpp + CuVpp + AgPhase	A	31	11	0,74	0,74	0,74	0,24
	B	11	11	0,50	0,50	0,50	0,17
	Average			0,62	0,62	0,62	0,21
CuPhase + NiVpp + CuVpp + AgPhase + NiPhase	A	33	10	0,77	0,79	0,78	0,32
	B	12	9	0,57	0,55	0,56	0,23
	Average			0,67	0,67	0,67	0,28
CuPhase + NiVpp + CuVpp + AgPhase + NiPhase + AgVpp	A	36	14	0,72	0,86	0,78	0,25
	B	8	6	0,57	0,36	0,44	0,18
	Average			0,65	0,61	0,61	0,21
TREES							
Features	Class	TP	FP	Precision	Recall	F-measure	MCC
CuPhase	A	38	20	0,66	0,90	0,76	-0,01
	B	2	4	0,33	0,09	0,14	-0,01
	Average			0,49	0,50	0,45	-0,01
CuPhase + NiVpp	A	33	14	0,70	0,79	0,74	0,16
	B	8	9	0,47	0,36	0,41	0,12
	Average			0,59	0,57	0,58	0,14
CuPhase + NiVpp + CuVpp	A	27	8	0,77	0,64	0,70	0,27
	B	14	15	0,48	0,64	0,55	0,20
	Average			0,63	0,64	0,63	0,23
CuPhase + NiVpp + CuVpp + AgPhase	A	34	12	0,74	0,81	0,77	0,27
	B	10	8	0,56	0,45	0,50	0,20
	Average			0,65	0,63	0,64	0,23
CuPhase + NiVpp + CuVpp + AgPhase + NiPhase	A	34	8	0,81	0,81	0,81	0,42
	B	14	8	0,64	0,64	0,64	0,30
	Average			0,72	0,72	0,72	0,36
CuPhase + NiVpp + CuVpp + AgPhase + NiPhase + AgVpp	A	30	9	0,77	0,71	0,74	0,29
	B	13	12	0,52	0,59	0,55	0,21
	Average			0,64	0,65	0,65	0,25
NB							
Features	Class	TP	FP	Precision	Recall	F-measure	MCC
CuPhase	A	29	9	0,76	0,69	0,73	0,27
	B	13	13	0,50	0,59	0,54	0,20
	Average			0,63	0,64	0,63	0,23
CuPhase + NiVpp	A	34	14	0,71	0,81	0,76	0,19
	B	8	8	0,50	0,36	0,42	0,14
	Average			0,60	0,59	0,59	0,16
CuPhase + NiVpp + CuVpp	A	31	9	0,78	0,74	0,76	0,32
	B	13	11	0,54	0,59	0,57	0,23
	Average			0,66	0,66	0,66	0,27
CuPhase + NiVpp + CuVpp + AgPhase	A	32	8	0,80	0,76	0,78	0,37
	B	14	10	0,58	0,64	0,61	0,27
	Average			0,69	0,70	0,69	0,32

Table 1 (continued)

SVM							
CuPhase + NiVpp + CuVpp + AgPhase + NiPhase	A	34	11	0,76	0,81	0,78	0,31
	B	11	8	0,58	0,50	0,54	0,22
	Average			0,67	0,65	0,66	0,27
CuPhase + NiVpp + CuVpp + AgPhase + NiPhase + AgVpp	A	31	11	0,74	0,74	0,74	0,24
	B	11	11	0,50	0,50	0,50	0,17
	Average			0,62	0,62	0,62	0,21

Fig. 6 Distribution of the characteristics extracted from the response of the electronic tongue for the different metals contained in the measurement probe, where classes A and C represent no defective and vinegary olive oils respectively



In each box, the centre mark indicates the median, and the lower and upper ends of the box indicate the 25th and 75th percentiles, respectively. Whiskers extend to the most extreme data points that are not considered outliers, and outliers are represented individually by the '+' symbol.

Results for the Binary Classification I are presented in Table 1. It shows the information provided by each of the six characteristics when they are used in the classification algorithms. For the three classifiers evaluated, it can be seen how the success rate is low when only the most discriminating features (CuPhase) is used (mean precision below 50%). On the other hand, when the five most discriminating characteristics are considered, the success rate is increased until reaching an average precision of 72% with the decision tree. When adding the least discriminating characteristic, AgVpp, to the vector of characteristics, the results did not improve. This algorithm was configured with a maximum number of split equal to 15 and using a split criterion based on the maximum deviance reduction (Ritschard 2007). In this case 34 and 14 oil samples with and without defect were respectively well classified and 8 misclassified.

Results for the Binary classification II

For this binary classification approach, a first ANOVA analysis was also carried out in order to identify the most discriminating characteristics between the classes evaluated (Class A and Class C). The results of this analysis have been graphed in the Fig. 6, where class A represents the distribution of the extracted characteristics for oils without defects and class C represents the distribution of the same characteristics for oils with vinegary defects. In this case, it can be seen that the differences between the medians of the different classes were greater than those obtained in the binary classification I. Specifically, the characteristic that presented the greatest differences was related to the nickel metal, NiVpp, with an F statistic of 29.18 and a p-value lower than 0.001. The following characteristics that provide more information when it comes to discriminating between classes were, in order, NiPhase (23.15–0.001), CuVpp (14,20–0.001), CuPhase (8,07–0.01), AgVpp (3,39–0.07) and AgPhase (2,17–0.14).

Table 2 shows the results obtained with the different classifiers evaluated for this Binary Classification II. In this case the best result for the SVM classifier with an average precision of 84%, the precision for class C being 93%.

Table 2 Classification results for the Binary Classification II

SVM							
Features	Class	TP	FP	Precision	Recall	F-measure	MCC
CuVpp	A	39	13	0,75	0,93	0,83	0,44
	C	13	3	0,81	0,50	0,62	0,35
	Average			0,78	0,71	0,72	0,39
CuVpp + CuPhase	A	39	13	0,75	0,93	0,83	0,44
	C	13	3	0,81	0,50	0,62	0,35
	Average			0,78	0,71	0,72	0,39
CuVpp + CuPhase + NiVpp	A	39	13	0,75	0,93	0,83	0,44
	C	13	3	0,81	0,50	0,62	0,35
	Average			0,78	0,71	0,72	0,39
CuVpp + CuPhase + NiVpp + NiPhase	A	41	15	0,73	0,98	0,84	0,46
	C	11	1	0,92	0,42	0,58	0,36
	Average			0,82	0,70	0,71	0,41
CuVpp + CuPhase + NiVpp + NiPhase + AgVpp	A	41	13	0,76	0,98	0,85	0,50
	C	13	1	0,93	0,50	0,65	0,40
	Average			0,84	0,74	0,75	0,45
CuVpp + CuPhase + NiVpp + NiPhase + AgVpp + AgPhase	A	41	17	0,71	0,98	0,82	0,41
	C	9	1	0,90	0,35	0,50	0,32
	Average			0,80	0,66	0,66	0,36
TREES							
Features	Class	TP	FP	Precision	Recall	F-measure	MCC
CuVpp	A	36	14	0,72	0,86	0,78	0,33
	C	12	6	0,67	0,46	0,55	0,26
	Average			0,69	0,66	0,66	0,29
CuVpp + CuPhase	A	37	14	0,73	0,88	0,80	0,36
	C	12	5	0,71	0,46	0,56	0,28
	Average			0,72	0,67	0,68	0,32
CuVpp + CuPhase + NiVpp	A	39	15	0,72	0,93	0,81	0,39
	C	11	3	0,79	0,42	0,55	0,30
	Average			0,75	0,68	0,68	0,35
CuVpp + CuPhase + NiVpp + NiPhase	A	30	7	0,81	0,71	0,76	0,40
	C	19	12	0,61	0,73	0,67	0,32
	Average			0,71	0,72	0,71	0,36
CuVpp + CuPhase + NiVpp + NiPhase + AgVpp	A	36	15	0,71	0,86	0,77	0,30
	C	11	6	0,65	0,42	0,51	0,23
	Average			0,68	0,64	0,64	0,27
CuVpp + CuPhase + NiVpp + NiPhase + AgVpp + AgPhase	A	40	17	0,70	0,95	0,81	0,36
	C	9	2	0,82	0,35	0,49	0,29
	Average			0,76	0,65	0,65	0,33
NB							
Features	Class	TP	FP	Precision	Recall	F-measure	MCC
CuVpp	A	38	11	0,78	0,90	0,84	0,46
	C	15	4	0,79	0,58	0,67	0,37
	Average			0,78	0,74	0,75	0,41
CuVpp + CuPhase	A	38	12	0,76	0,90	0,83	0,44
	C	14	4	0,78	0,54	0,64	0,35
	Average			0,77	0,72	0,73	0,39
CuVpp + CuPhase + NiVpp	A	35	11	0,76	0,83	0,80	0,39
	C	15	7	0,68	0,58	0,63	0,31
	Average			0,72	0,71	0,71	0,35
CuVpp + CuPhase + NiVpp + NiPhase	A	34	9	0,79	0,81	0,80	0,42
	C	17	8	0,68	0,65	0,67	0,33
	Average			0,74	0,73	0,73	0,38

Table 2 (continued)

SVM							
CuVpp + CuPhase + NiVpp + NiPhase + AgVpp	A	30	10	0,75	0,71	0,73	0,31
	C	16	12	0,57	0,62	0,59	0,24
			Average	0,66	0,66	0,66	0,28
CuVpp + CuPhase + NiVpp + NiPhase + AgVpp + AgPhase	A	32	8	0,80	0,76	0,78	0,41
	C	18	10	0,64	0,69	0,67	0,32
			Average	0,72	0,73	0,72	0,37

Discussion of the obtained results

The predictive classification was higher in the binary classification methods that works with Class A and Class C. This improvement in prediction may be due to the fact that the number of samples with low intensity of vinegary defect was lower than the number of samples with the same intensity of musty defect.

Based on the results obtained, integrating the sensor into the virgin olive oil production process could be evaluated to quickly detect the presence of the vinegary defect and prevent it from being mixed in the cellar with flawless oils. The authors obtained similar results in (Velooso et al., 2018), in which the experiments were carried out with another e-tongue technology (lipid membrane sensor). They demonstrated the feasibility of applying a potentiometric e-tongue (with lipid cross-sensitivity polymeric membranes) in combination with chemometric tools, for the successful discrimination of olive oils with negative organoleptic attributes (fusty, rancid, wet-wood and winey-vinegary). They reach an average correct class prediction of 92%. However, from authors point of view, the meticulous preparation of the oil samples and the reduced useful life of the sensors would make it difficult to integrate them into the production process.

The greatest limitation of the method proposed relies on the sensitivity of the sensor to discriminate samples that do not have a marked defect. In particular, the proposed e-tongue does not identify defects which have intensity value less than 2 according to IOC. In Fig. 2, it could be seen the number of samples with a low intensity (<2) for musty and vinegary defects. There are 8 and 4 samples with this defect values respectively, which are the number of badly classified samples. Based on the results, the sensor could be used in the process line to detect the defect when it is present with a medium-high intensity level. The accuracy is significantly lower than that obtained in (Lerma-García et al., 2010). In this work, the authors used an electronic nose to detect the musty defect, reaching 85% of correctly classified samples. However, in this work the samples used were sunflower oil, they were artificially created and the time used to carry out each measurement was around 10 min. Similar results were achieved in (Marchal et al., 2021) although

these were obtained using a different technology based on gas detection through metal oxide sensors. In this case, the authors obtained a success rate of 88% when classifying oil samples with defects among oil samples without defects. In this case they did not consider the type of defect. Other authors (Teixeira et al., 2021) also used gas sensors for extra virgin olive oils commercial classification according to the perceived fruitiness intensity with a success rate of 97%. Instead they did not use oils with defects.

Conclusion

In this study, the use of a voltammetric electronic tongue for the identification of organoleptic defects on olive oil samples has been evaluated. To increase the conductivity of the oil samples, they were mixed with distilled water and the measurement was carried out using three working electrodes: nickel, silver and copper. Three classification algorithms (Support Vector Machines, Naïve Bayes and Classification Trees) were tested to evaluate the differences between the features extracted from the analog signals of each electrode. When discerning between non-defective olive oil samples and samples with musty-type defects, the best result was obtained with the classification tree algorithm, obtaining an average success rate of 72%. In this case it was necessary to use the signals acquired by all the electrodes (CuPhase + NiVpp + CuVpp + AgPhase + NiPhase) and only 8 samples per class were misclassified. In general, better results were obtained when detecting the vinegary type defect. In this case, using the vector support machine algorithm, the success rate was 84% and only one defective sample was misclassified. The most discriminating metal being nickel with its NiPhase characteristic, although it was also necessary to use all the metals. In both cases, the validation method used was 5-fold cross validation.

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