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Evaluation the effect of extracted time conditions on the phenolic content of olive pastes from *cv.* Arbequina and discrimination using a lab-made potentiometric electronic tongue

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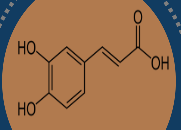
INTRODUCTION

Malaxation time

Olive paste

Extraction process

Olive Oil



Total Phenolic Content

Quality can be enhanced

Optimization of technological process could improve the quality of olive oils

Traditional tecniques of analysis

Determination of Total Phenolic Content

Limitations

- **Need for technicians**
- **High cost of equipment and reagents**
- **Time-consuming**
- **Difficult implementation in production lines**

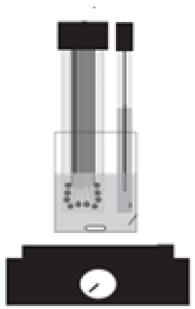
WORK OBJECTIVES

- Infer about the best malaxation time of olive pastes to obtain extra virgin olive oil with the highest total phenolic content (TPC);

- Assess the use of the E-tongue as a single-run, fast and cost-effective analytical device to estimate total phenolic content in olive pastes during the oil extraction process

This capability could provide indirectly correlations with the malaxation time effect on the TPC of the *cv.* Arbequina oils industrially extracted

Malaxation process



Potentiometric lab-made E-tongue was applied to evaluate *cv.* Arbequina pastes malaxed during different times (0, 15, 30, 45 and 60 minutes)

Electronic tongue

Complementary analytical device to conventional techniques of analysis in order to meet the needs of the olive oil industry

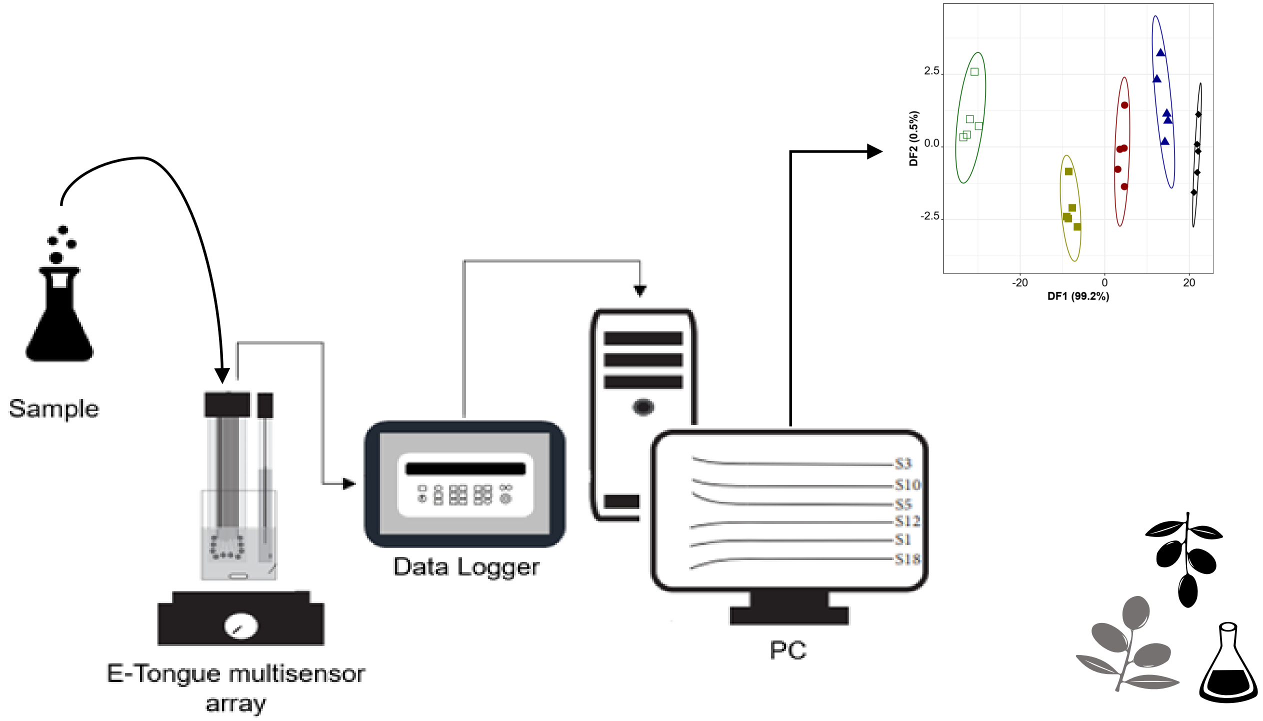
E-tongue

- ☑ Quick analysis tool
- ☑ Green technology
- ☑ Economic analytical device

Working principle

Potentiometric lab-made electronic tongue (E-tongue) comprising 40 non-specific lipid polymeric sensor membranes

Sensors	• Compounds interact with the sensor membranes included in the device. • Electrical properties change leading to diferences in sensing signal.
Data Logger	• Electrical signals are transferred to the signal processing unit.
PC	• Electrical signals are converted to an electrochemical signals and processed using chemometric tools.



E-tongue: Olive oil applications

- Assess geographic origin
- Olive cultivar recognition
- Monitoring quality and oxidative stability during storage
- Assess oil shelf-life
- Determine the intensity of the bitter sensation
- Assess physicochemical and sensory parameters

- **Physicochemical and sensory simultaneous assessment of olive oils**

Rodrigues *et al.*, 2019 https://doi.org/10.1016/j.talanta.2019.01.055

- **Perception of olive oil sensory defects**

Veloso *et al.*, 2018 https://doi.org/10.1016/j.talanta.2017.08.066

- **Unmasking EVOO defects**

Harzalli *et al.*, 2018 https://doi.org/10.1016/j.compag.2017.12.016

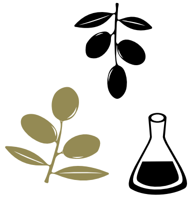
- **Discrimination olive oil samples by cultivar and geographical origin**

Slim et al., 2017 https://doi.org/ 10.1007/s00217-017-2856-8

Souayah *et al*,. 2017 https://doi.org/10.1007/s11746-017-3051-6

- **Effect of malaxation temperature on the physicochemical and sensory quality**
- **of *cv.* Cobrançosa olive oil and its evaluation using an electronic tongue**

Marx et al., 2021a https://doi.org/10.1016/j.lwt.2020.110426



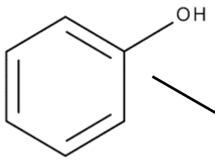
More recently

Estimating hydroxytyrosol-tyrosol derivatives amounts in *cv.* Cobrançosa olive oils based on the electronic tongue analysis of olive paste extracts

- **Estimating hydroxytyrosol-tyrosol derivatives amounts in *cv.* Cobrançosa olive oils based on the electronic tongue analysis of olive paste extracts**

Marx et al., 2021b https://doi.org/10.1016/j.lwt.2021.111542

Phenolic compounds in olive pastes



Hydroxybenzene
(Phenol)

Biological activity
Anti-inflammatory
Antioxidant

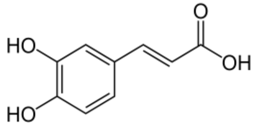
Phenolic compounds

Structure

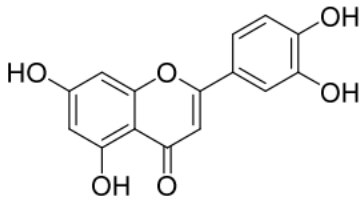
- Aromatic ring with one (or more) hydroxyl group
- Simple molecules (low molecular weight)
- Complex polymers (high molecular weight)

High importance in antioxidant activity

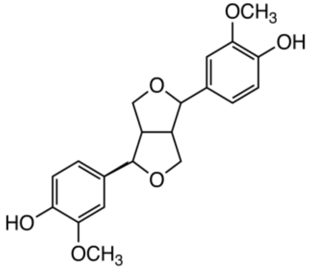
Examples



Phenolic acid



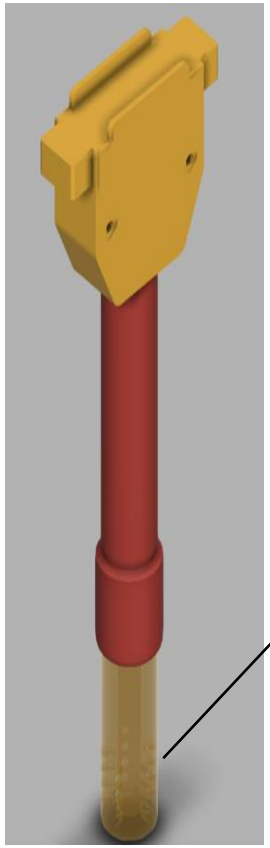
Flavonoid



Lignan

An antioxidant's activity is determined by its reactivity as proton or electron donating agent

Potentiometric determination of phenolic compounds in olive pastes



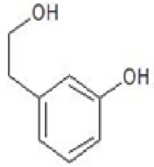
Membrane composition: Lipid additives + Plasticizer additives

Lipid-polymeric membranes

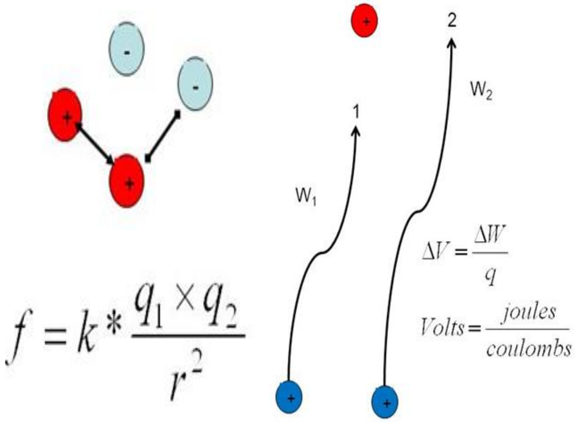
Negative and positive polarity

Polar and nonpolar regions

Tyrosol molecule
(phenolic alcohol)



Electrostatic interactions
Coulomb's Law



MATERIALS AND METHODS

Olive pastes collection

Olive → Leaf removal and olive washing → Milling → **Malaxation**

T0
T15
T30
T45
T60

Cv. Arbequina olive pastes collected in Trás-os-Montes region – Portugal.

Traditional tecnique of analysis

Total phenols content

- Spectrophotometric Analysis
  (g GAE / Kg olive paste)
  Folin-Ciocalteu method

Method proposed by Singleton and Rossi (1965)

Potentiometric determination of phenolic compounds in olive oils

1. Olive pastes polar phenol extraction

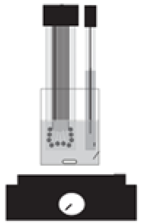
Olive pastes

- First extraction: *n*- Hexane
- Then, aqueous methanolic solution ($MeOH/H_2O$ 80:20 v/v)
- Centrifugation and polar fraction separation

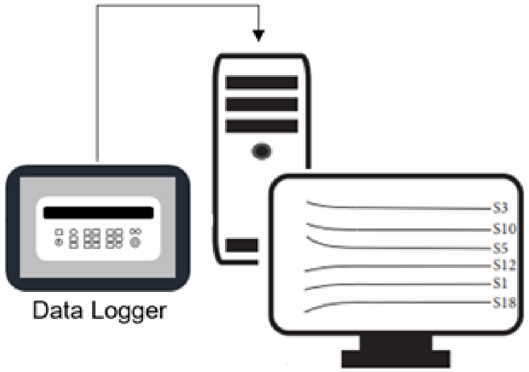
2. Potentiometric analysis

5 min of analysis

Polar phenol extract



E-tongue multisensor array



3. Data treatment - Chemometric tools

Linear discriminant analysis (LDA) to evaluate the correct discrimination olive pastes based on the best subsets of E-tongue sensors selected using the simulated annealing (SA) algorithm.

Leave-one-out cross-validation (LOO-CV) variant to evaluate the predictive performance of the classification model and the repeated K-fold-CV.

Linear discriminant analysis was established:

- **Potentiometric profiles recorded by the 40 E-tongue sensors**

RESULTS AND DISCUSSION

Evaluation of the TPC of olive pastes

Table 1: Total Phenolic Content (mean ± standard deviation) of *cv.* Arbequina olive pastes industrially collected at different malaxation times (0, 15, 30, 45 and 60 minutes).

Parameter	T0	T15	T30	T45	T60	P-value	R-Pearson
Total phenolic content (TPC, g GAE/kg olive oil)	**2.21±0.019^{A}**	**2.18±0.016^{A}**	**2.17±0.040^{A}**	**2.04±0.027^{B}**	**1.99±0.029^{B}**	**<0.0001**	**-0.910**

P-values for the one-way ANOVA.
R-Pearson coefficients: between each parameter and the malaxation time
Means (n = 5) in the same line with the same uppercase letter are not significantly different from a statistical point of view according to the Test of Tukey, at a significance level of 0.05

TPC: significant differences according to the malaxation time

RESULTS AND DISCUSSION

Estimating TPC concentration of olive pastes based on the potentiometric E-tongue analysis of olive paste extracts

CORRELATION

TPC concentration (g GAE/Kg olive paste) and potentiometric signals from E-tongue

$0.836 \geq R^2 \leq 0.998$

SENSITIVITY

Log of TPC concentration (g GAE/Kg olive paste) and potentiometric signals from E-tongue

+0.0037 to +0.376 mV/decade
−0.185 to −0.042 mV/decade

E-TONGUE

Could be applied to contribute to the industrial decision of the best malaxation time of olive pastes to obtaining an olive oil with a high content of phenolic compounds

RESULTS AND DISCUSSION

Discriminating olive pastes according malaxation time

E-tongue-LDA-SA model

11 sensors

S1:1, S1:8, S1:14, S1:17, S1:18, S1:20; S2:2, S2:3, S2:4, S2:5 and S2:18

Correct discrimination of all the olive pastes according to the malaxation time (sensitivities of 100% for training and leave-one-out cross-validation) and 91±12% for repeated K-fold-CV.

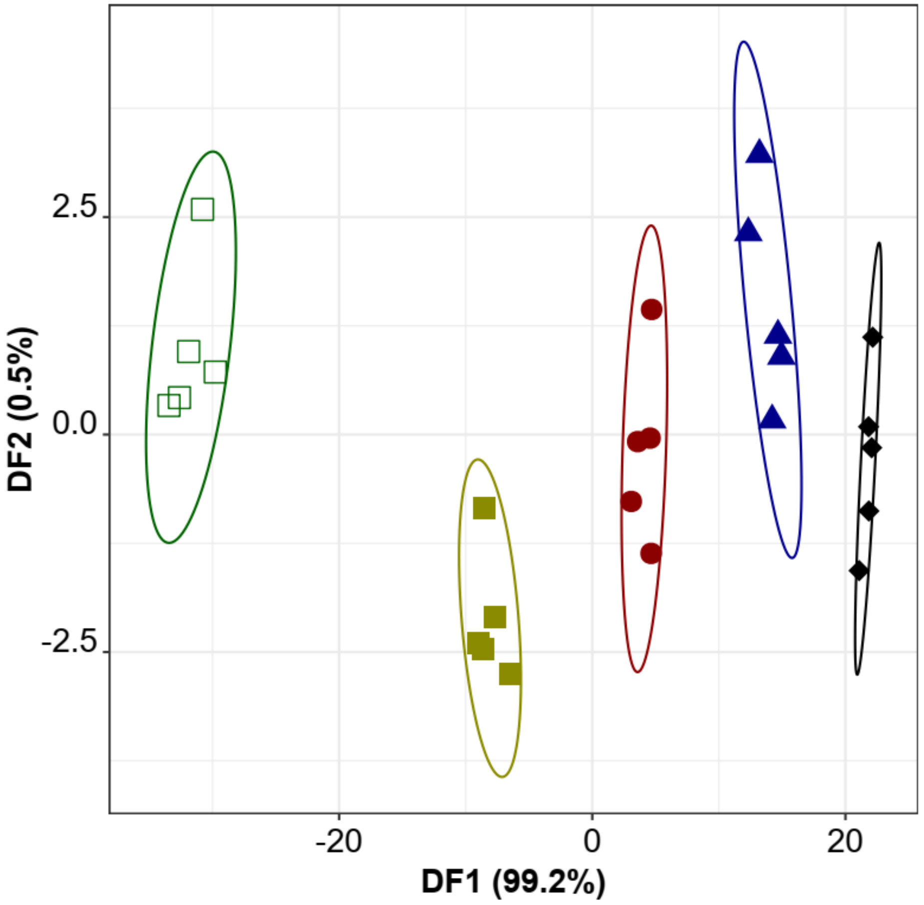


Fig. 1 LDA-SA model performance regarding the supervising classification of *cv.* Arbequina olive pastes extracted at 0 min (T0 □); 15 min (T15 ■); 30 min (T30 •); 45 min (T45▲) and 60 min (T60 ♦) based on the potentiometric signals gathered by eleven E-tongue lipid sensor membranes (1st array: S1:1, S1:8, S1:14, S1:17, S1:18, S1:20; 2nd array: S2:2, S2:3, S2:4, S2:5 and S2:18), selected using the SA algorithm from a set of 40 sensors.

CONCLUSIONS

- ✓ Malaxation time of 0, 15 and 30 minutes did not show significant changes in TPC concentration;
- ✓ After 45 minutes of malaxation, the TPC concentration of was significantly reduced.

The E-tongue could be applied for:

Estimating TPC concentration in olive pastes

↓

This findings can contribute to the industrial decision of the best malaxation time of olive pastes to obtaining an olive oil with a high content of phenolic compounds

TOTAL PHENOLIC CONTENT
↓
SHELF-LIFE RELATED PARAMETER

E-tongue

Complementary to conventional analytical techniques, acting as:

➢ **Quality control and monitoring tool for the olive oil industry.**

Future perspectives

Scenario for the next years ...

Dissemination of the E-tongue system:

- Closer approximation of devices with consumers / industry
- Development of user-friendly portable interfaces

Technology based on high precision sensors, quick analysis, customized according to the client's application.

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THANK YOU FOR YOUR ATTENTION!

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LAQV requimte LABORATÓRIO ASSOCIADO PARA A QUÍMICA VERDE

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