



**XXI Encontro  
Sociedade Portuguesa  
de Eletroquímica**

**XVIII Encontro  
Ibérico  
de Eletroquímica**

**XXI Meeting of the Portuguese Electrochemistry Society  
&  
XVIII Iberian Electrochemistry Meeting  
Abstract Book**

**XXI Encontro da Sociedade Portuguesa de Eletroquímica  
&  
XVIII Encontro Ibérico de Eletroquímica  
Livro de Resumos**

**Bragança, Portugal ◀ 14-17 setembro 2016**



## Title

XXI Meeting of the Portuguese Electrochemistry Society &  
XVIII Iberian Electrochemistry Meeting

## Título

XXI Encontro da Sociedade Portuguesa de Eletroquímica &  
XVIII Encontro Ibérico de Eletroquímica

## Event Abbreviation / Abreviatura do Evento

SPE2016

## Coordination / Coordenação

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## Edition / Edição

Instituto Politécnico de Bragança · 2016  
5300-253 Bragança · Portugal  
Tel. (+351) 273 303 200 · Fax (+351) 273 325 405  
<http://www.ipb.pt>

## Imaging services / Serviços de imagem

Atilano Suarez (Instituto Politécnico de Bragança, Portugal)

## URI

<http://hdl.handle.net/10198/12931>

## ISBN

978-972-745-213-2



## PC13

### Qualitative evaluation of Tunisian olive oils using an electronic tongue and chemometric tools: a prospective study.

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Olive oil commercialization has a great impact in the regional economy of several countries including Tunisia. It is a high-value food product, quite prone to frauds. So, it is important to establish analytical techniques that can ensure labeling correctness regarding olive oil quality as well as its origin, namely concerning the olive(s) cultivar(s) used in the production, which is of major importance for monovarietal olive oils. Traditional analytical techniques like those based on chromatography are quite expensive, time-consuming, not portable and difficult to implement in-situ, considering the usual harsh environments of the olive industry. In this work, the feasibility of using an electronic tongue as a classification tool for discriminating Tunisian olive oils according to their quality level (i.e., extra virgin olive oil, virgin olive oil or lampante olive oil) and olive cultivar (i.e., Chetoui, Shali and others, according to the label information) was evaluated for the first time. Olive oil quality was assessed quality parameters (free acidity, peroxide values,  $K_{232}$  and  $K_{270}$  extinction coefficients) and on the organoleptic evaluation carried out by a sensory panel parameters (according to the International Olive Council directives). The potentiometric signal profiles recorded with the electrochemical multi-sensor device during the electrochemical analysis of olive oils' hydroethanolic extracts ( $\approx 5$  min), coupled with linear discriminant models, established based on the most informative sub-sets of sensors, selected by a simulated annealing algorithm, were able to satisfactorily perform olive oils discrimination according to:

- (i) Olive cultivar: sensitivities of 88% for leave-one-out cross-validation and mean sensitivities of 79% for the repeated K-folds cross-validation (4 folds with 10 repeats), achieved with a multivariate model based on the information gathered by 20 sensors of the electronic tongue; and,
- (ii) Quality level: sensitivities of 91% for leave-one-out cross-validation and mean sensitivities of 84% for the repeated K-folds cross-validation (4 folds with 10 repeats), achieved with a multivariate model based on the information gathered by 26 sensors of the electronic tongue.

Overall, the results show the satisfactory performance of a potentiometric electronic tongue containing cross-sensitivity lipid membranes as sensors, which may be tentatively attributed to the capacity of the electrochemical device in discriminating olive oils with different polar compounds contents, which are related to specific sensory attributes of olive oils such as bitterness and pungency. Furthermore, the present study, concerning Tunisian olive oils analysis using an electronic tongue, confirms the results previously reported in the literature for olive oils from other geographical origins.

# QUALITATIVE EVALUATION OF TUNISIAN OLIVE OILS USING AN ELECTRONIC TONGUE AND CHEMOMETRIC TOOLS: A PROSPECTIVE STUDY

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## INTRODUCTION

- ✓ Olive oil commercialization has a great impact in the regional economy of several countries including Tunisia.
- ✓ It is a high-value food product, quite prone to frauds.
- ✓ Traditional analytical techniques are quite expensive, time-consuming, not portable and difficult to implement in-situ, due to the harsh environments of the olive industry.
- ✓ In this work, the feasibility of using an electronic tongue as a classification tool for discriminating Tunisian olive oils

## ELECTRONIC TONGUE

Potentiometric system  
(all-solid-state electrodes)

20 lipidic polymeric membranes (**x2**)  
Ag/AgCl reference electrode  
Data acquisition with DataLogger Agilent

Each **lipidic polymeric membrane** contains:

32% of PVC;  
65% of plasticizer;  
3% of additive compound.

### Additive compound

- [1] Octadecylamine
- [2] Oleyl alcohol
- [3] Methyltriethylammonium chloride
- [4] Oleic acid

### Plasticizer

- [A] Bis(1-butylpentyl) adipate
- [B] Dibutyl sebacate
- [C] 2-Nitrophenyl-octylether
- [D] (2-ethylhexyl)phosphate
- [E] Dioctyl phenylphosphonate

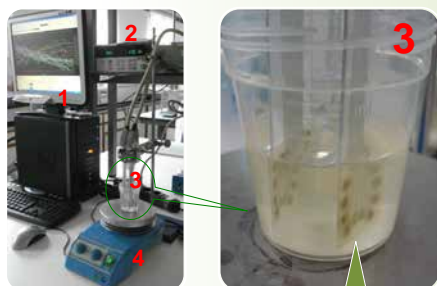


Figure 1 – Multi-sensor analytical system:

- 1 - PC for data acquisition;
- 2 - DataLogger Agilent;
- 3 - Electronic tongue;
- 4 - Magnetic stirrer.

Double multi-sensor system:  
40 sensors

## Electronic tongue analysis

### TUNISIAN OLIVE OILS

Quality: **EVOO (3); VOO (4) & LOO (36)**

(according to physico-chemical & sensory analysis)

Cultivar: **Chetoui cv. (11); Sahli cv. (26) & others cvs. (4)**

(according to the label information)

Extraction with H<sub>2</sub>O:EtOH (80:20 v/v),  
to obtain a polar compounds rich-solution

## OBJECTIVES

### ELECTRONIC TONGUE (multi-sensor system)

Chemical sensors with high stability and cross-sensitivity  
to different substances in solution

### TO OBTAIN

Olive oils' signals profiles corresponding to a  
*fingerprint* of sample matrix

### TO APPLY

Chemometric methods:

- Linear discriminant analysis (LDA)
- Simulated annealing (SA) variable selection algorithm
- Leave-one-out cross-validation (LOO-CV)
- Repeated K-folds-CV (repeated K-folds-CV)

### TO ALLOW

Olive oils' identification/classification according to:

- Olive oil quality (EVOO, VOO & LOO)
- Olive cultivar (Chetoui, Sahli & others)

## RESULTS

### Establishment of the best E-tongue-LDA-SA models:

→ variable selection with simulated annealing (SA) algorithm

→ sub-set with minimum number of sensors => maximum correct classification,

- LOO-CV

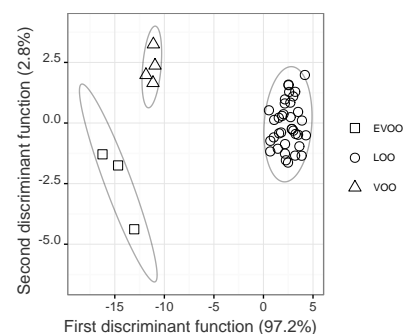
- repeated K-folds-CV: K=4 folds  $\left\{ \begin{array}{l} 75\% \text{ data for training} \\ 25\% \text{ data for internal validation} \end{array} \right\} \times 10 \text{ repeats}$

### i) Olive oils' quality discrimination: EVOO, VOO & LOO

→ model with 26 potentiometric sensor signals

→ 91% of predictive correct classifications for LOO-CV

→ 84% of predictive correct classifications for repeated K-folds-CV

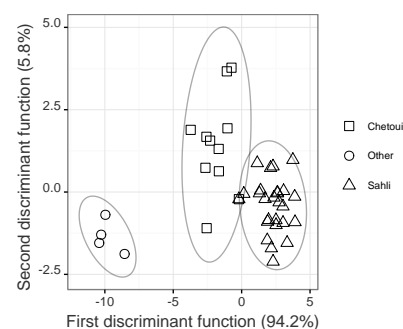


### ii) Olive oils' discrimination according to Tunisian cultivars: Chetoui, Sahli & others

→ model with 20 potentiometric sensor signals

→ 88% of predictive correct classifications for LOO-CV

→ 79% of predictive correct classifications for repeated K-folds-CV



## CONCLUSIONS

- The potentiometric E-tongue coupled with a LDA-SA procedure demonstrated to be a fast and cost-effective tool for :

→ **Tunisian olive oils' predictive classification according to olive cultivar.**

→ **Tunisian olive oils' predictive classification according to quality grade.**

- The overall results achieved confirmed the E-tongue potential for olive oil analysis, previously reported by our research group [1-6] as well as other research groups [7-12].

### Acknowledgements

This work was co-financed by Project POCI-01-0145-FEDER-006984 - Associated Laboratory LSRE-LCM funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), by national funds through FCT - Fundação para a Ciência e a Tecnologia; and by the strategic funding of UIDB/04469/2013 unit. Nuno Rodrigues thanks FCT, POPH-OREN and FSE for the Ph.D. Grant (SFRH/BD/104038/2014).

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