EMEC 10
CHEMISTRY TOWARDS AN INFINITE ENVIRONMENT

Electrochemical Taste Sensor for Unmasking Extra-Virgin Olive Oils Adulterated with Rancid or Winey-Vinegary Olive Oils

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INTRODUCTION

✓ Olive oils may be graded according to its overall physicochemical composition and sensorial attributes as extra-virgin (EVOOs), virgin (VOOs) or lampante olive oils (LOOs).

✓Olive oils are a food product quite prone to frauds, thus protection legal regulations have been implemented by the European Union Commission.

✓Unfortunately, the admixture of expensive olive oils with low quality oils aiming fraudulent economic revenue is still a common practice difficult to detect using the official methods.

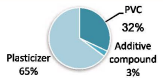
✓ In this work, it is evaluated, the performance of a lab-made potentiometric electronic tongue (**E-tongue**) for assessing **EVOOs adulterations** with olive oils for which intense **sensory defects** (**rancid** or **winey-vinegary, WV**) could be perceived by trained sensory panelists.

ELECTRONIC TONGUE (E-tongue)

Potenciometric array
(all-solid-state electrodes)

20 lipidic polymeric membranes (**×2**)
Ag/AgCl reference electrode
Data acquisition with DataLogger Agilent

Each **lipidic polymeric membrane contains**:



Additive compound
[1] Octadecylamine
[2] Oleyl alcohol
[3] Methyltrioctylammonium chloride
[4] Oleic acid

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

Electronic Tongue Analysis

OLIVE OILS

Physicochemical Analysis
Free Acidity, Peroxide Value, UV-Vis Extinction Coefficients (K_{232}, K_{270}, ΔK)

Sensory Analysis
(trained panelists)

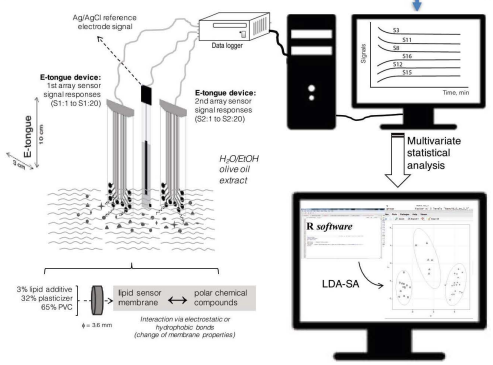
E-tongue
Potentiometric analysis of hydroethanolic extracts (H_2O:EtOH (80:20, v/v)

QUALITY GRADE CLASSIFICATION:

Unadulterated olive oils → EVOOs
2.5% up to 10% adulteration (rancid or WV) → VOOs
≥ 20% adulteration (rancid or WV) → LOOs

SENSORY ANALYSIS

Trained panelists were not able to assess low adulteration levels (≤ 5% of rancid or WV admixing)



AIMS

ELECTRONIC TONGUE

↓

Comprising

Chemical sensors → high stability and cross-sensitivity to different polar substances

↓

To obtain

Olive oils potentiometric profiles → **unique *fingerprint*** *unadulterated and intentionally adulterated olive oils*

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To analyze with

Chemometric methods:
- Linear discriminant analysis (LDA)
- Simulated annealing (SA) variable selection algorithm
- Leave-one-out cross-validation (LOO-CV)

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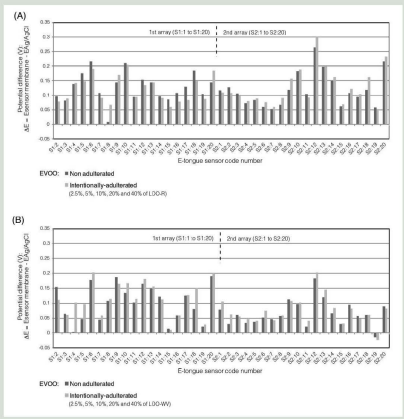
To achieve

Successful adulteration detection predictive rates of EVOOs with intense rancid or WV sensory defects for a **repeated K-fold-CV (10 repeats; 4 folds** → ensuring that 25% of the original data is left for internal validation purposes)

E-tongue potentiometric profiles



E-tongue potentiometric mean signal profiles of unadulterated and intentionally-adulterated EVOO:
(A) LOO-rancid (2.5% up to 40%, v/v)
(B) LOO-WV (2.5% up to 40%, v/v)

RESULTS

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

→ Sub-set sensors selection using a variable selection simulated annealing (SA) algorithm
→ Sub-set with minimum number of sensors → maximum correct classification, LOO-CV
→ Internal-validation: repeated K-fold-CV

Olive oils' adulteration detection

i) Rancid sensory defect:

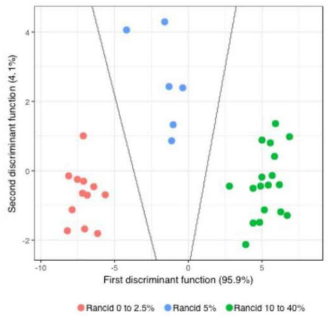
Adulteration groups:
- rancid adulteration ≤ 2.5%
- 5% rancid adulteration
- 10% ≤ rancid adulteration ≤ 40%

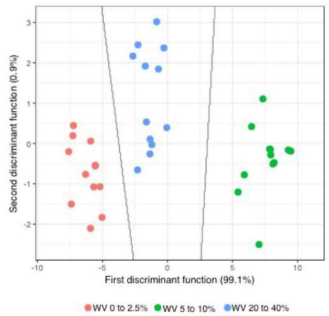
→ E-tongue-LDA-SA model: 19 sensor signals
→ 100% for original grouped data (**FIGURE**)
→ 92% of correct classifications for LOO-CV
→ **84±4% (from 79% to 94%) for repeated K-fold-CV**
→ Selected sensors: S1:1, S1:2, S1:7, S1:9, S1:10, S1:11 to S1:13, S1:17; S2:1, S2:5, S2:6, S2:9, S2:10, S2:13, S2:14, S2:17; S2:19

ii) Winey-vinegary sensory defect:

Adulteration groups:
- WV adulteration ≤ 2.5%
- 5% ≤ WV adulteration ≤ 10%
- 20% ≤ WV adulteration ≤ 40%

→ E-tongue-LDA-SA model: 20 sensor signals
→ 100% for original grouped data (**FIGURE**)
→ 100% of correct classifications for LOO-CV
→ **92 ± 4% (from 89% to 100%) for repeated K-fold-CV**
→ Selected sensors: S1:2, S1:3, S1:6, S1:13 to S1:15, S2:1, S2:2, S2:6 to S2:14, S2:18; S2:19





CONCLUSIONS

- The E-tongue-LDA-SA can be used as a taste sensor device for the successful detection of EVOOs adulterated with LOOs containing intense sensory defects such as rancid and winey-vinegary (≥ 2.5% adulteration).
- Physicochemical quality parameters, were not efficient to detect intentionally admixing of rancid or winey-vinegary olive oils to EVOOs, allowing classifying adulterated olive oils (up to 20%) as VOOs.
- Sensory analysis was a more efficient tool, restricting VOO classification to admixing up to 10% and being able to detect adulterations greater than 2.5% or 5% for rancid or winey-vinegary olive oils, respectively.

Acknowledgements
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