Inorganic composition and redox profile as a novel approach for oil authentication studies

INORGANIC COMPOSITION AND REDOX PROFILE AS A NOVEL APPROACH FOR OIL AUTHENTICATION STUDIES

Agnese Giacomino[a], Simone Provenzano[b], Wala Sarah Zreg[a], Andrea Ruo Redda[a], Eleonora Conca[b], Carmela La Gioia[b], Mery Malandrino[b], Ornella Abollino[b]

[a]*Department of Drug Science and Technology, University of Torino*
[b]*Department of Chemistry, University of Torino*
agnese.giacomino@unito.it

Valorizzazione dei prodotti Italiani derivanti dall'OLiva attraverso tecniche analitiche INnovative

Determination of the authenticity of extra virgin olive oils (EVOOs) has become increasingly important in recent years following some adulteration and contamination scandals.
This work (VIOLIN project, supported by AGER foundation) focused on the evaluation of the possibility to consider inorganic content and/or the redox profile as possible markers of EVOOs.

INORGANIC COMPONENT_methods

Sample homogenisation (Sonication; Stirring)
Microwave digestion
0.5 g of sample
+
H_2O_2/HNO_3 mixture
↓
Cooling at room temperature
↓
Dilution to 30 ml with water

ICP-AES → Mayor elements

HR-ICP-MS → Cu, Fe, Mn, Ni, Zn and Rare earths

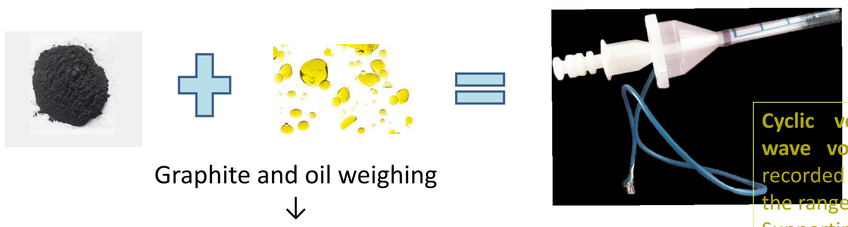
Microwave digestion alone 

Homogenisation + Microwave digestion (**Experimental design**) 

<16%

REDOX PROFILE_methods

EVOO modified carbon paste electrodes (EVOO-CPE)



Graphite and oil weighing
↓
Homogeneization
↓
Packing of the paste in the body of the electrode
↓
Inserting an electric contact (copper wire)
↓
Inserting in an oven at 60 °C
↓
Stabilization (3 days covered with parafilm and in the dark)

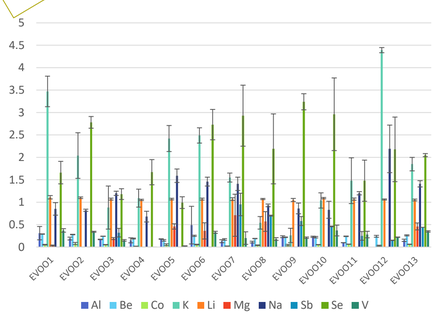
Cyclic voltammetry and square wave voltammetry profiles were recorded varying the potential in the range 0-1.3 V.
Supporting electrolyte: HCl 0.1 M

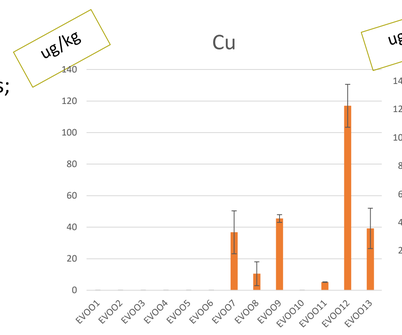
The profiles obtained with EVOOs were **compared with that of other vegetable oils**: olive oil, linseed oil, peanut oil, sunflower oil and rice oil.

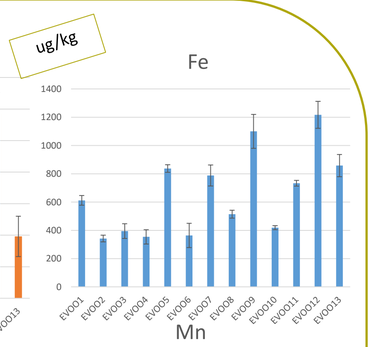
CPEs were prepared using **mixture of EVOO and other types** of oil to value the real capability of the technique to discriminate possible adulterations.

INORGANIC COMPONENT_results

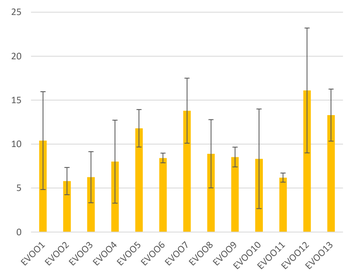
- Concentrations below 1 mg / kg were obtained for Al, Be, Co, Mg, Sb and V;
- K, Li and Se had higher concentrations;
- Na varied depending on the sample considered.

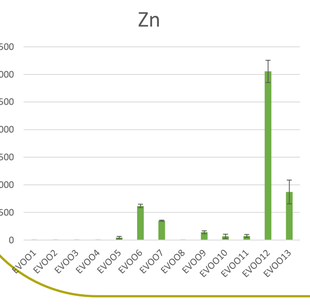


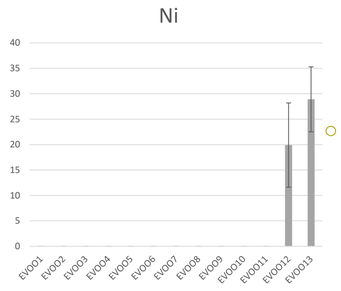




- The content of Cu, Fe, Mn, Ni and Zn ranged from a few units to hundreds of ug / kg, with a few exceptions.



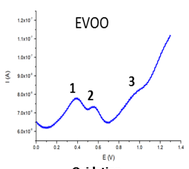




- Only Ce, Er, Gd, La, Nd, Sc, Sm, and Y were determined in concentrations of the order of ng / kg, whereas the other REEs were undetectable.

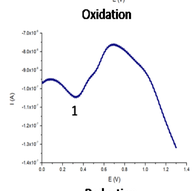
REDOX PROFILE_results

- In the voltammograms obtained for the EVOO samples there are from one to three oxidation peaks at about 0.4 V, 0.6 V and 1.1 V; the first two linked to polyphenolic compounds, while the last one is attributed to tocopherols.
- In the cathodic sense, on the other hand, one or two reduction peaks are observed at about 0.3 V and 0.5 V due to the polyphenolic compounds.



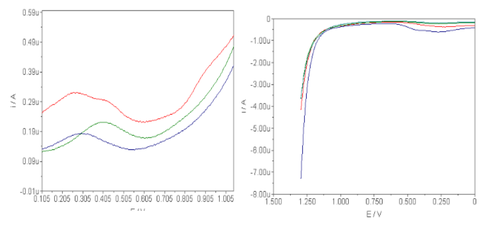
Oxidation

Peak 1 0.4 V
Peak 2 0.6 V
} Polyphenols
Peak 3 1.1 V
} Tocopheerols



Reduction

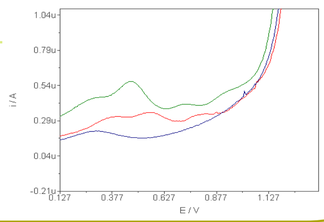
Peak 1 0.3 V
} Polyphenols



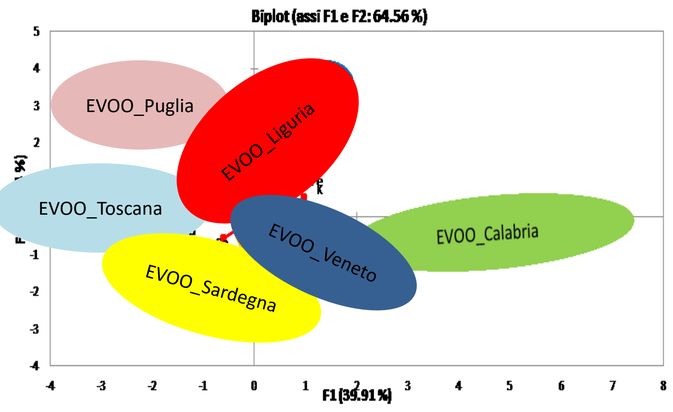
(EVOO, sunflower oil and peanut oil)

From the comparison of the profiles obtained, it is possible to observe differences in the number of peaks present, in their height and in the potential to be observed, which highlighted the diversity in the content and nature of the antioxidant compounds of the oils with different plant origins.

EVOO
sunflower oil
mixture EVOO:sunflower oil = 4:1



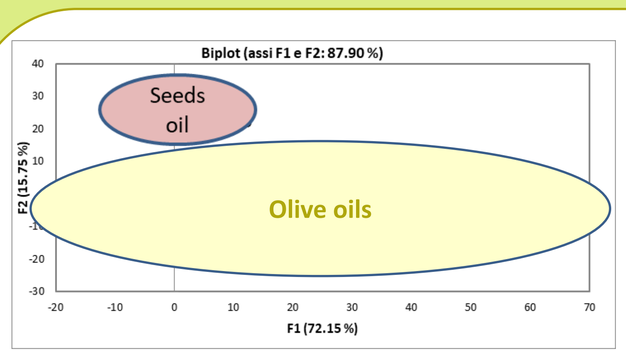
INORGANIC COMPONENT_chemometrc treatment



The metal content depends of the conditions in which the oils has been produced, from the composition of soil and water to the conditions of production, conservation and transport.

Considering the concentrations of Na, Fe, K, Al, Se, Li, Mn and Zn, a grouping of EVOOs is obtained based on the region of origin.

REDOX PROFILE_chemometric treatment



The features observed in the voltammograms reflect the reactions of electroactive compounds (such as polyphenols), which are present in the oils mixed with the carbon matrix. For this reason, the voltammetric responses of the electrodes are specific for each type of oil.

Voltammetry does not seem to allow a distinction between the region of origin of several EVOOs.
The only clear separation highlighted by the biplot chart obtained considering the results of voltammetry was that between EVOOs and oil having different vegetable origin .
It is important to underline that it is reported "olive oils" since adding to the dataset some olive oils (and not extravirgin) they are grouped in the same cluster of the EVOOs.

INORGANIC COMPONENT_conclusions

Inorganic composition seems to be an useful marker for the assessment of the **geographical origin** of an EVOO.

Reference
Apetrei et al., Sensors and Actuators B, 111–112(2005) 403-409

REDOX PROFILE_conclusions

Voltammetry coupled with **EVOO-CPEs** seems to have a good ability to distinguish the **plant species of origin**.
The technique presents enormous potential from the standpoint of **monitoring the state of conservation** and the **organoleptic properties** of the oils and their by-products.