Développement de stratégies analytiques inorganiques pour l'authentification géographique des huiles d'olive tunisiennes

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Development of inorganic analytical strategies for the geographical authentication of Tunisian olive oils

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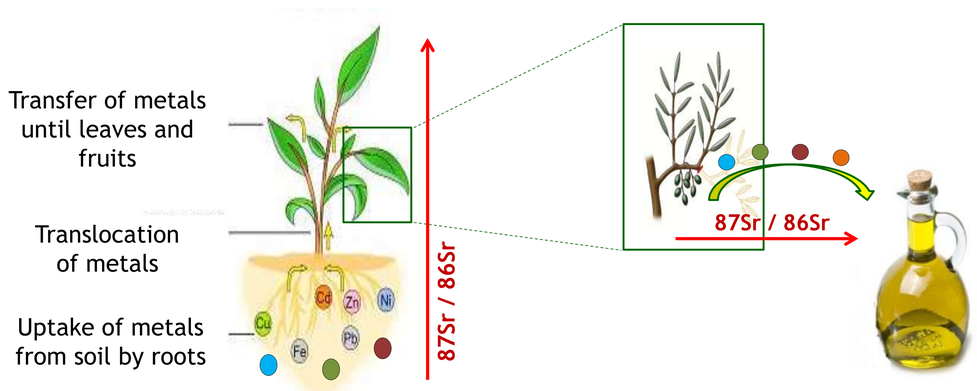
INTRODUCTION

Olive oil, an important component in the Mediterranean diet, is among the foods most affected by counterfeits. Tunisian extra virgin olive oil (EVOO), widely appreciated for its high quality, is therefore subject to the risk of fraud. This is why researchers have become more and more interested in authenticating this precious product by trying to develop advanced analytical techniques. Previously, olive oil was most often the subject of organoleptic and sensory analyzes (K Ben Hassine et al.,2014) which is not always discriminating and quick for monitoring origin. More recently, research has focused more on the analysis of trace metals by means of spectroscopic analysis (M beltran et al.,2015; F Damak et al., 2019) . Indeed, a wide range of metals is a good means for geographical tracing because they constitute the original soil like Sr, Rb and Li. Others are associated with human activities such as Pb, Cd (atmospheric pollution), Cu , Zn and Fe (agricultural practices). However, this analytical control is not always discriminating and the information on the geographical origin is not precise. This is why we have resorted more recently to the heavy isotopes which intervene in the biogeochemical cycles of the environment such as strontium (Sr) which has proven its reliability in the traceability of numerous agrifood products (S Medini et al.,2015; V Susanne et al.,2010).
The aim of this study is to develop a method allowing an irrefutable discrimination on the geographical origin of an olive oil through a multi-elemental and/or isotopic analysis.

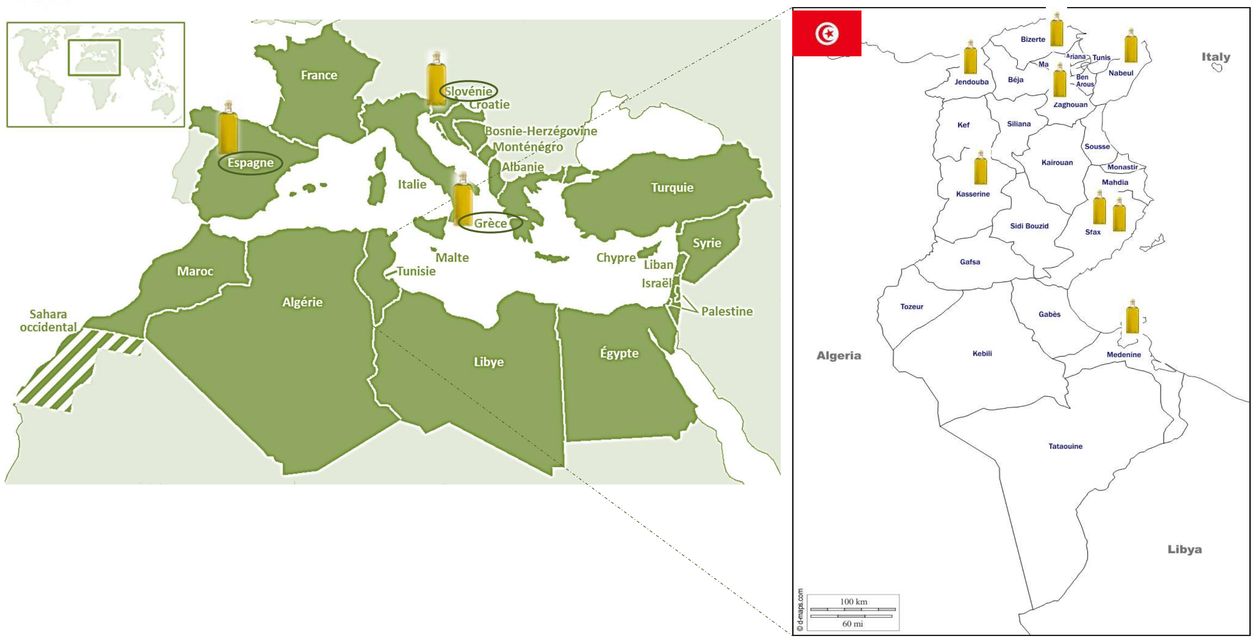


AIM OF THE STUDY

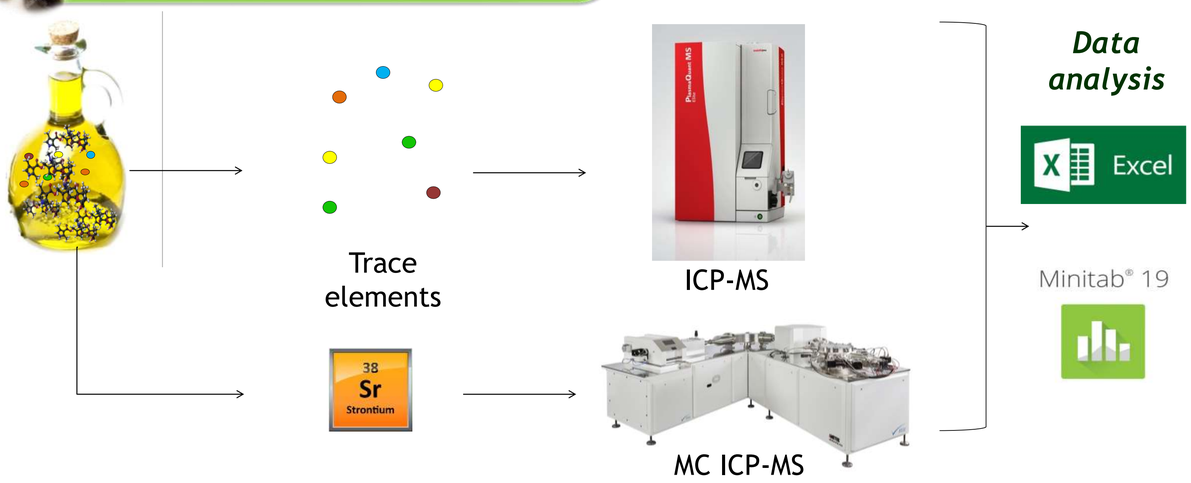
- Development of a efficient sample preparation method for precise determination of the concentrations of trace elements in olive oil samples using ICP-MS.
- Development of a reliable method for determining the isotopic ratio of Sr in olive oil.

=> Discrimination of olive oils according to their geographical origin.

SAMPLES



METHODOLOGY



MULTI-ELEMENTAL ANALYSIS

A. Analytical method

0,5 g of olive oil and CRM
+ 5 mL nitric acid
+ 0,5 mL Hydrogen peroxyde

Microwave digestion
Time: 30 min
Temperature: 220°C

Ultrawave- Milestones

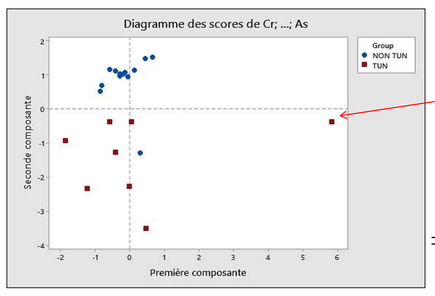
Clear solutions

ICP-MS analysis

PlasmaQuant MS Elite - Analytik Jena

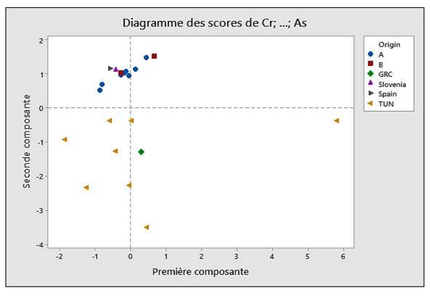
B. Results

The Principal Component Analysis (PCA) was applied to the concentration of seven elements (As, Cr, Fe, Li, Mn, Pb and Sr).



AD, Tunisia

large amount of pomace residues
⇒ the metals concentrations are modified (Poscic et al., 2019)



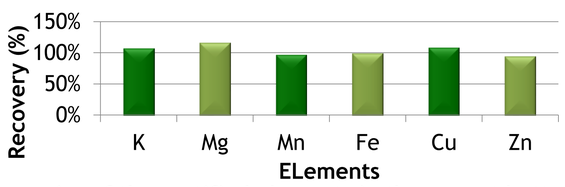
PC1 vs PC2 score plot of Tunisian and non Tunisian EVOO samples

Influence of variables on discrimination

Element	PC1	PC2	PC3
Cr	0,15305	-0,54603	-0,08361
Mn	-0,55411	-0,29441	0,20073
Li	0,27248	-0,53542	-0,07879
Sr	0,31583	0,07887	0,73730
Pb	-0,30948	0,02678	0,58306
Fe	-0,36497	-0,50396	0,08091
As	0,51631	-0,25998	0,23746

❖ *CRM Recovery*

Peanut butter
NIST® SRM® 2387



Recoveries of the certified elements in the peanut butter

DEVELOPMENT OF ISOTOPIC ANALYSIS

A. Analytical method

Olive oil / Acid mixture (HNO3 2% + HCl 0,1%)

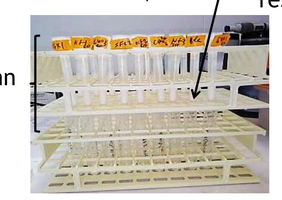
Agitation on a Shaking plate

phase separation by aspiration using a pipette

Microwave digestion of the acid extract
Time: 30 min
Temperature: 220°C

Ultrawave- Milestones

Eichrom Sr spec resin



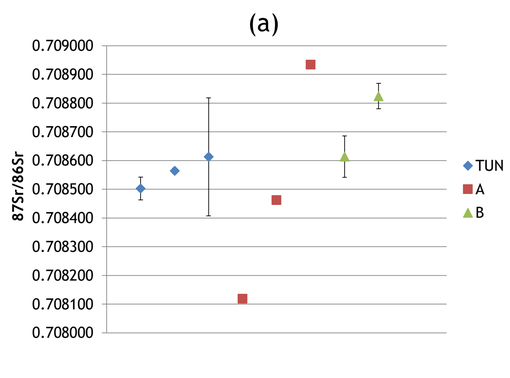
Sr separation on specific resin

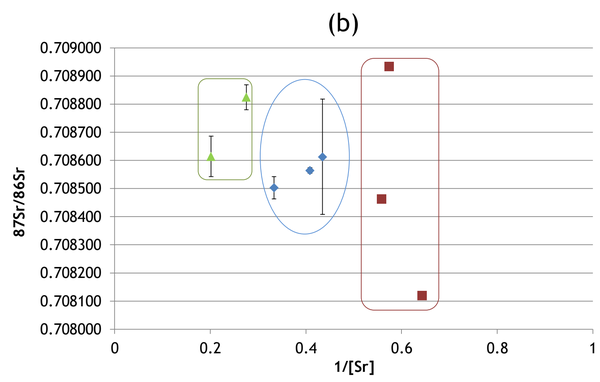
column

MC ICP-MS
Nu instruments

Determination of the isotopic ratio 87Sr / 86Sr

B. Results





(a) Ratios of 87Sr/86Sr in some EVOO samples from different origins
(b) Ratios of 87Sr/86Sr as a function of 1/Sr concentrations in EVOO samples

NB.Only the samples with recovery* higher than **50%** have been represented on the graph.
*The percentage of Sr recovered after column separation.

Conclusion

Olive oil is a complex matrix which requires an intensive pre-treatment for the separation of trace elements from the rest of the organic charge. For a better comprehension of the results, several factors must be taken into account such as the filtration of the oil which removes components rich in trace elements. The results showed that the Principal component analysis (PCA) might be a good technique for the differentiation of Tunisian and foreign olive oils. However PCA doesn't allow the authentication of each sample group according to their geographical origin. The combination of Sr concentration with its isotopic ratio (87Sr/86Sr) allowed to better discriminate each group of samples according to their provenance which highlights the importance of the Sr isotope ratio as a powerful tool for a traceability study although the low content of Sr and the high organic charge of olive oil made it difficult to separate Sr. Further studies must be carried out to optimize the extraction of Sr for isotopic analysis.