HELLENIC REPUBLIC
National and Kapodistrian University of Athens

TrAMS Trace Analysis and Mass Spectrometry Group

BRUKER

9th International Symposium on RECENT ADVANCES IN FOOD ANALYSIS
November 5–8, 2019 • Prague, Czech Republic

Potential of Trapped Ion Mobility combined with LC-HRMS in Food Authenticity Studies: Identification and Characterization of Secoiridoids Isomers found in Greek Extra Virgin Olive Oil

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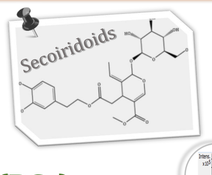
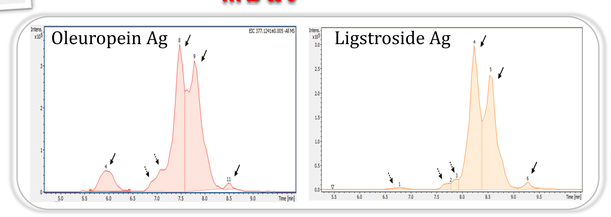
Introduction

Squalene
Phytosterols
Aliphatic fatty alcohols
Triterpene alcohols
Tocopherols
Triterpene acids
Phenolic Compounds (PCs)



- Secoiridoids highly contribute to health claim enhancement

...but



Different **isomeric peaks** are detected

REGULATION

EU Reg. 432/2012

EVOOs, rich in **PCs**, (Hyd. and its derivatives) contribute to **health protection**

Scope

- **Separation** of isomeric compounds, crucial in olive oil health claim
- Isomers **identification**
- **Discrimination** of olive oil samples from different agricultural backgrounds (variety, geographical origin)

Samples

- 48 samples of Koroneiki variety from 3 different **geographical origins** in Greece (Peloponnese, Lesvos, Crete)
- 33 samples of 5 different **Greek varieties**: Koroneiki, Kolovi, Adramytiani (Lesvos), Chiotiki (Chios), Thrumba (Samos)

Materials & Methods

Schematic workflow

Sample treatment

0.5g of olive oil → MeOH:H_2O 80:20% (v/v) →  1 min Vortex → Centrifugation →  Extraction →  Filtration (0.22μm) → **UPLC-timsTOF-Pro** (Powered by PASEF)

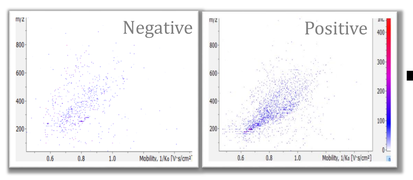
Data treatment

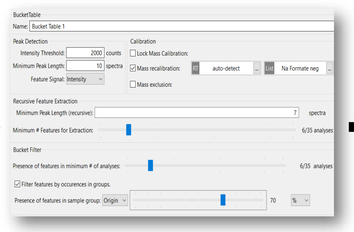
MetaboScape 4.0
4D feature finder (T-ReX 4D)

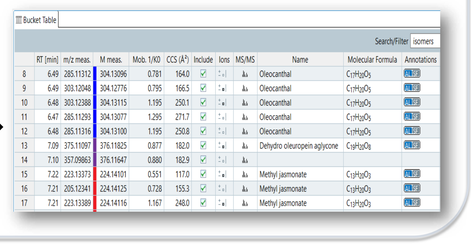
Data preprocessing (calibration, bucketing, filtering, scaling,...)

Creating bucket table

Non-targeted data extraction



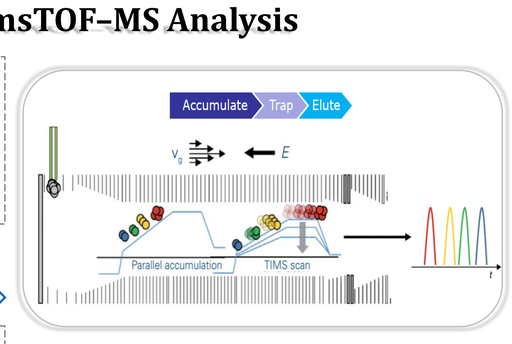




UHPLC-timsTOF–MS Analysis

LC method
Bruker C18 column (2.1 × 100 mm, 1.8μm)
Mobile Phase and Flow Gradient
Temperature: 40°C

Take a closer look!



timsTOF method
Ionization mode: Negative & Positive
Scan Range of Mass: 50-1000 m/z
$1/k_0$: 0.45-1.80 V×s/cm^{-2}
ICC: 5M
Ramp time: 100 ms
TIMS Spectra rate: 9.26 Hz

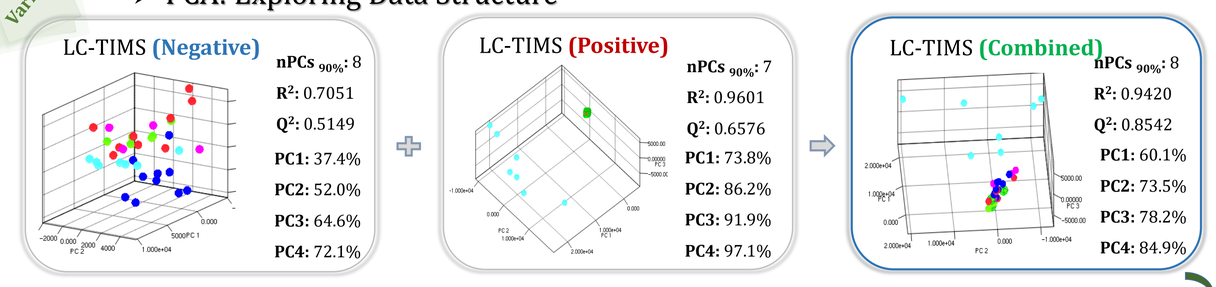
- ✓ Separation, based on the **3D size** and **charge** of the compound
- ✓ Increased peak capacity by **integrated separation** dimension

Results & Discussion

Discrimination - Untargeted Approach

Variety

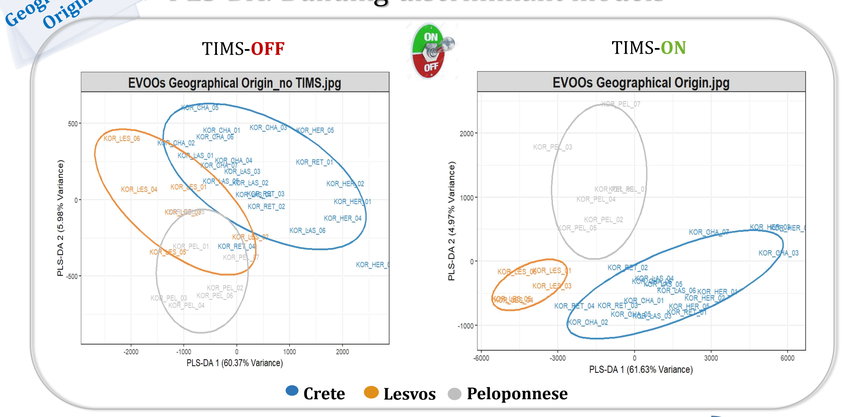
➢ PCA: Exploring Data Structure

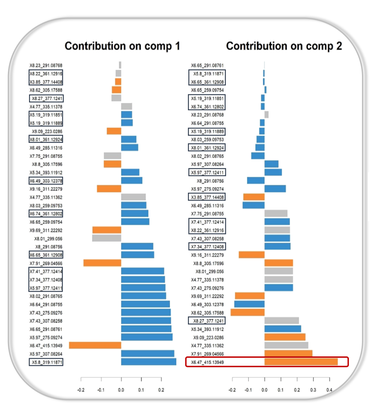


Variety discrimination combining both polarities acquisition data

Geographical Origin

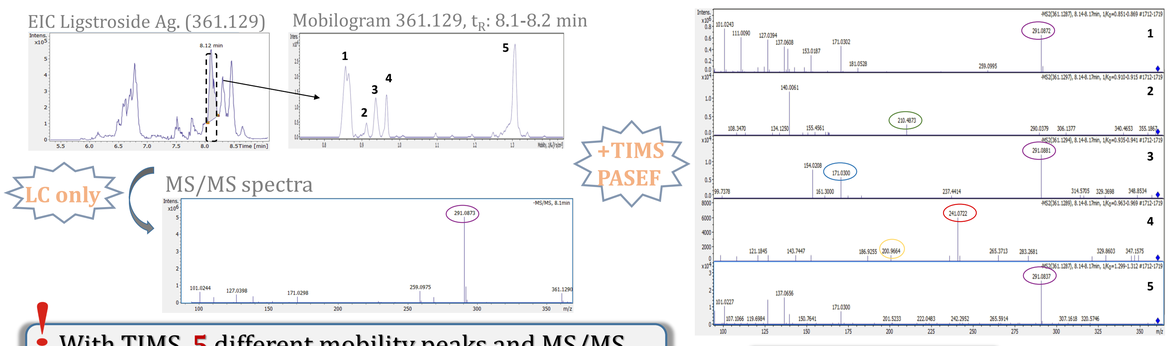
➢ PLS-DA: Building discriminant models





Using TIMS mobility dimension, geographical origin discrimination is clearly enhanced → Isomers as potential **authenticity markers**

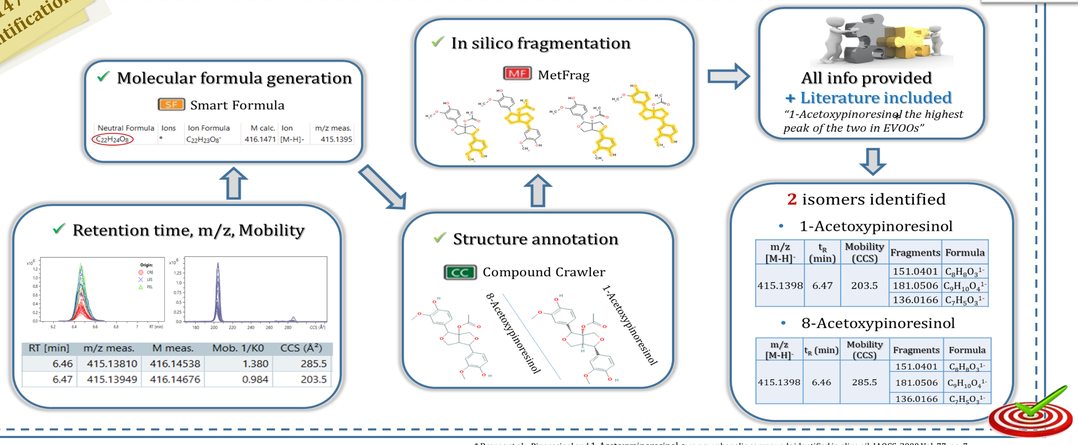
Separation of isomeric compounds



With TIMS, **5** different mobility peaks and MS/MS spectra are detected from **1** chromatographic peak → **5** indicative isomers

Isomers Identification

415.147 m/z identification



Structure elucidation

* Brenes et al., Pinoresinol and 1-Acetoxypinoresinol, two new phenolic compounds identified in olive oil, JAOCS, 2000 Vol. 77, no. 7

Conclusions

- ✓ The extra dimension of ion mobility enabled the separation of isomeric compounds
- ✓ Large amount of chemical information retrieved (t_R, m/z, CCS) using non-targeted data extraction
- ✓ Identification of unknowns compounds was achieved, applying a structure elucidation-aimed workflow
- ✓ Application of chemometric tools (PCA, PLS-DA) for EVOOs variety and geographical origin discrimination

We acknowledge support for the olive oil sampling by the projects: "Emblematic Action, The Olive Road" and "Novel wide-scope research for the promotion of N. Aegean olive oil and olive products through the designation of their unique characteristics and bioactive content"

Emblematic Action "The Olive Road"
NORTH AEGEAN REGION