Development of GC-IMS-based fingerprinting methods to support honey authenticity

Samuele Pellacani, Daniele Tanzilli, Marina Cocchi, Raniero Marabottini, Angela Napolitano, Rebecca Barbieri, Giorgia Gazzoli, Francesca Martone, Lorenzo Strani, Noemi Coppola, Caterina Durante

UNIVERSITAS STUDIORUM MUTINENSIS ET REGIENSIS 1175

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

The project

Analytical and chemometrics challenges

Assessing the peak resolution

Preliminary results

Future prospectives

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

CONSORZIO TUTELA

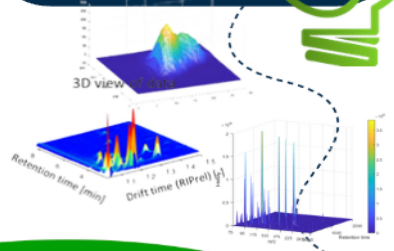
FONDAZIONE DI MODENA

ICQRF

Sampling

Acquisition of fingerprinting signals

NIR
UV-VIS
GC-IMS
EES
RAMAN



Machine Learning

Development of authenticity models

The project

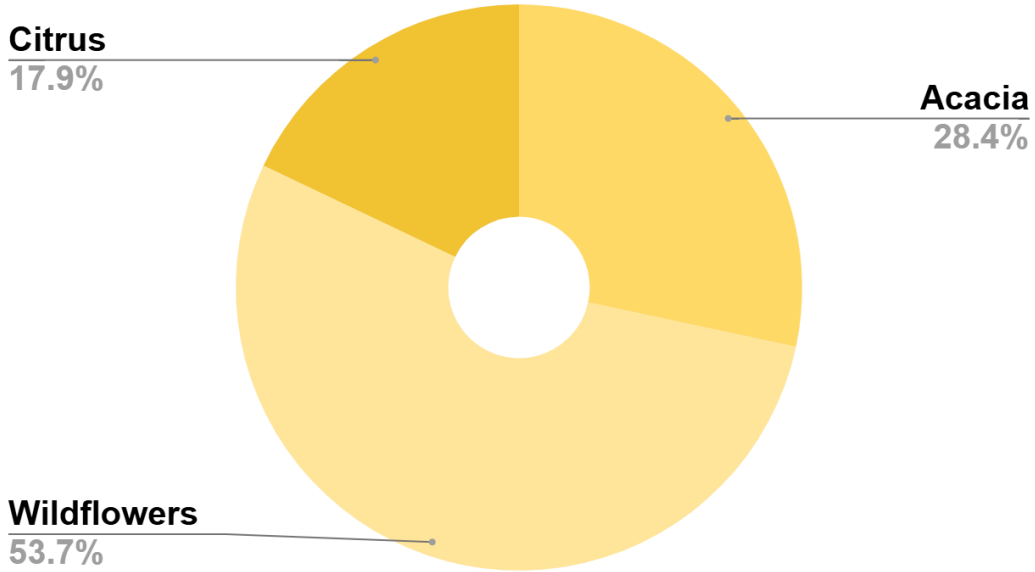
Analytical and chemometrics challenges

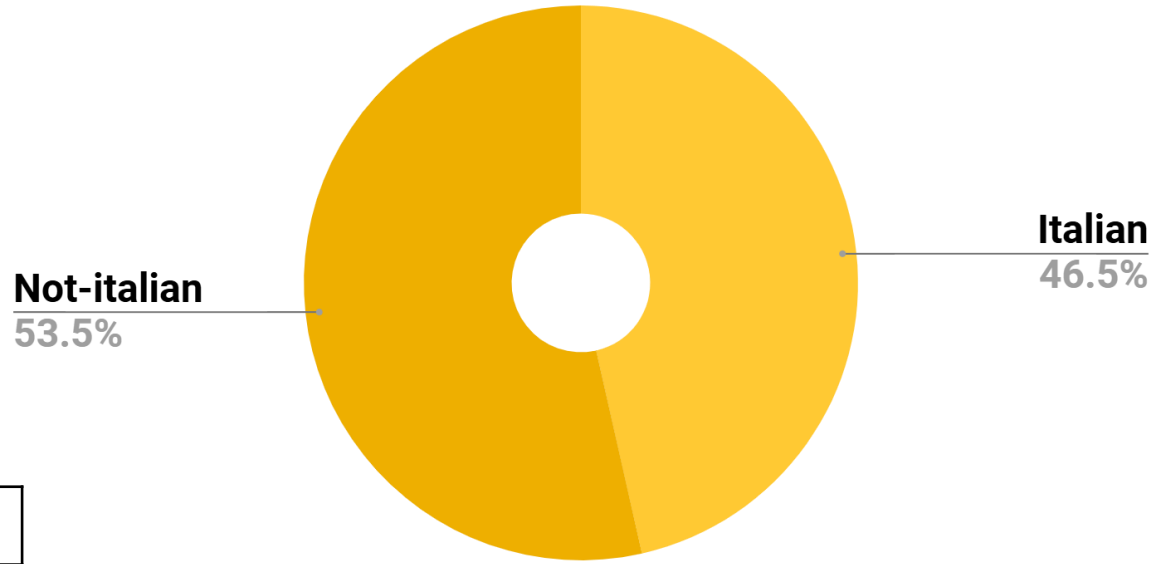
Assessing the peak resolution

Preliminary results

Future prospectives

Sampling





Italian	31
Not-Italian	36

The project

Analytical and chemometrics challenges

Assessing the peak resolution

Preliminary results

Future prospectives

Gas-Chromatography – Ion Mobility Spectrometry (GC-IMS)

GC-IMS FlavourSpec © (G.A.S.)

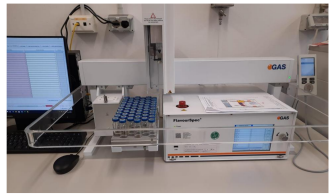
The project

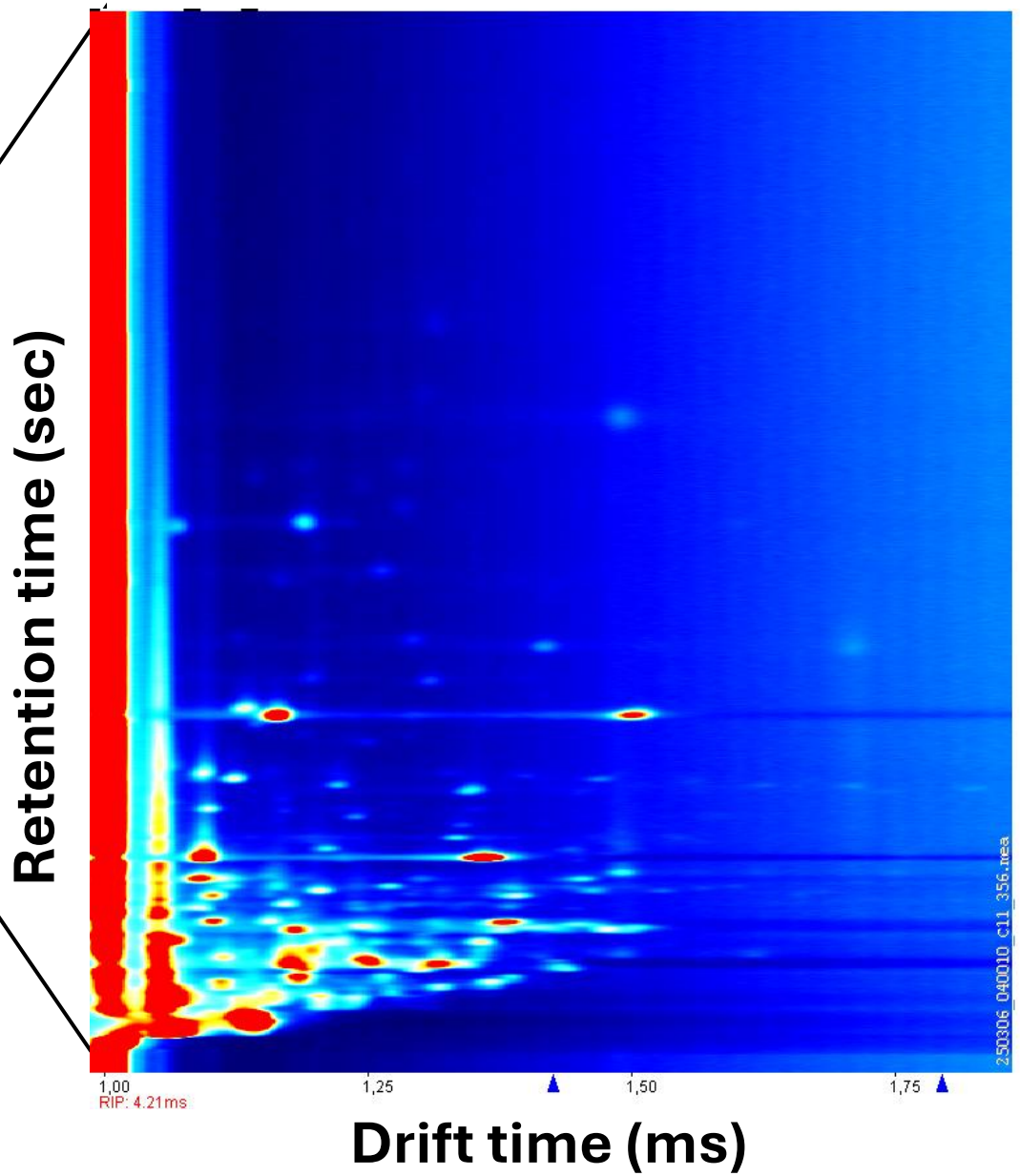
Analytical and chemometrics challenges

Assessing the peak resolution

Preliminary results

Future prospectives





The project

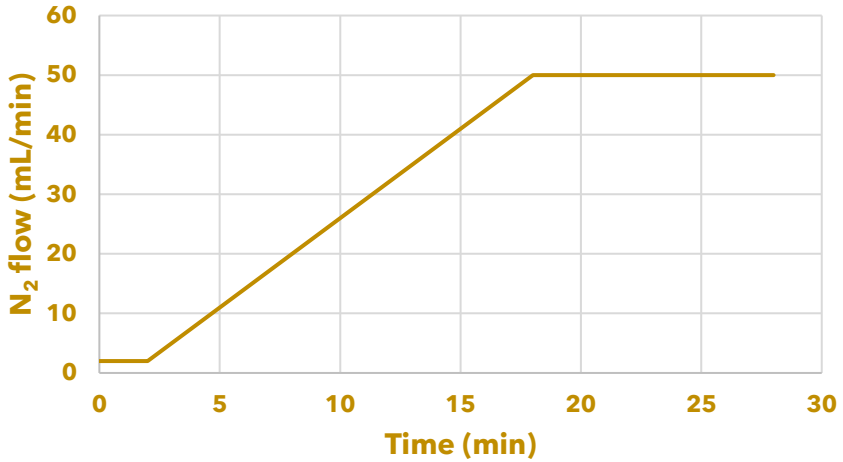
Analytical and chemometrics challenges

Assessing the peak resolution

Preliminary results

Future prospectives

The instruments works at constant temperature



Memory effect[1]

Two blanks between samples

Long sequence (67 samples + blanks)

Control samples, one every 10 samples to look for instrumental drift

[1]Jurado-Campos et al., "Usage considerations for headspace-gas chromatography-ion mobility spectrometry as a suitable technique for qualitative analysis in a routine lab" *Journal of Chromatography A,* **2021**, 1640, 461937.

iCoshift alignment

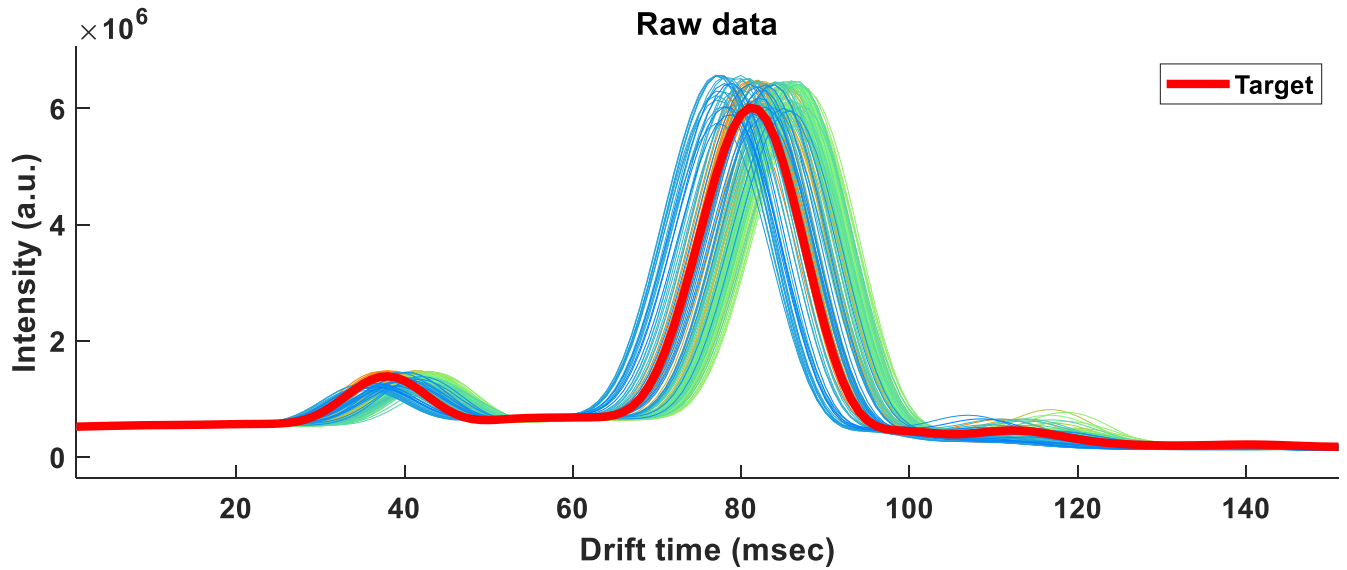
The project

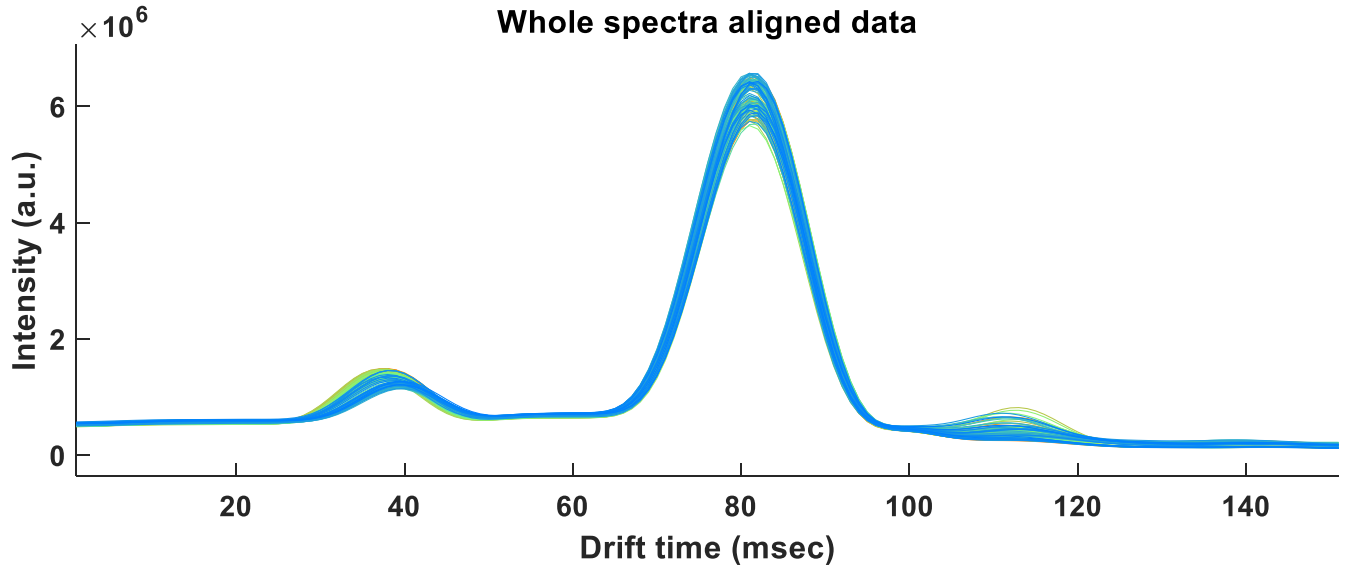
Analytical and chemometrics challenges

Assessing the peak resolution

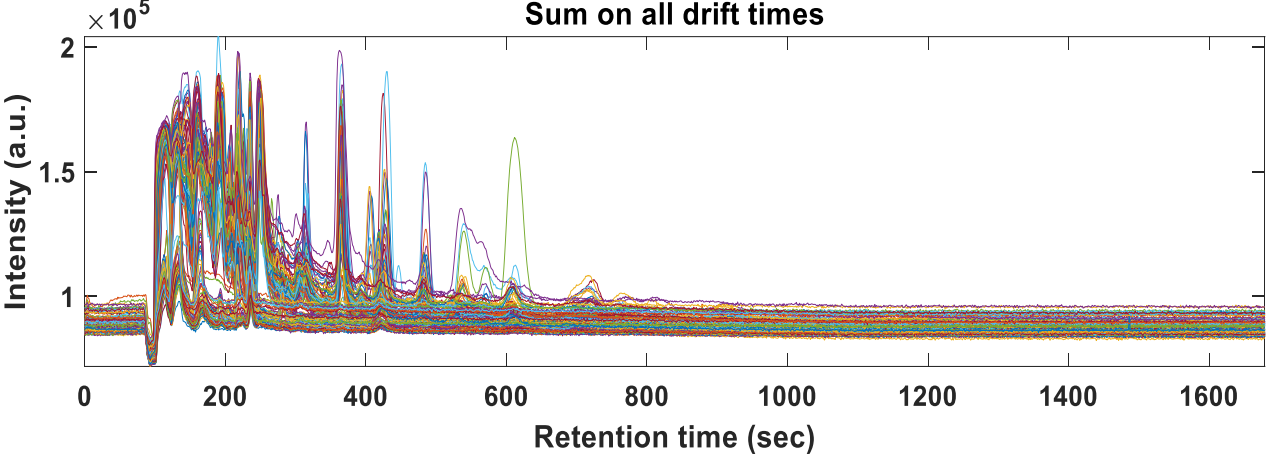
Preliminary results

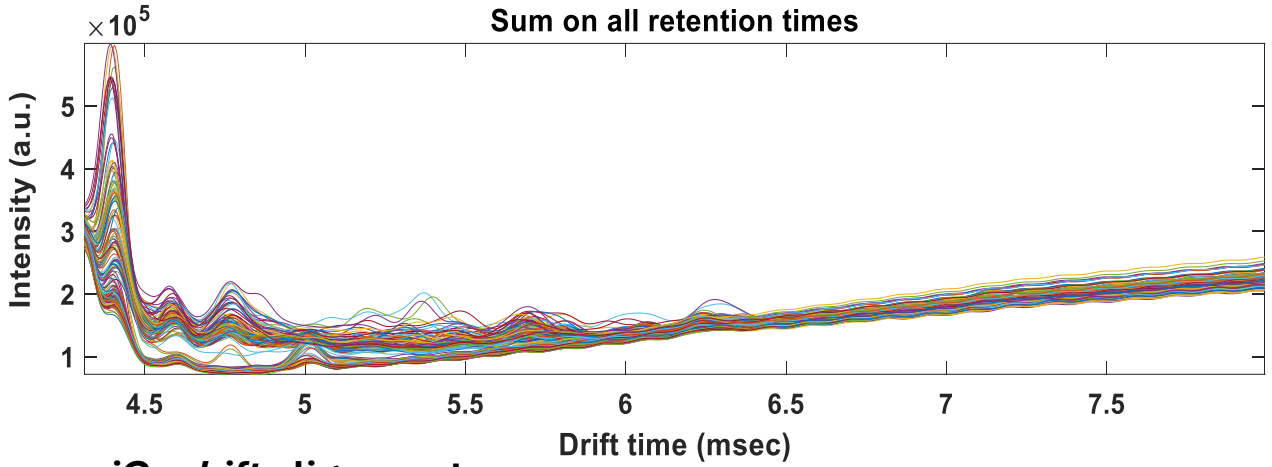
Future prospectives



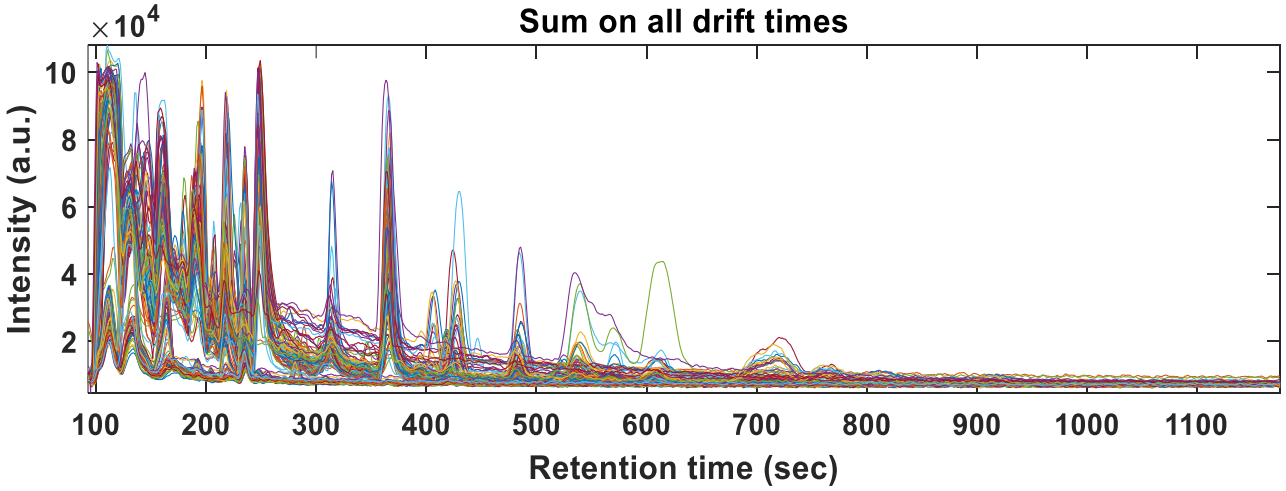


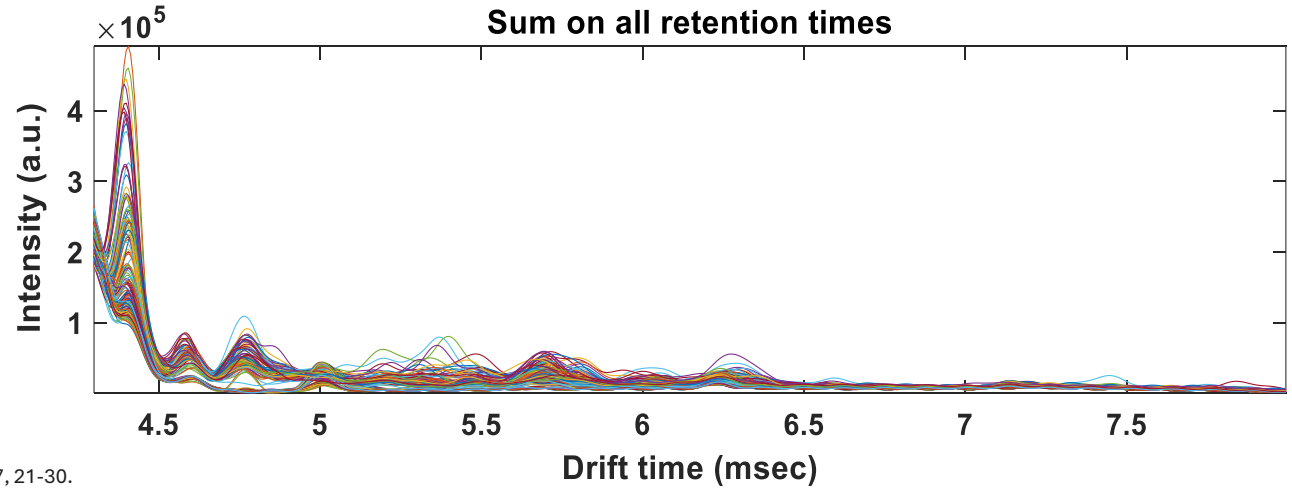
Alignment applied to the rest of the spectra





- ***iCoshift* alignment**
- **ROI selection**
- **Smoothing on retention times (SavGol, width = 11, order = 2)**
- **Smoothing and baseline correction on drift times (asymmetric least squares, default parameters[2])**





[2]Hans F.M. Boelens, Reyer J. Dijkstra, Paul H.C. Eilers, Fiona Fitzpatrick, Johan A. Westerhuis. *Journal of Chromatography A,* **2004**, 1057, 21-30.

The project

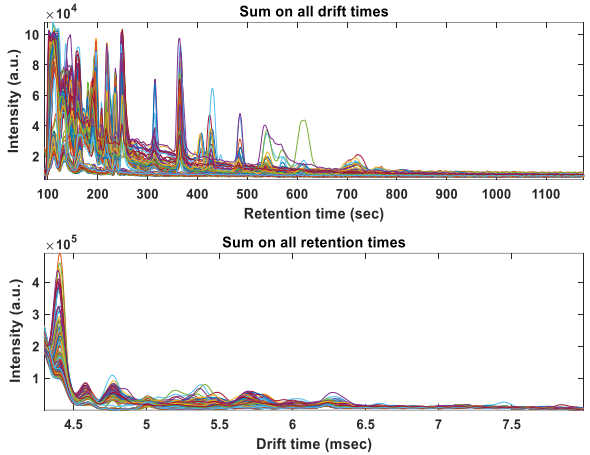
Analytical and chemometrics challenges

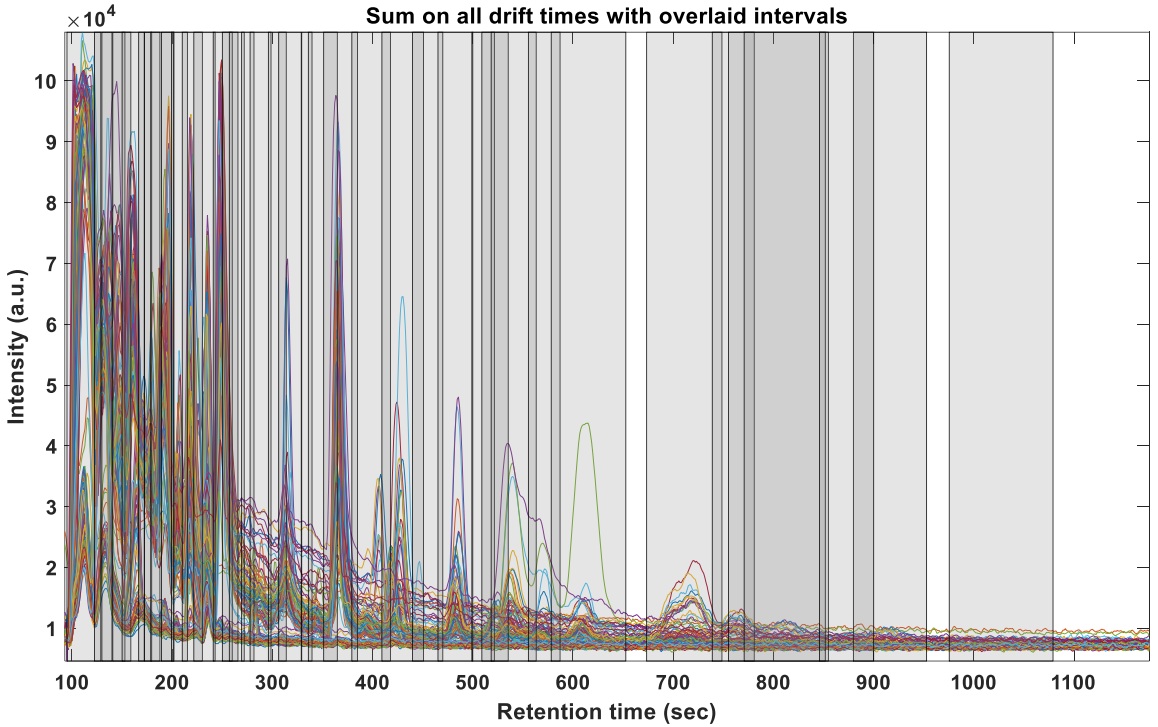
Assessing the peak resolution

Preliminary results

Future prospectives

Definition of 38 intervals





Peak deconvolution:
MCR-ALS[3] (nonnegativity and unimodality constraints)
PARAFAC2 (nonnegativity constraint)

[3]Parastar et al., Non-targeted volatilomics for the authentication of saffron by gaschromatography-ion mobility spectrometry and multivariatecurve resolution. *Food Chemistry*, **2025**, 465, 142074

The project

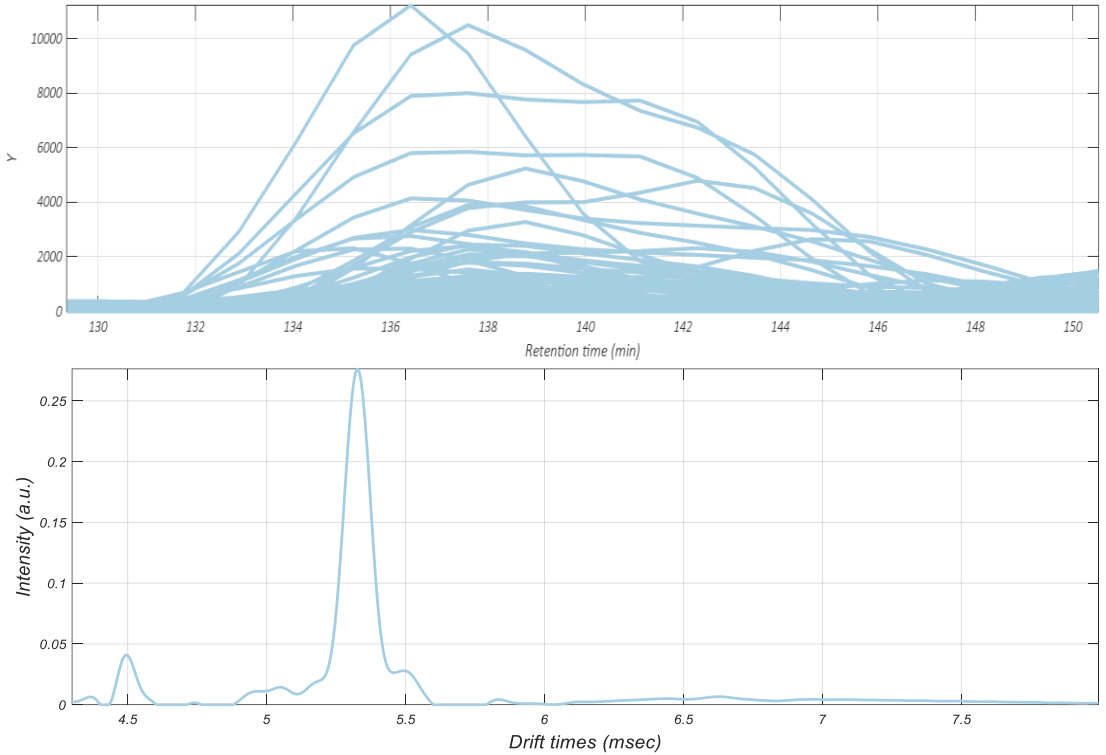
Analytical and chemometrics challenges

Assessing the peak resolution

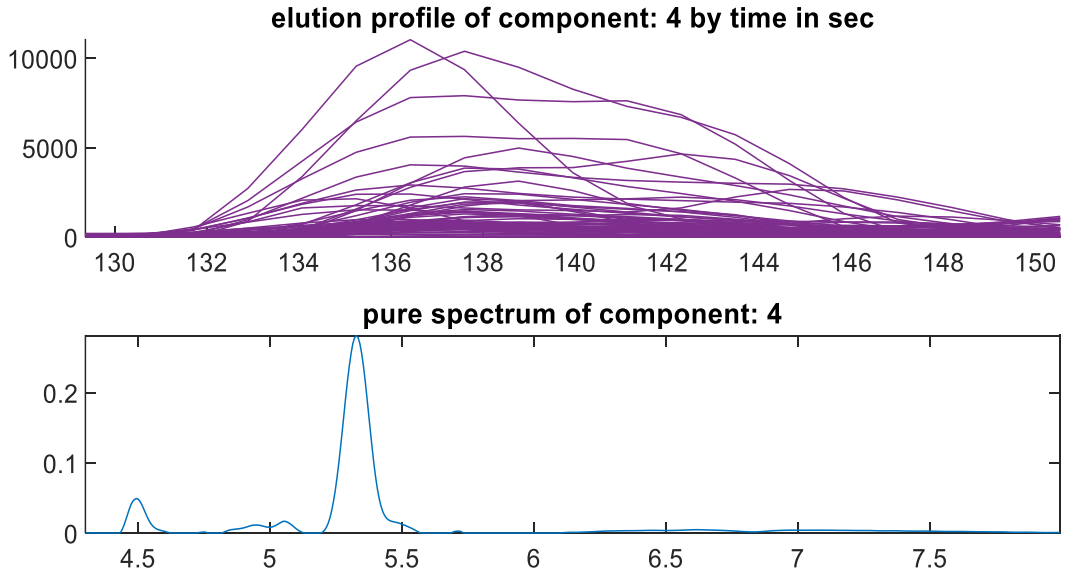
Preliminary results

Future prospectives

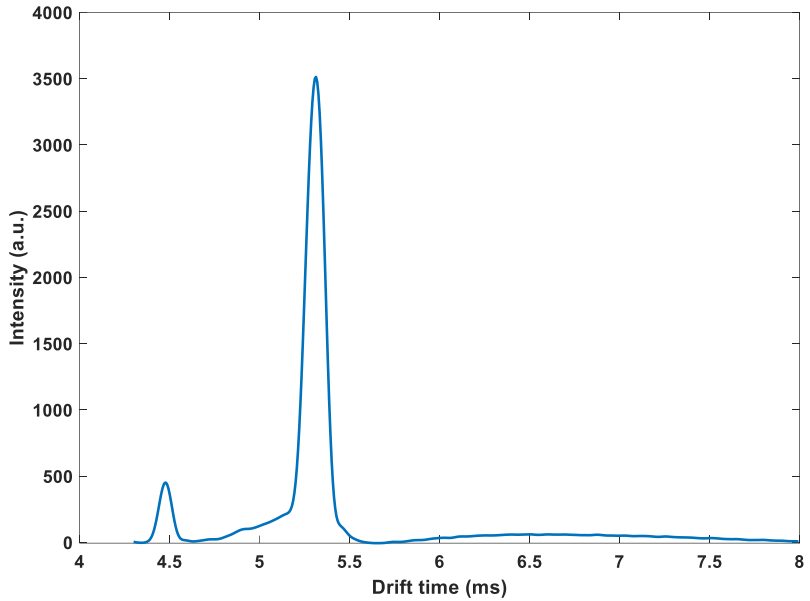
PARAFAC2 deconvolution



MCR-ALS deconvolution



Standard: 1-butanone



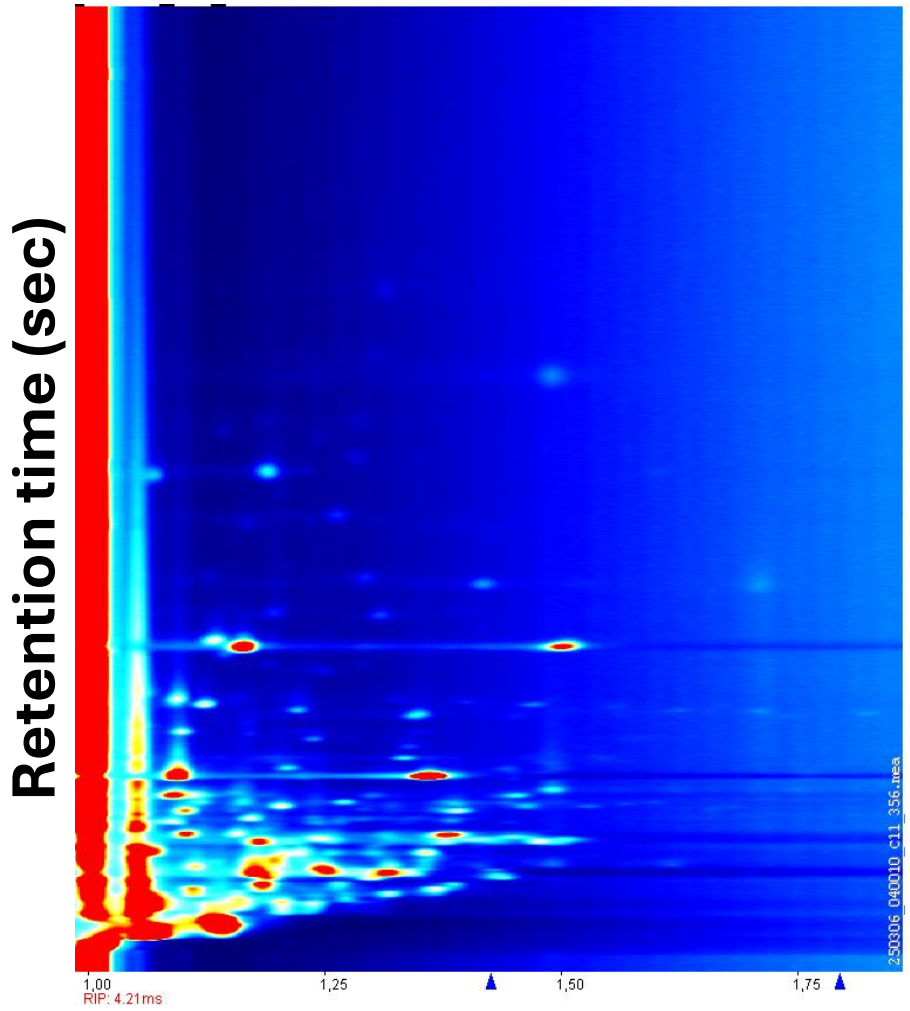
The project

Analytical and chemometrics challenges

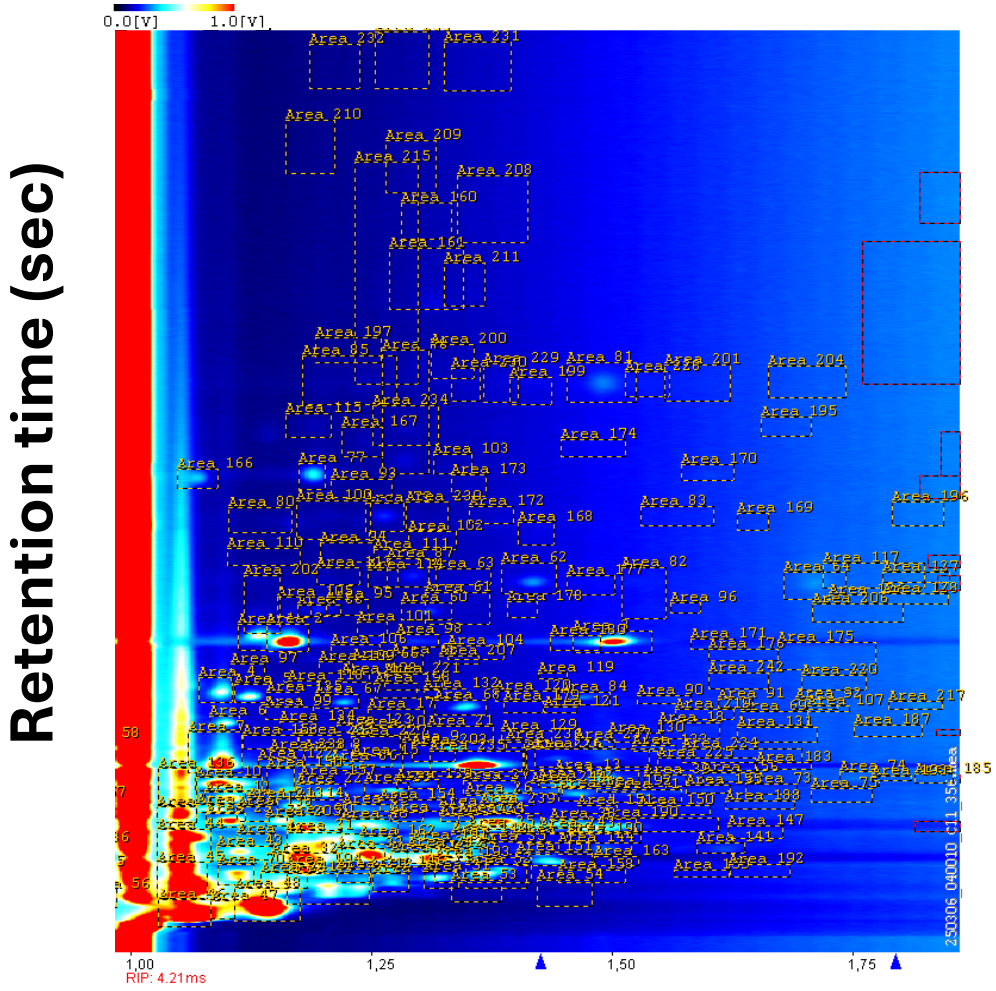
Assessing the peak resolution

Preliminary results

Future prospectives



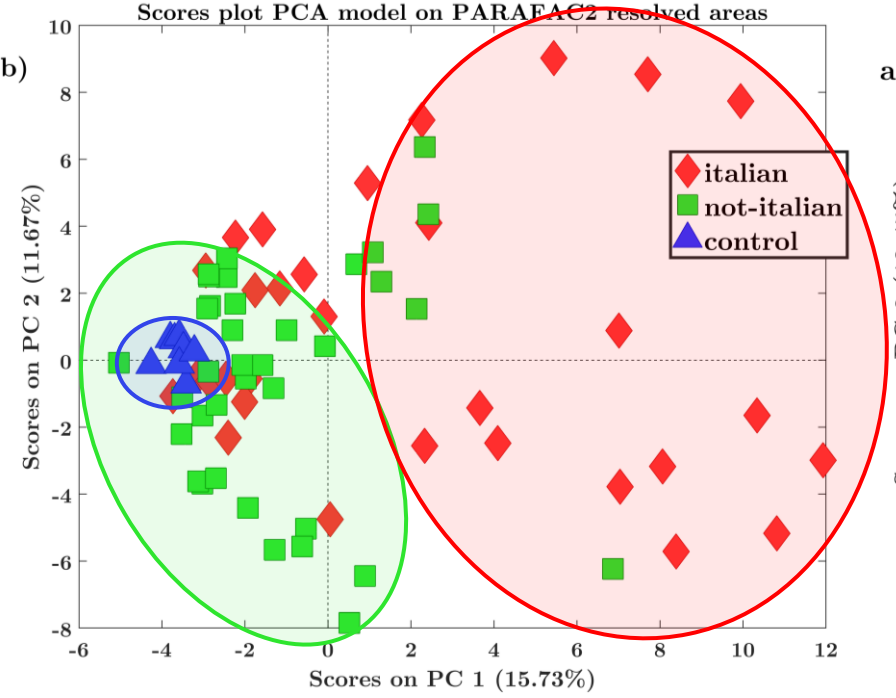
Vocal software



244 intervals!!

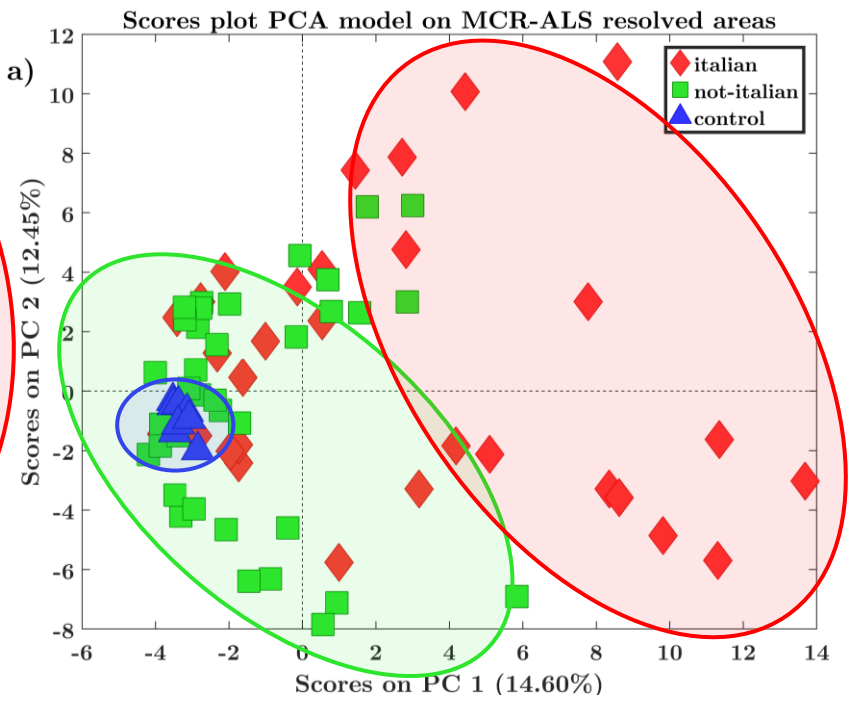
Principal Component Analysis (PCA)

PARAFAC2 resolved areas



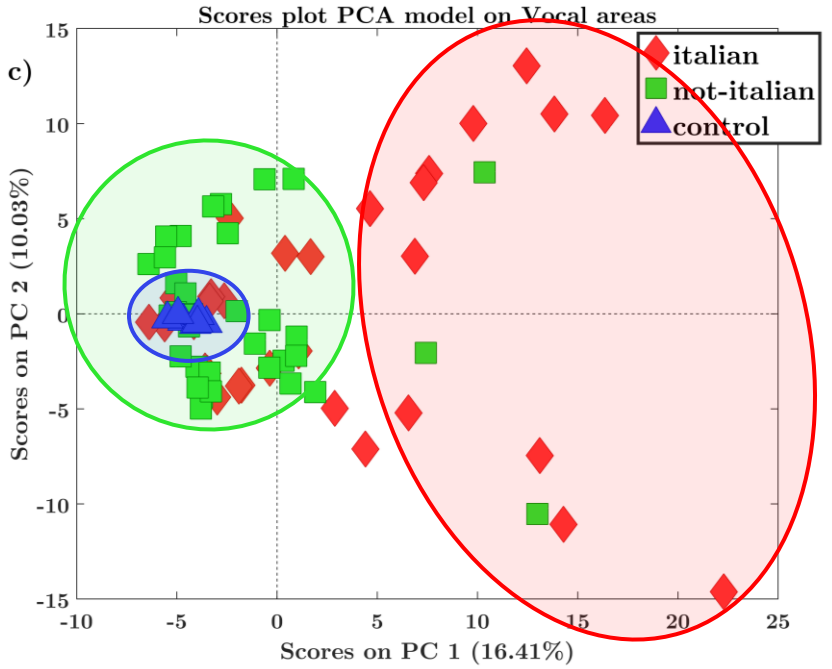
Area matrix (75 x 108)

MCR resolved areas



Area matrix (75 x 114)

Vocal areas



Area matrix (75 x 244)

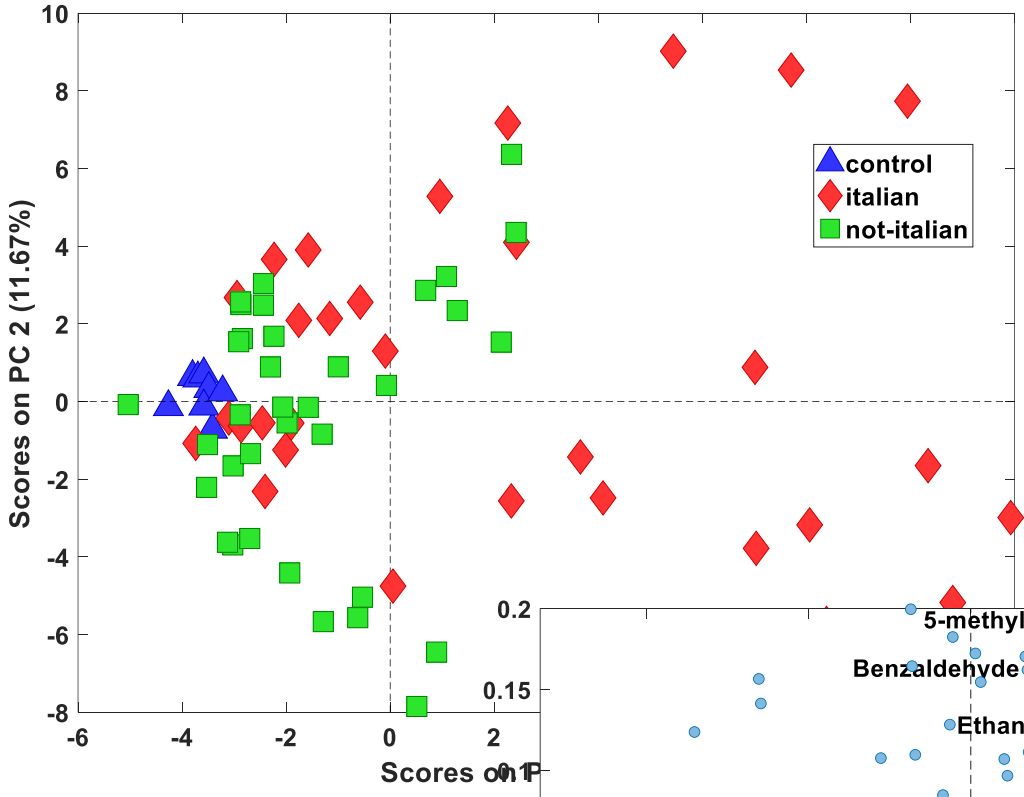
The project

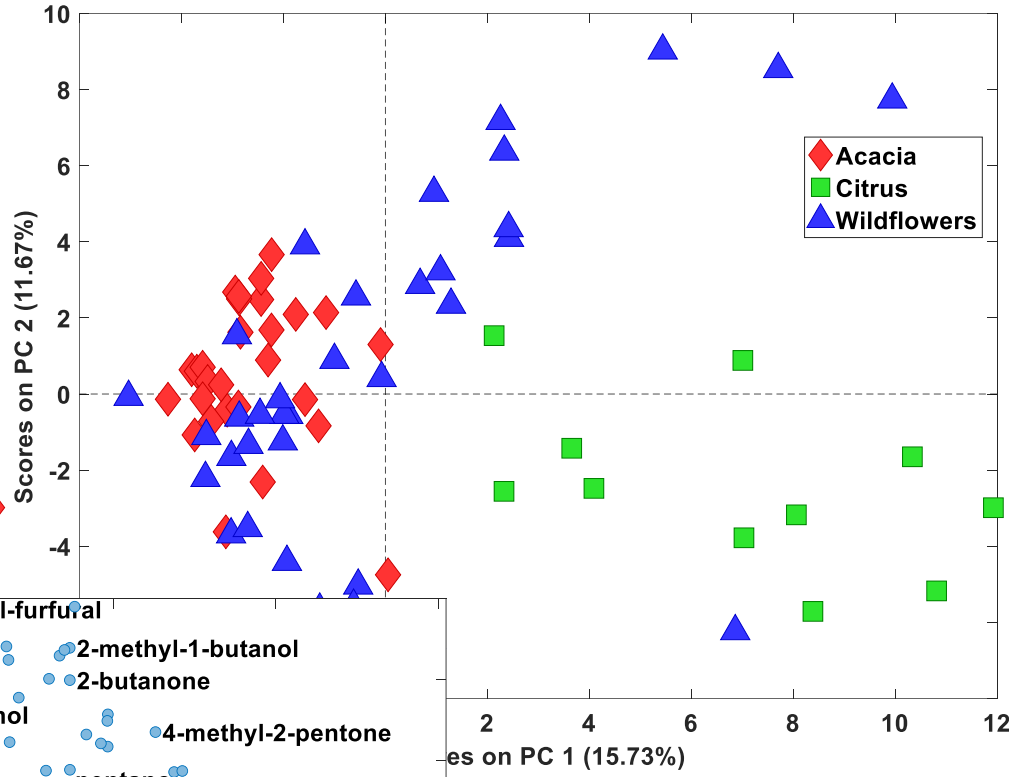
Analytical and chemometrics challenges

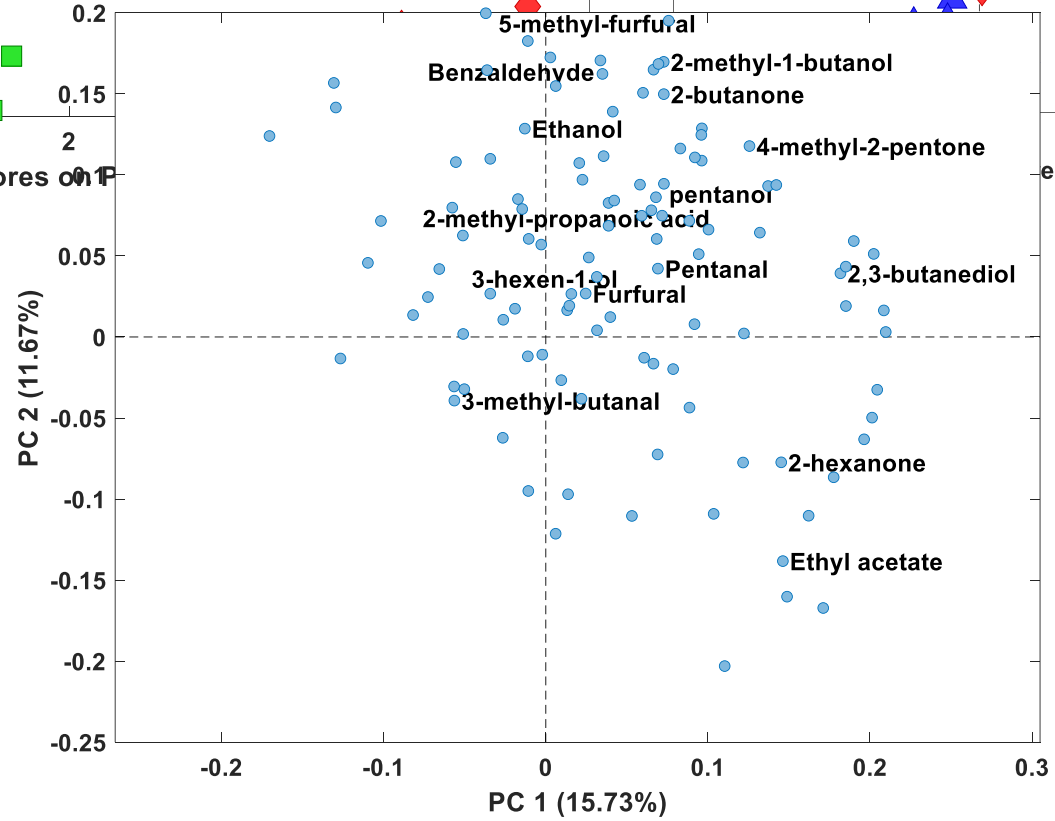
Assessing the peak resolution

Preliminary results

Future prospectives







!!

Identification based solely on RI and DT, standards confirmation needed!!!

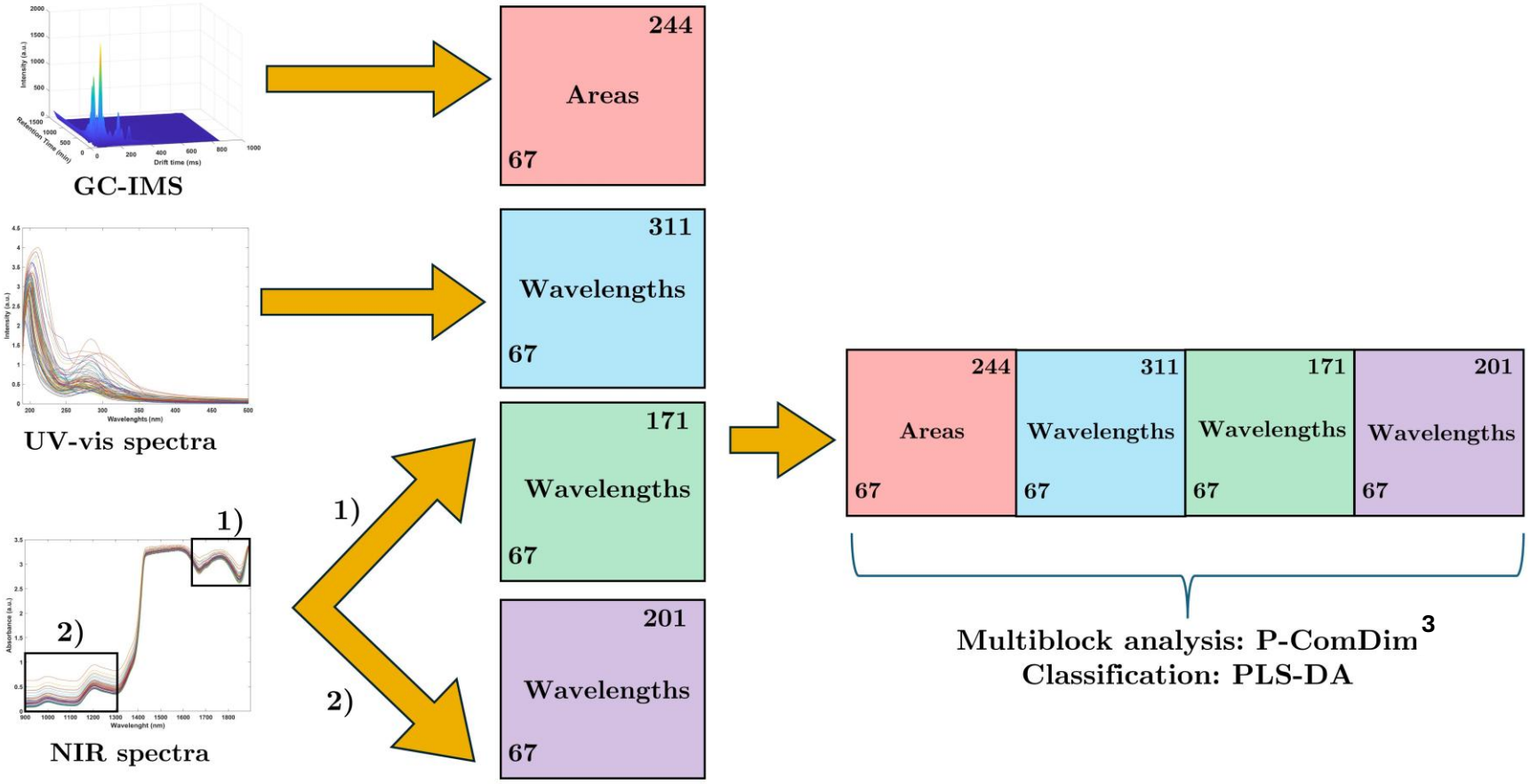
The project

Analytical and chemometrics challenges

Assessing the peak resolution

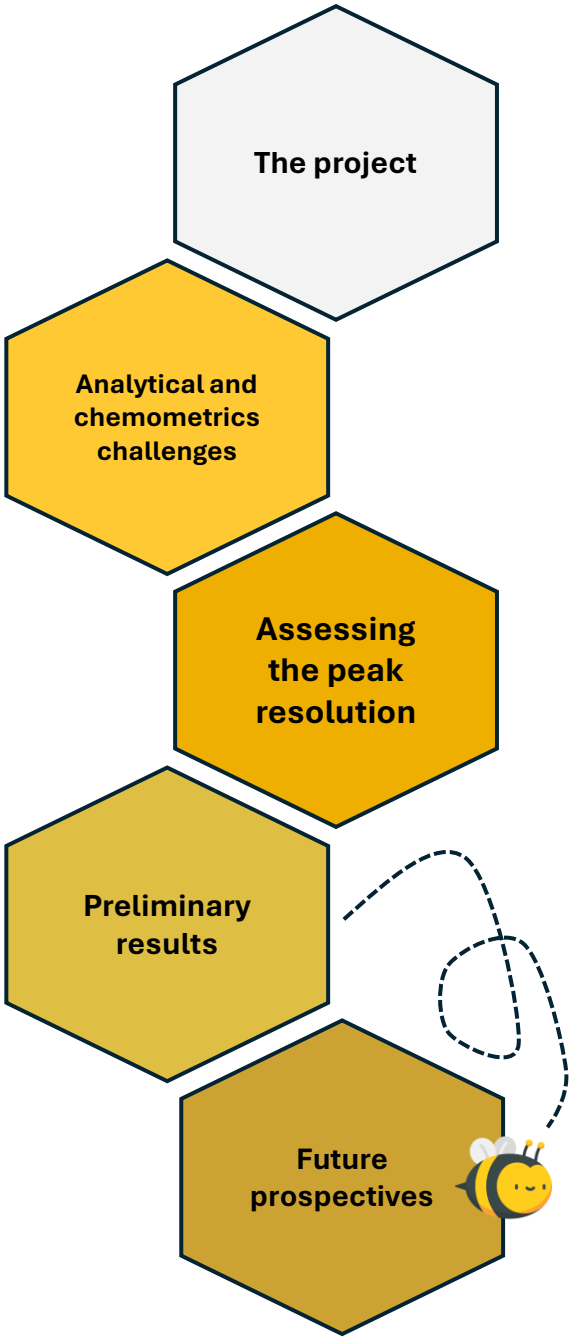
Preliminary results

Future prospectives



Dataset	Classification model	Preprocessing	Latent Variables	% Correctly classified			
				Training set		Test set	
P-ComDim	PLS-DA	Autoscaling	5	95	100	82	90

[3] V. Cariou, E. M. Qannari, D. N. Rutledge, E. Vigneau. "ComDim: From multiblock data analysis to path modeling". Food Quality and Preference, 2018, 67: pp. 27–34. doi: 10. 1016/j.foodqual.2017.02.012.



- MCR-ALS and PARAFAC2 proved to be effective for the decomposition and resolution of GC-IMS data
- After careful preprocessing, GC-IMS data can be analysed using the same chemometric techniques as GC-MS, demonstrating that the same level of automation can be achieved
- GC-IMS partially separates Italian and Not-Italian samples and it is significantly influenced by the botanical origin
- GC-IMS combined with spectroscopic techniques allows for a good classification of Italian honey
- More acacia, wildflowers and citrus honey samples will be analysed for properly develop and validate a classification model

UNIVERSITAS STUDIORUM MUTINENSIS ET REGIENSIS 1175

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

Consorzio Tutela Aceto Balsamico Tradizionale di Modena

FONDAZIONE DI MODENA

DIPARTIMENTO ICQRF
ISPETTORATO CENTRALE DELLA TUTELA DELLA QUALITÀ E REPRESSIONE FRODI DEI PRODOTTI AGRO-ALIMENTARI

ACETO BALSAMICO DI MODENA
CONSORZIO TUTELA

UNIVERSITAS STUDIORUM MUTINENSIS ET REGIENSIS 1175

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

Consorzio Tutela Aceto Balsamico Tradizionale di Modena

FONDAZIONE DI MODENA

DIPARTIMENTO ICQRF
ISPETTORATO CENTRALE DELLA TUTELA DELLA QUALITÀ E REPRESSIONE FRODI DEI PRODOTTI AGRO-ALIMENTARI

ACETO BALSAMICO DI MODENA
CONSORZIO TUTELA