



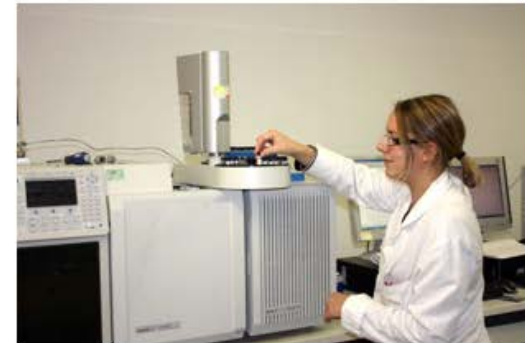
Routine detection and interpretation of anomalies using multivariate and non-targeted methods

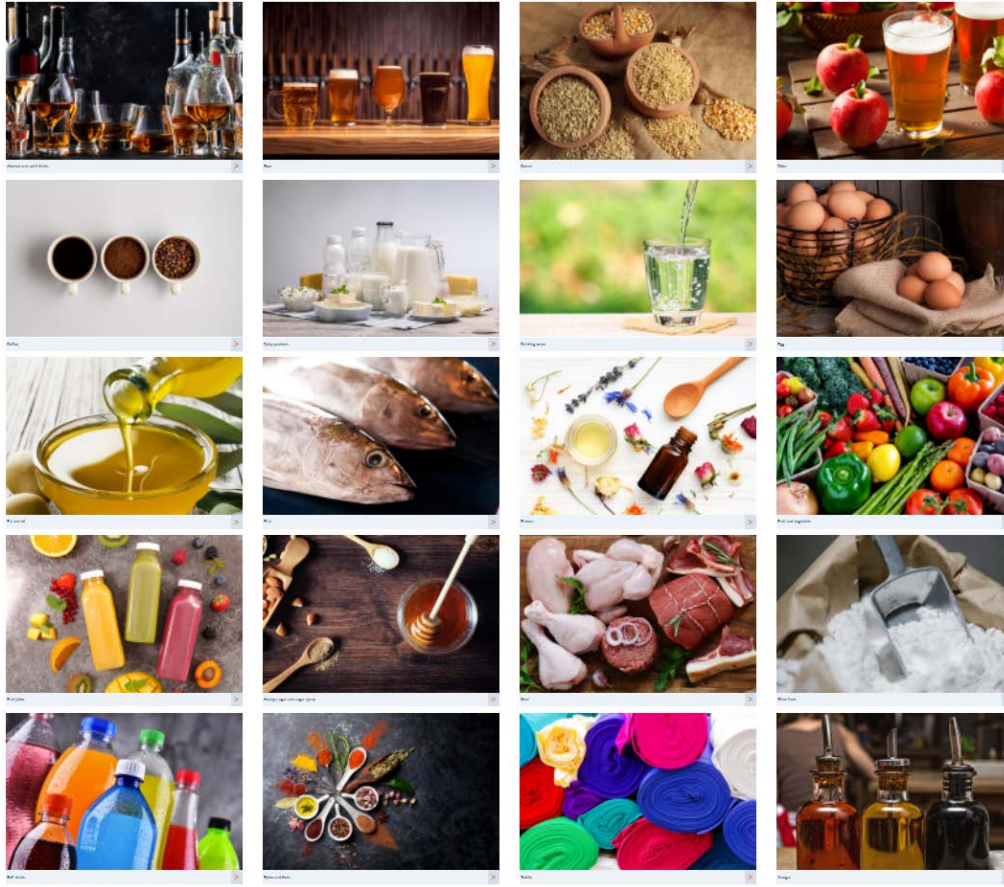
Dr. Eric Jamin
Eurofins Authenticity Competence Center,
Nantes (France)

Authenticity testing pioneers since 1987



Nantes, France
60 staff members
1500 m²





Frequent requests

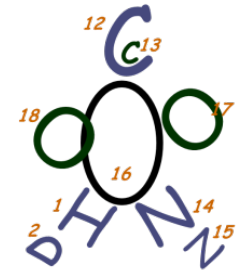
- Sugar addition
- Water addition
- Botanical origin
- Geographical origin
- Fruit content
- Undeclared additives
- Labelling check
- Naturality (high value compounds)
- Purity (high value compounds)
- Production process

All food ingredients are potentially at risk of fraud
> use of advanced methods and broad screening approaches



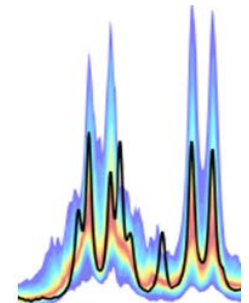
- **Stable isotopes**

- Molecules origin, natural products geo origin



- **Profiling methods**

- Whole matrices fingerprint, non-targeted approach

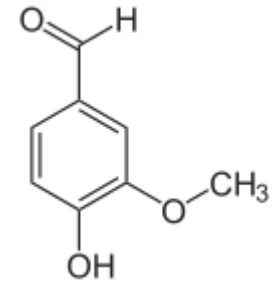
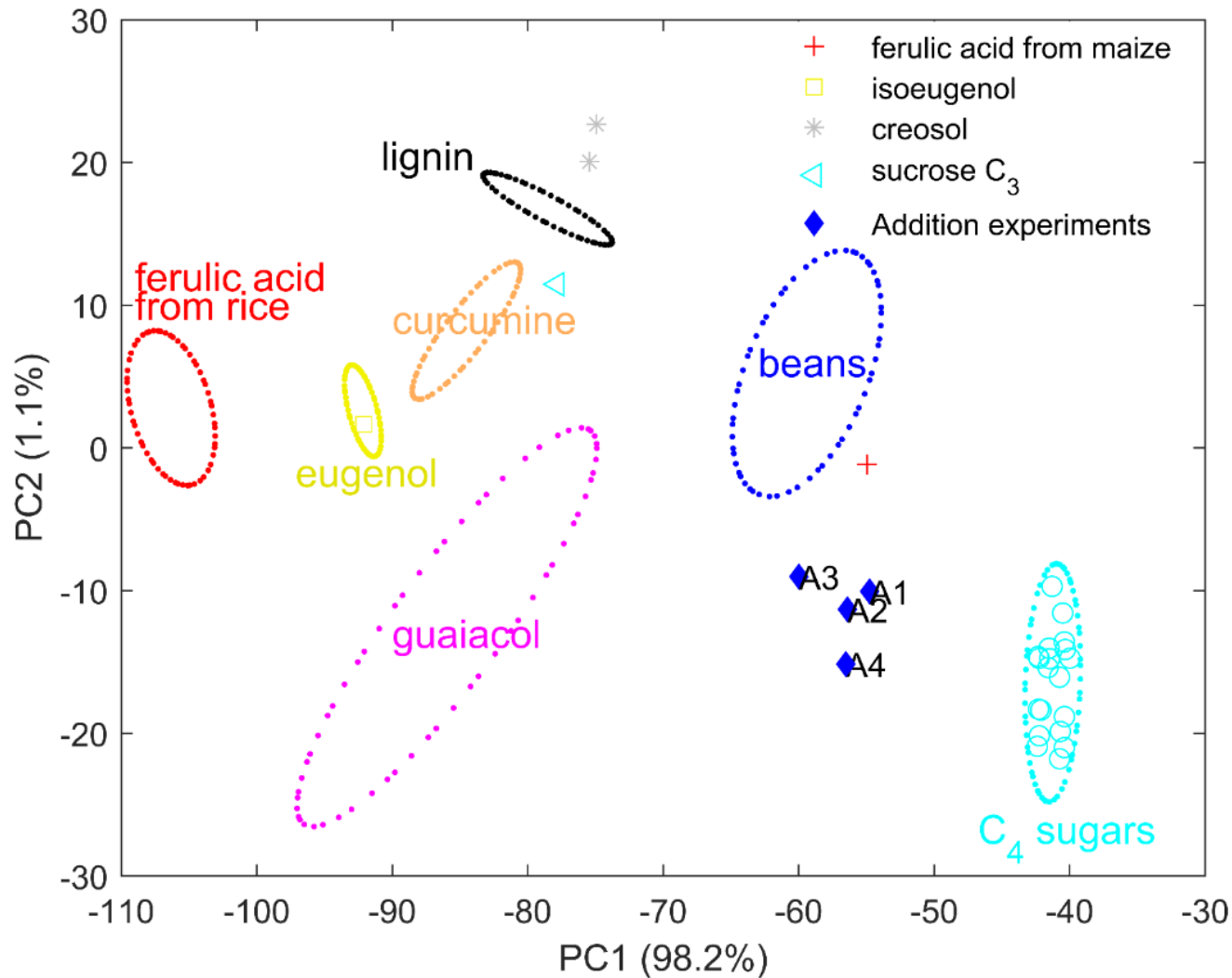


- **Chemical composition methods**

- Identification & quantification of defined compounds



Multivariate approach applied to stable isotope data: application to vanillin



C13-IRMS
Global ratio
+
C13 SNIF-NMR
Site-specific ratios

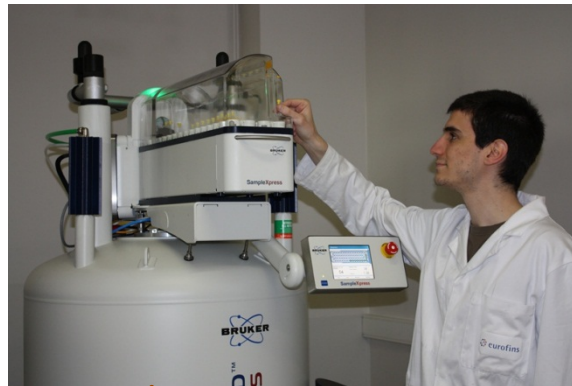
Food Control 130 (2021) 108345
<https://doi.org/10.1016/j.foodcont.2021.108345>

NMR profiling Using High Resolution ^1H NMR power

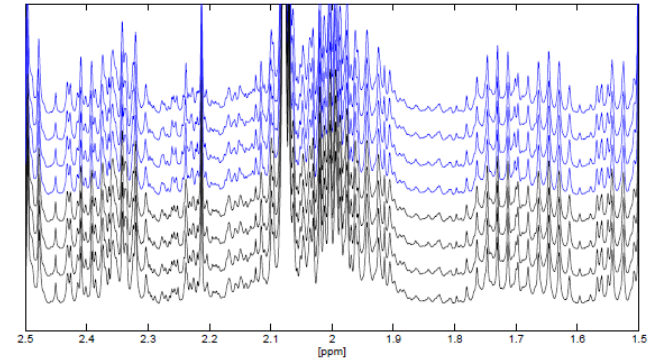
Solvent infusion/ filtration



^1H NMR



Data processing



A wide range of applications:



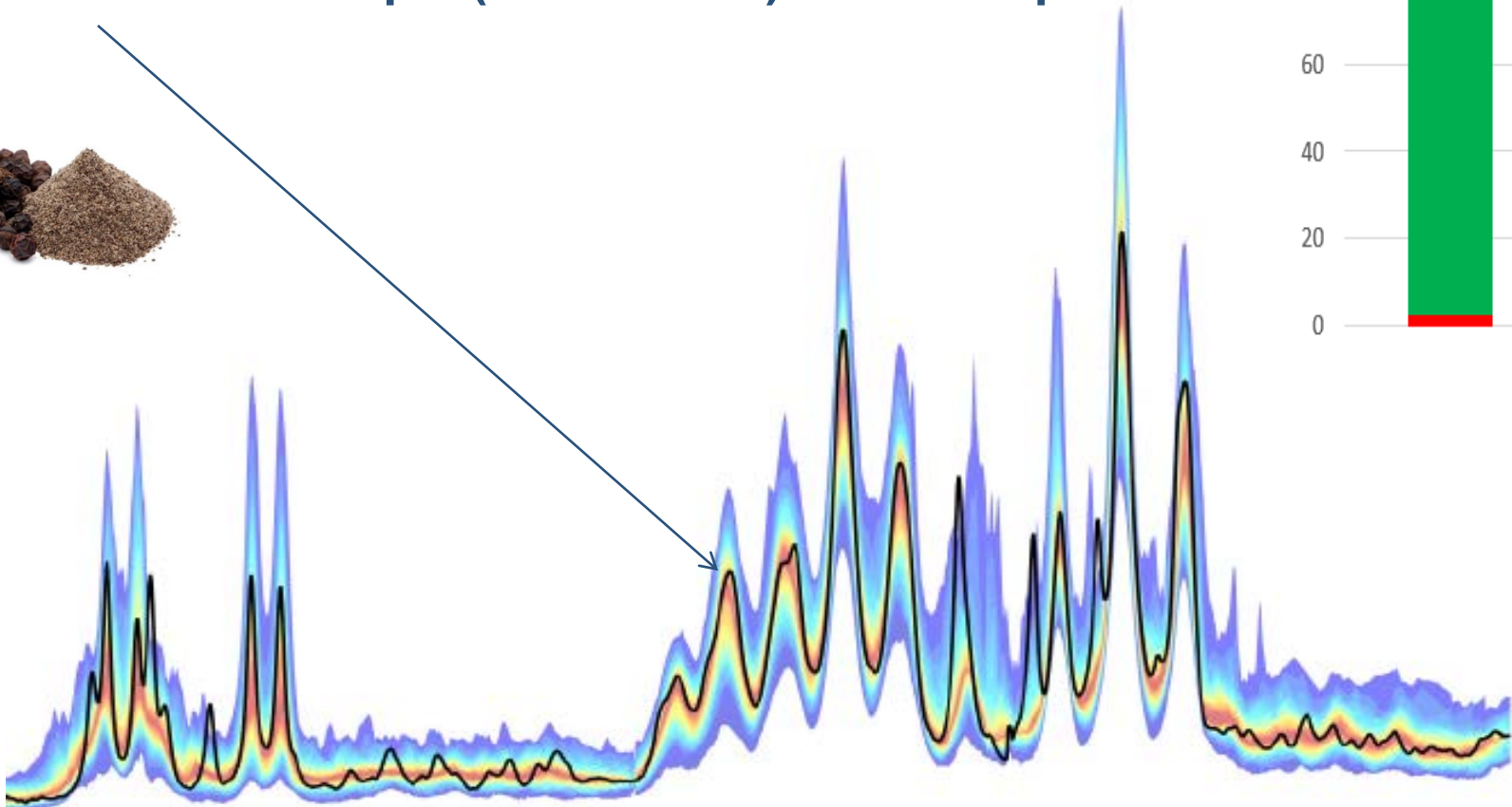
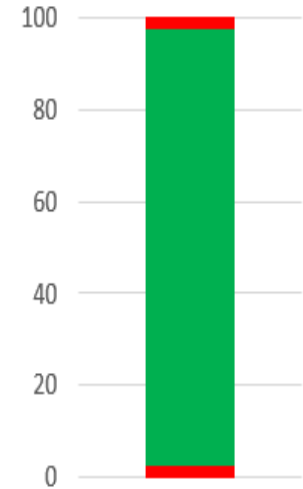
Univariate approach: spectral envelopes



- **Example 1: Black Pepper (^1H)**
- **The tested sample (black curve) fits in the profile**

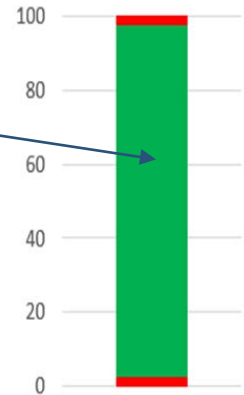


95% quantiles

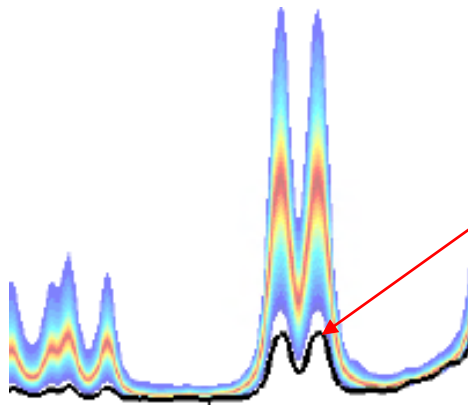




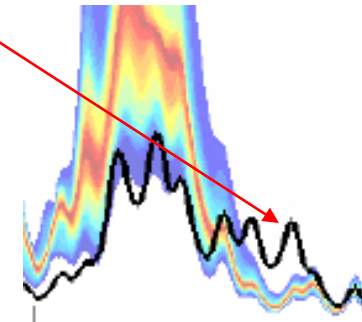
Interpretation limits based on 95% quantiles of reference honey populations



Adulterated honeys



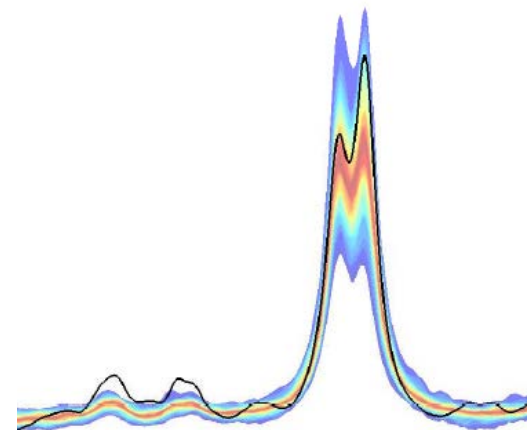
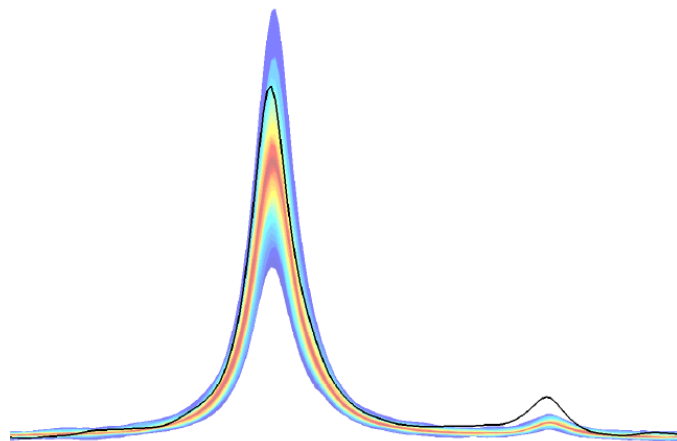
**Indirect detection:
Dilution effects**



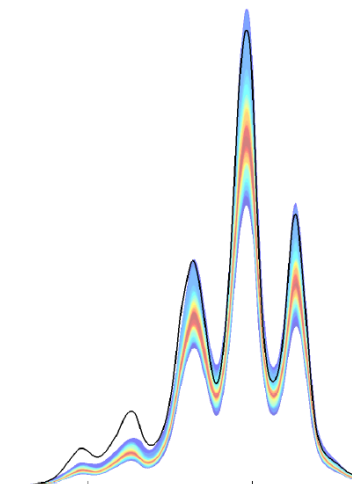
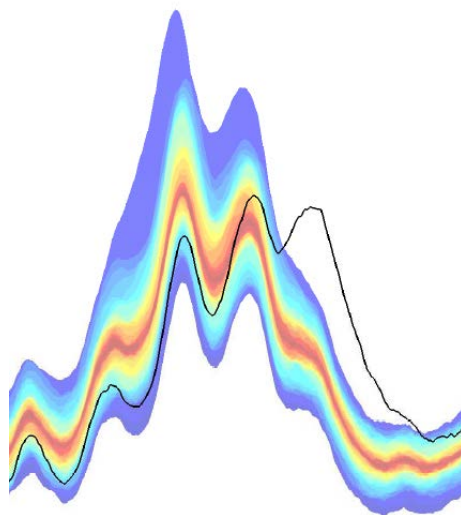
**Direct detection:
Markers of sugar syrup addition**

Anomalies detection examples: Avocado oil adulterated with rapeseed oil

^{13}C -NMR



^1H -NMR



LC-HRMS

LC - High Resolution Mass Spectrometry



Capable of separating mass fragments at the fifth decimal place (exact mass) where MS/MS instrumentation was limited to single-digit mass unit

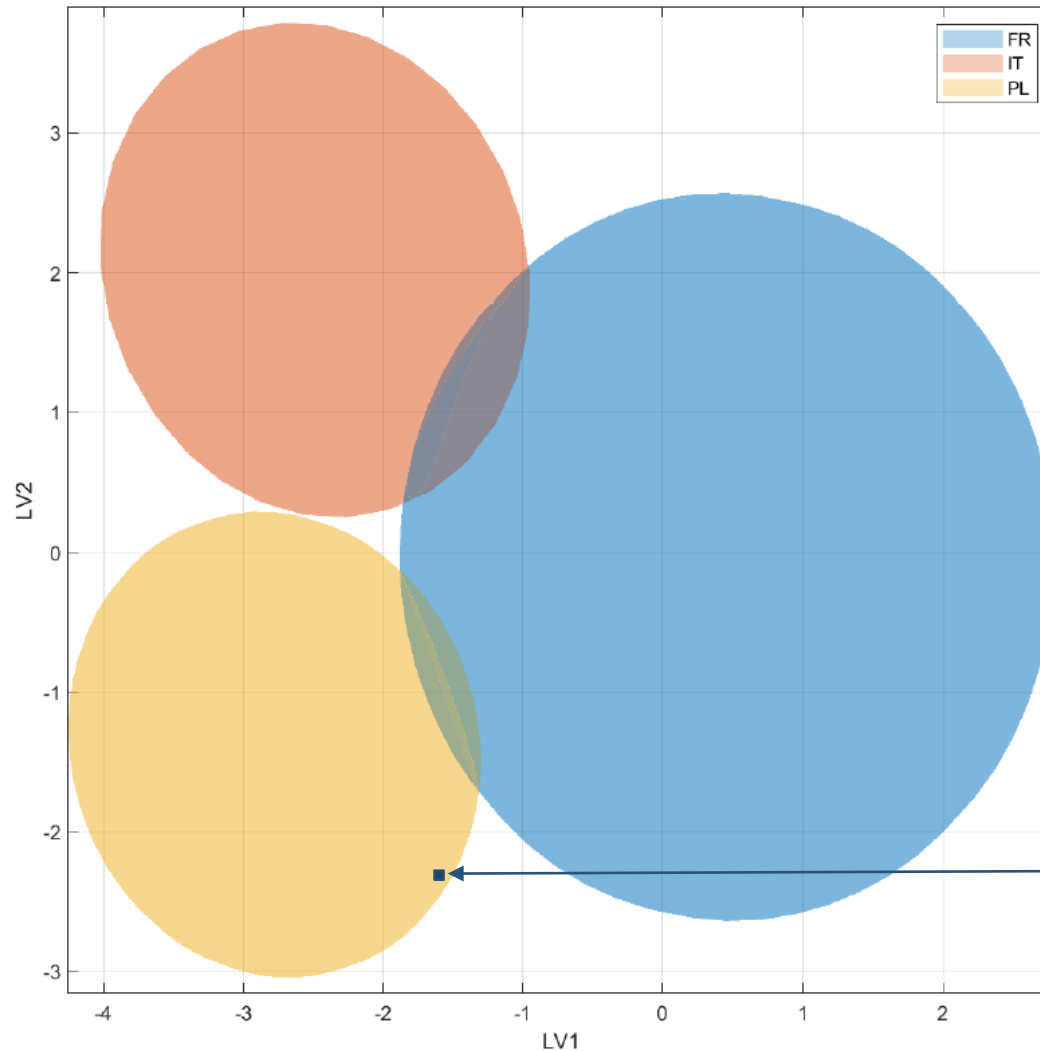
- **Target Analysis:** Detection of known markers
- **Non-target Analysis:** Detection of unknown substances, also retrospectively
- **Food Authenticity:** Non-target profiling and identification of non-natural compounds which can be used to detect manipulation or adulteration

Geographical origins: classification rates / confusion matrices



	NMR alone	IRMS alone	RMN + IRMS
Specificity	80%	87%	90%
Sensitivity	68%	93%	91%

Geographical origins: practical use of multivariate models

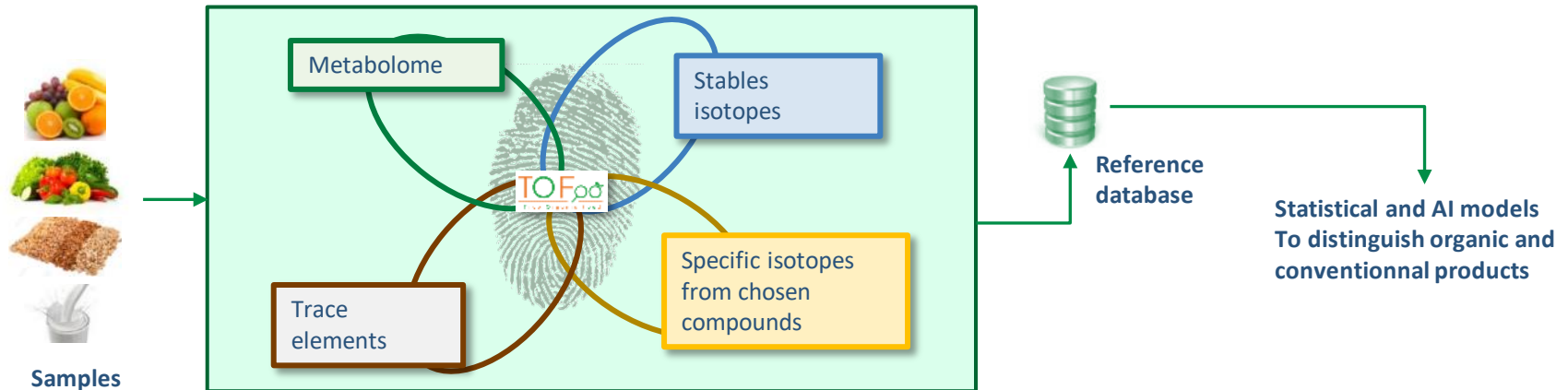


*Linear Discriminant Analysis
95% confidence ellipses*

**Tested sample
Is untypical for
FR
Consistency with
Italian model:
95%**

A French collaborative research project 2020-2025

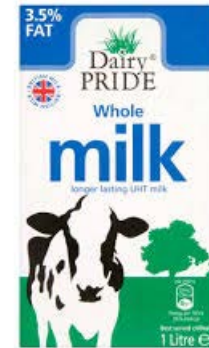




Laboratory analytical instruments optimised to catch « organic markers »

- Databases containing **hundreds of reference samples** (50% organic – all over France).
- **Two analytical techniques** chosen for each food product to get robust results.
- Several models tested to **identify organic or conventional markers**.
- Choices of models depending on the performances – with the highest score of well classified products (globally and for the organic samples) using new samples.

More than 4000 samples collected over 4 years

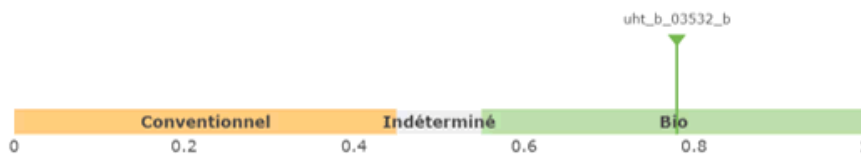


Application of the models developed in TOFOO® and based on hundreds of reference samples

CONCLUSION

Isotopic deviations and NMR spectra of this sample are in agreement with an organic production mode, based on our reference data.

The proximity of this sample with the reference group of « Organic agriculture » is illustrated below : $P=0.78$



NB: the more the sample is close to 1, the more it is close to the organic reference group.
The more the sample is close to 0, the more it is close to the conventionnal reference group. In the grey area, no conclusion will be given.

Performances

UHT milk and tomatoes

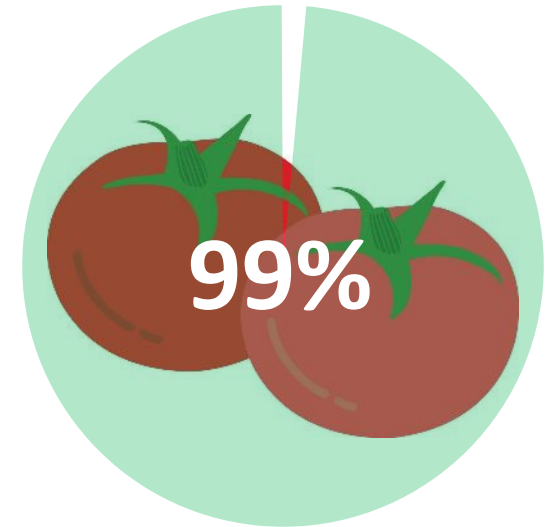
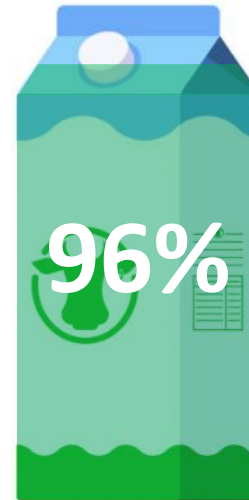
Two techniques to analyse the composition of UHT milk and tomatoes :

- IRMS (Isotopic Ratio with Mass Spectrometry),
- ¹H NMR profiling (Nuclear Magnetic Resonance).



Models built on hundreds of food products representing the market (UHT whole, skimmed and semi-skimmed milk, different origins and varieties of tomatoes, colors, cherry tomatoes, origin, etc.).

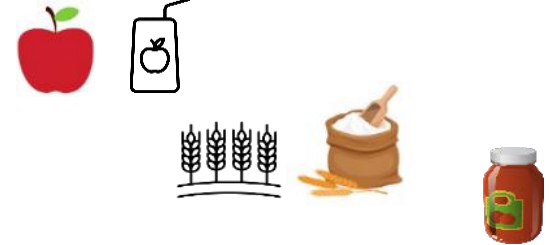
Test on new samples :



Well classified samples

New offers releases:

- Q2: Apple fruits and apple juice (NMR and LC-HRMS)
- Q3: Wheat and flour (IRMS and LC-HRMS)
- Q3: Processed Tomatoes (NMR and IRMS)



- EU enlargement (same organic regulation):
 - Validated for milk and tomatoes

Other organic products:

- Projects are being discussed for other commodities
- Extension to non EU countries can be part of such projects too

Follow the TOFoo project!



Discover our website: www.tofoo-project.com

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Routine detection and interpretation of anomalies using multivariate and non-targeted methods

Dr. Eric Jamin
Eurofins Authenticity Competence Center,
Nantes (France)

authenticity@eurofinsFR.com