Chemometrics in method validation – why?

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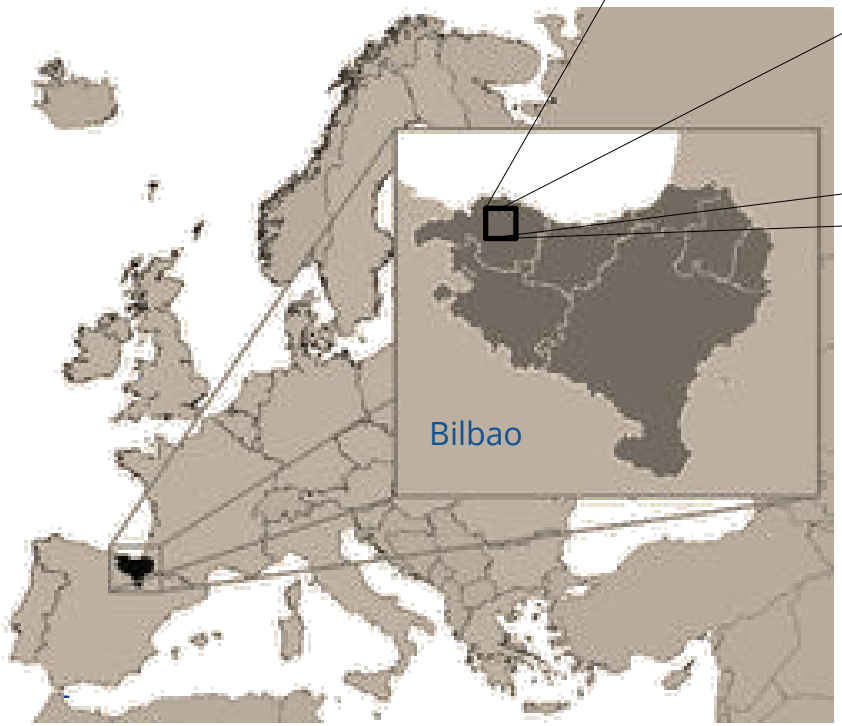
10th May 2016, Gent
Eurachem 2016

Joint Research Centre
the European Commission's
in-house science service

Early career scientist – Who am I?



PhD in analytical chemistry in 2013
'New analytical strategies for the characterization of bioactive compounds'

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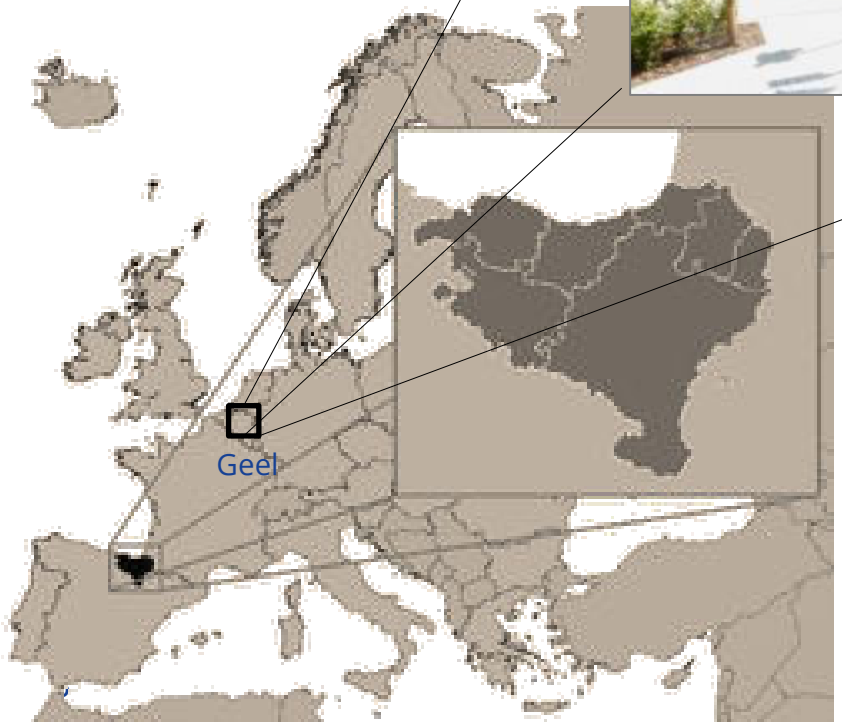
Early career scientist – Who am I?



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Institute for Reference Materials and Measurements

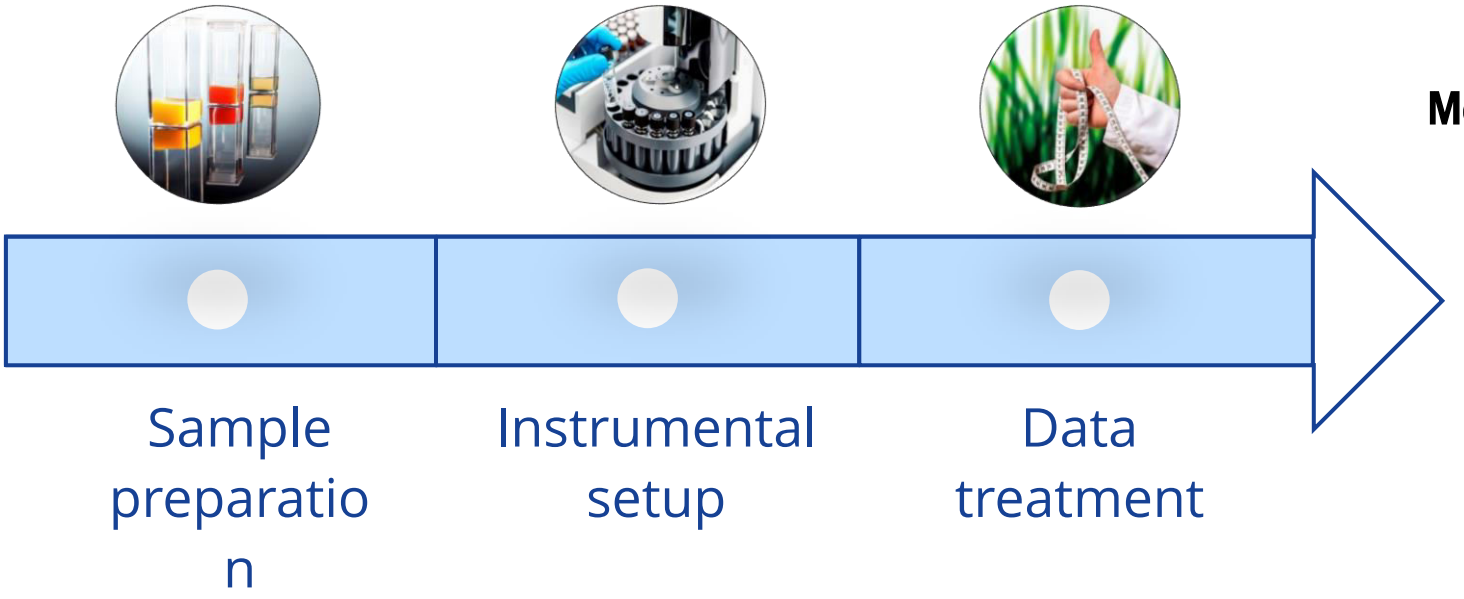
Since 2013
Research fellow in the JRC-IRMM

European Commission

Outline

- Chemometrics in method validation-why?
- Briefly, what is chemometrics
- Where can we apply chemometrics, how?
- Applicability of chemometrics, some examples
- Conclusions

Chemometrics in method validation – why?



Where can we apply chemometrics?

DoE for getting the best /optimum analyte disposition

Sample preparation

DoE for getting the best working conditions in our method & validate

Instrumenta method

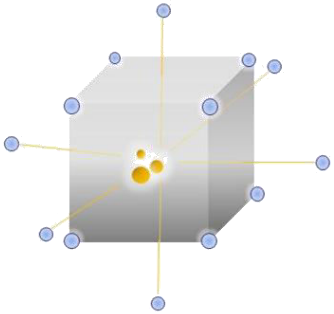
Multivariate data or image analysis

Data treatment

HOW?

What is DoE? And what advantages does

Design of Experiments = DoE



Screening designs – Full Factorial Design (**FFD**)

Information of the statistically significant parameters

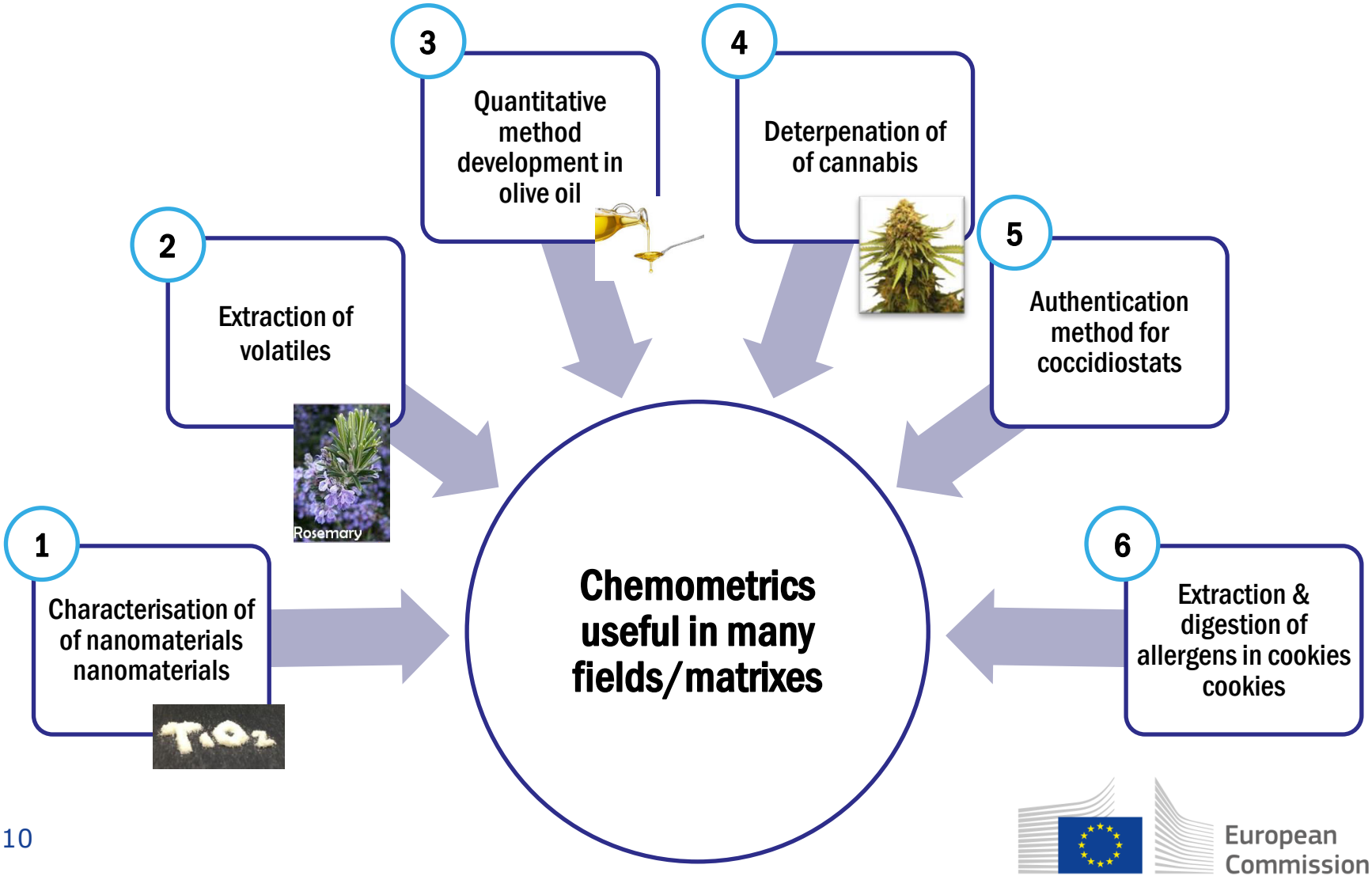
Optimisation Design – Central Composite Design (**CCD**)

Optimum conditions of the system and the interactions among the parameters

Maximum information - minimum Nº of experiments

Interaction between parameters

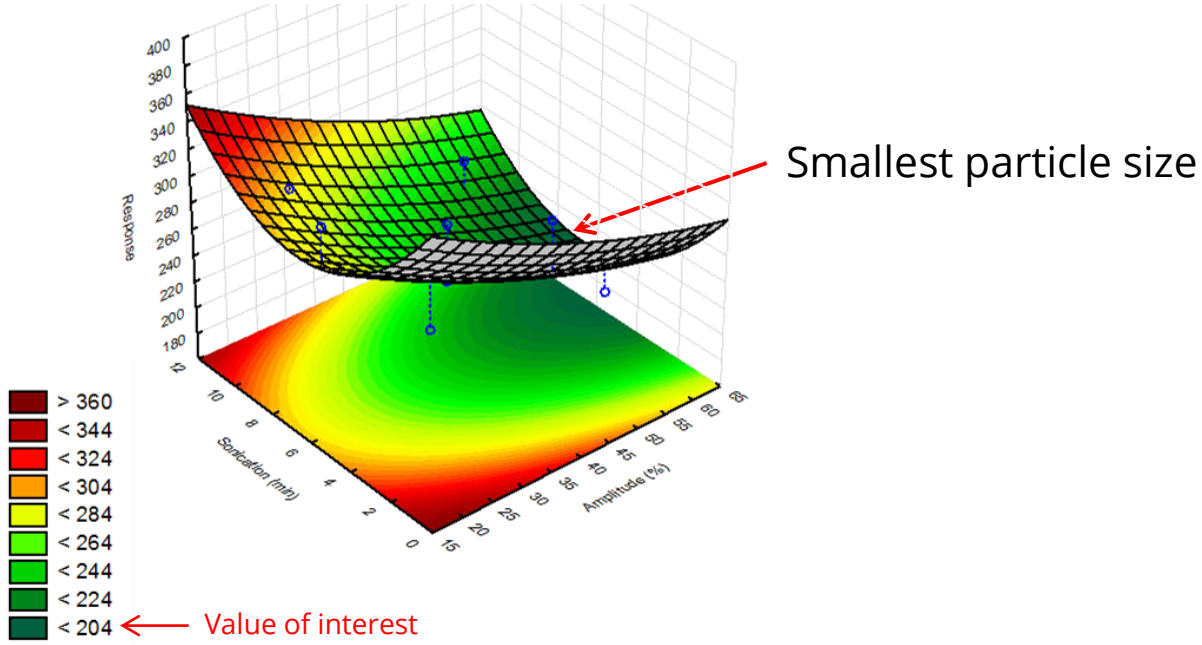
Applicability of chemometrics, some examples



Example 1: characterisation of nan

Optimise the **dispersion** of TiO_2 into minimum dispersible units

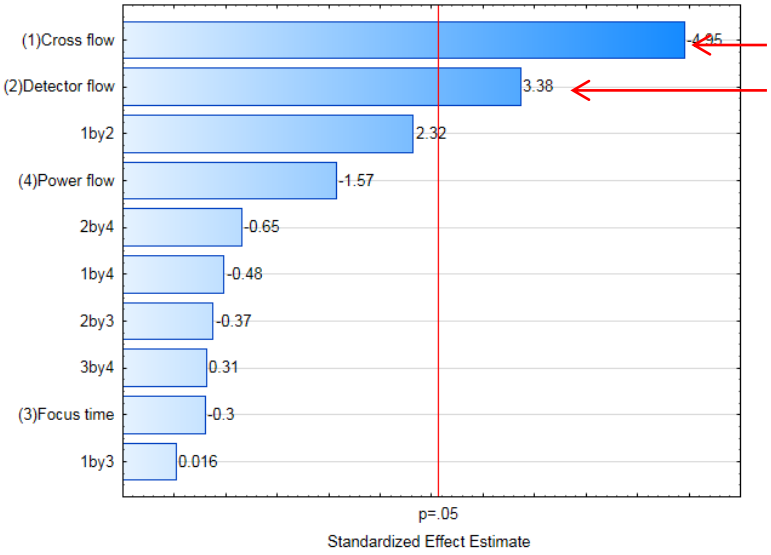
Focused Ultrasound



Example 1: characterisation of nanomaterials

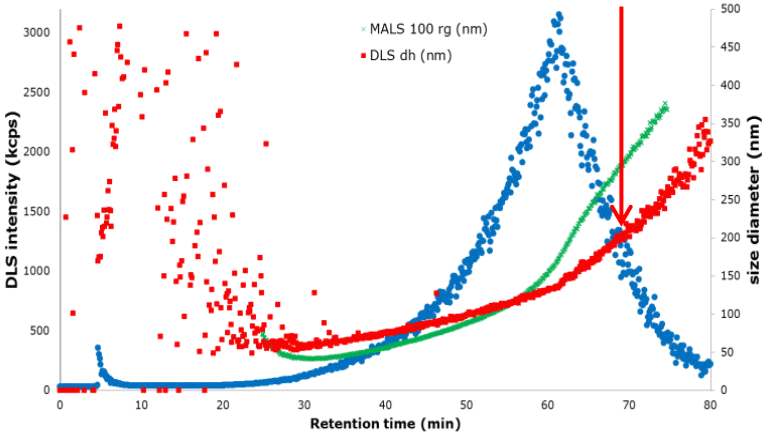
Optimise an AF4 method that can **separate** a polydisperse TiO_2 material

FFD - Pareto diagram with the significant variables



Variables to be studied in a CCD

Particle size 200nm= Value of interest



Fractogram of TiO_2 under optimised conditions

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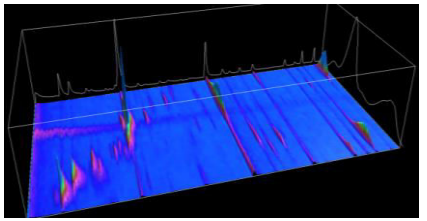
Example 2: volatiles

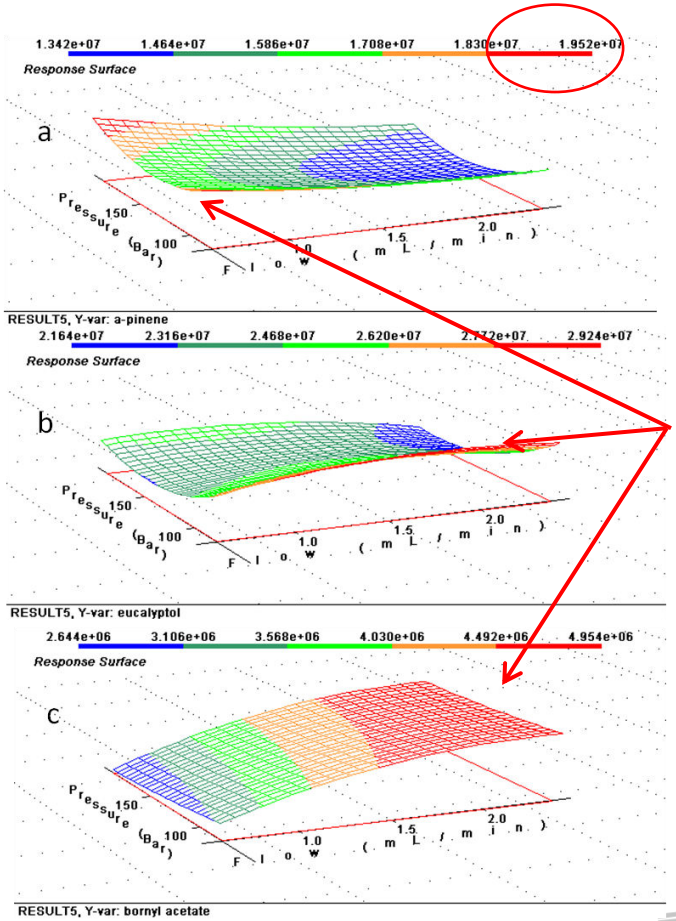


AIM

Develop & optimise a **quantitative method** for extracting aromas from plants by means of SFE or FUSE

1) Screening - FFD

2) Optimisation - CCD



15 volatiles

Highest amount = Value of interest

J.Omar, et al. Food Analytical Methods 6 (2013), 1611-1620, Optimization of FUSE and SFE of Volatile Compounds and Antioxidants from Aromatic Plants

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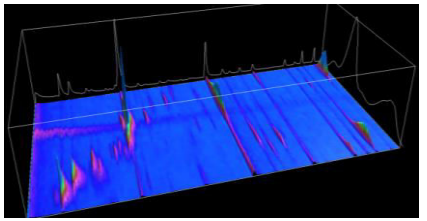
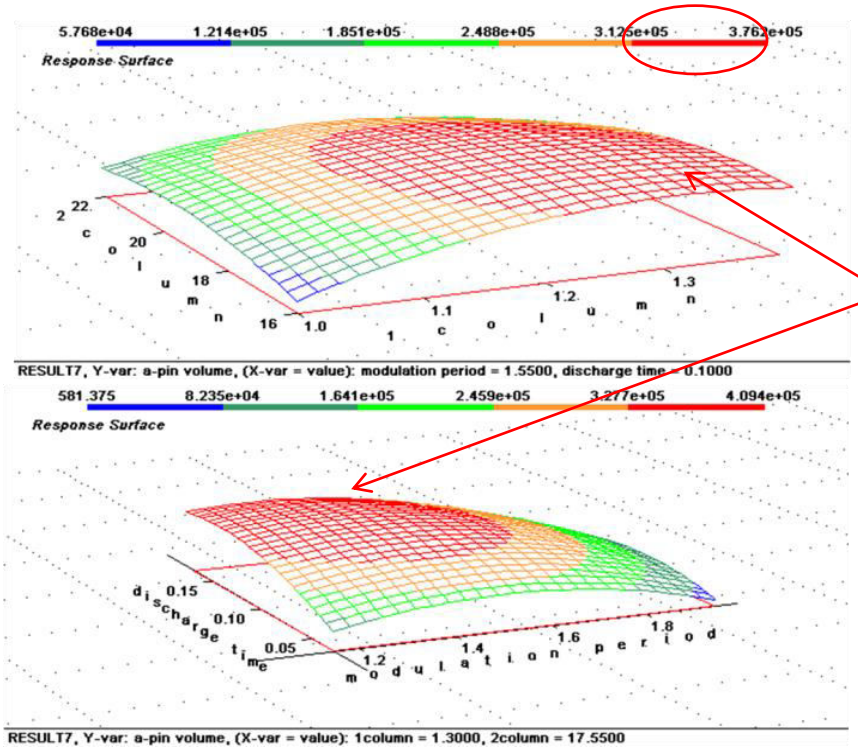
Example 2: volatiles & antioxidants

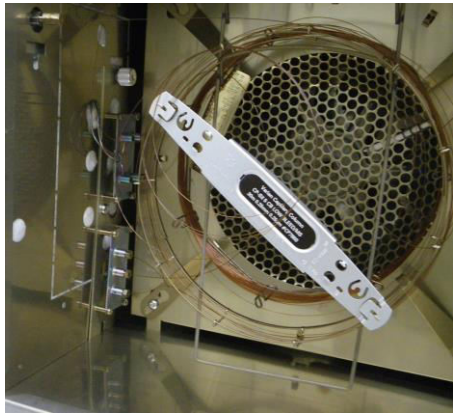


AIM

Optimise a GCxGC-MS **separation method** that suits all volatiles



Highest intensity =
Value of interest



GCxGC-MS
microfluidic modulator

J.Omar, et al. Talanta 88 (2012) 145– 151, *Optimization of comprehensive two-dimensional gas-chromatography (GC×GC) mass spectrometry for the determination of essential oils*

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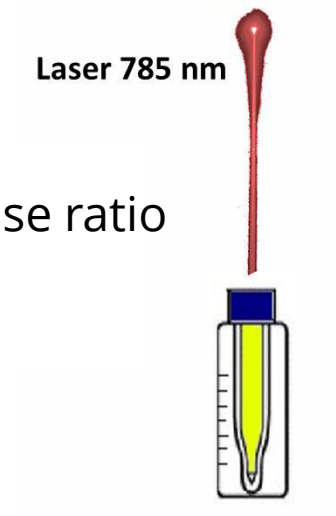
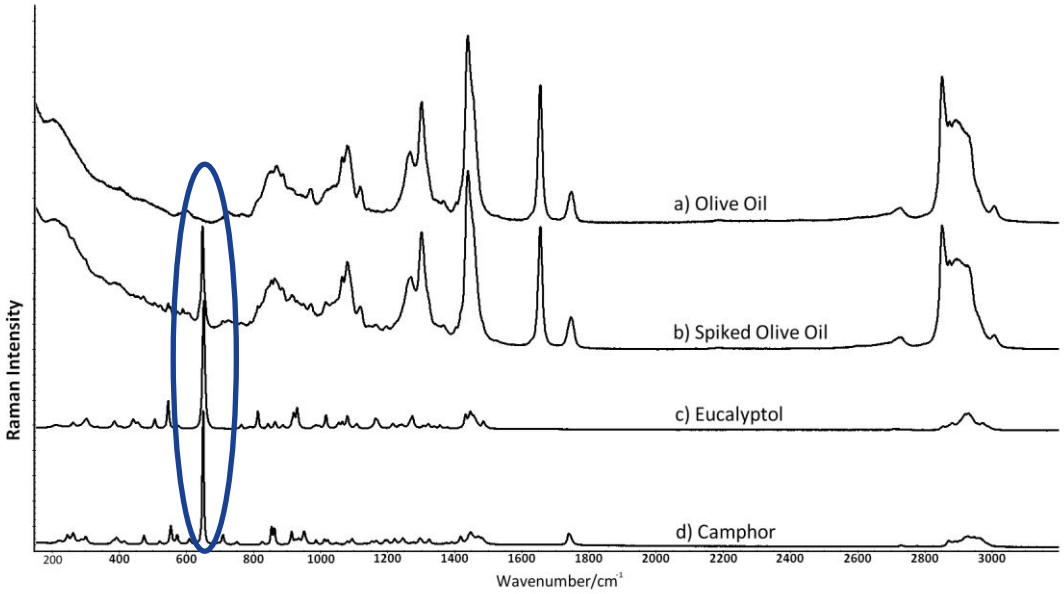
Example 3: aromas in olive oil

AIM

Optimise the **measuring conditions** of a Raman method

We look for the highest signal of the spectra
Without burning the sample
The shortest acquisition time with an acceptable signal/noise ratio





J.Omar, et al. Journal of Raman Spectroscopy 43 (2012) 1151-1156, Quantitative analysis of Essential oils from rosemary in virgin olive oil using Raman spectroscopy and chemometrics

Example 3: aromas in olive oil

AIM

Develop a **quantitative Raman** method for volatiles in olive oil

Wavenumber range

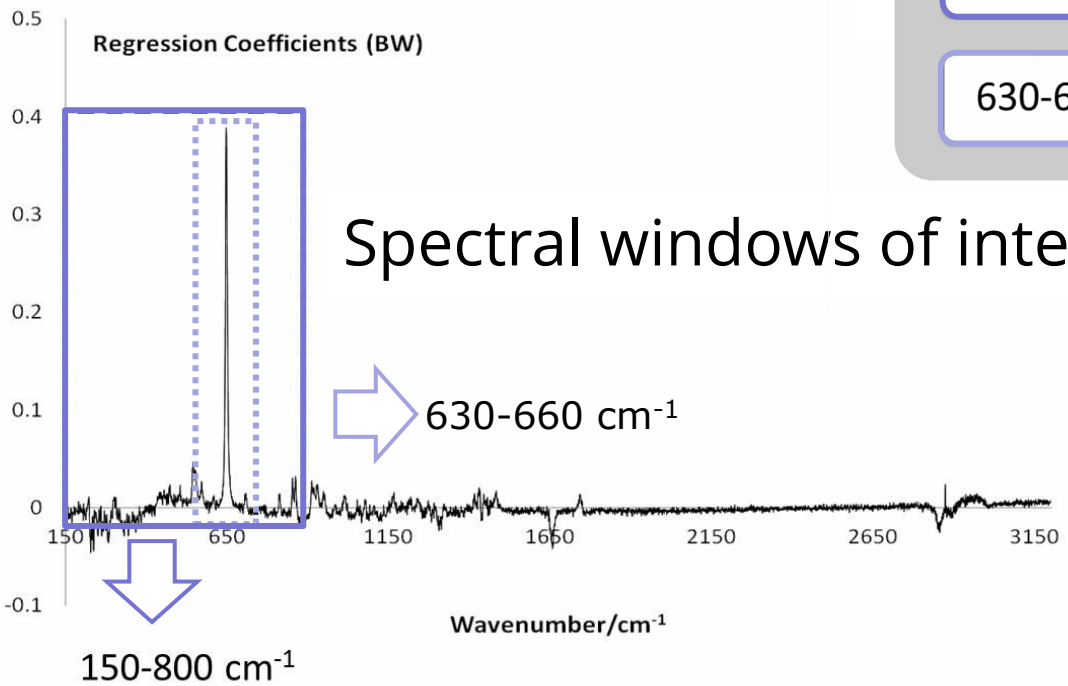
150-800cm $^{-1}$

630-660cm $^{-1}$

Spectral pre-processing

- None
- Normalize
- Baseline
- 1st derivative
- SNV

Combinations of pre-processings



Spectral windows of interest

630-660 cm^{-1}

150-800 cm^{-1}

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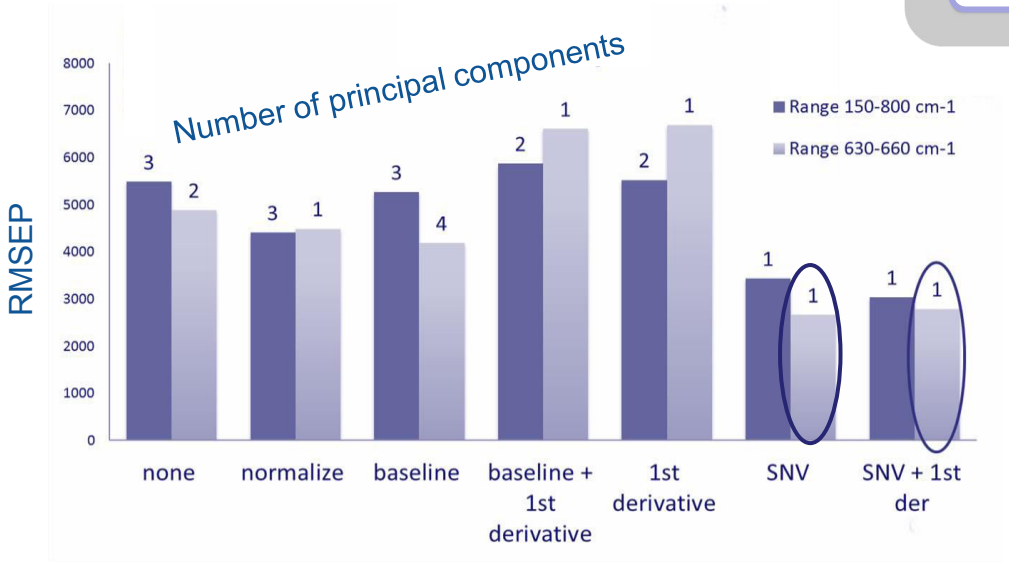

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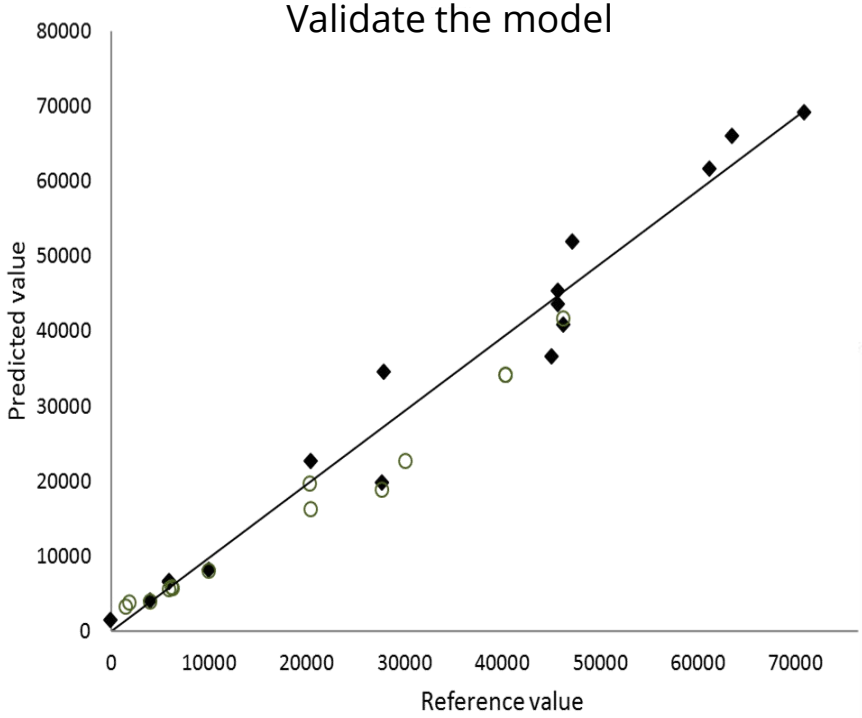
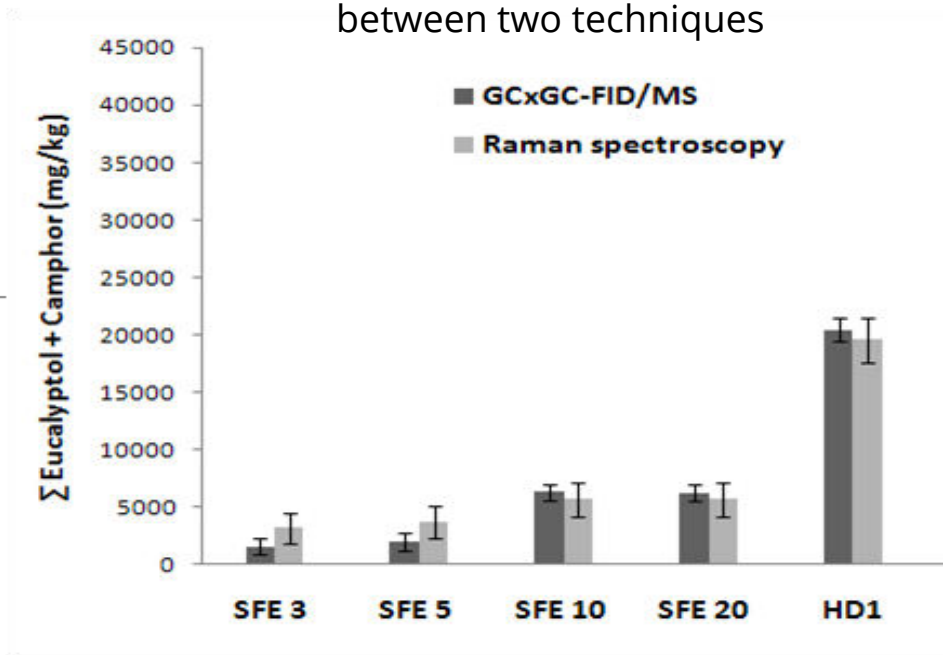
Example 3: aromas in olive oil

Validate the model



Compare real sample concentrations between two techniques



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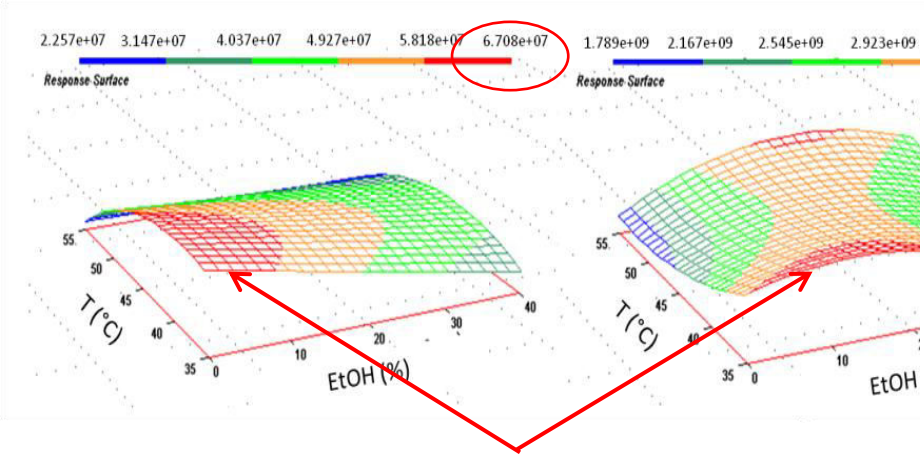
Example 4: deterpenation of can

AIM

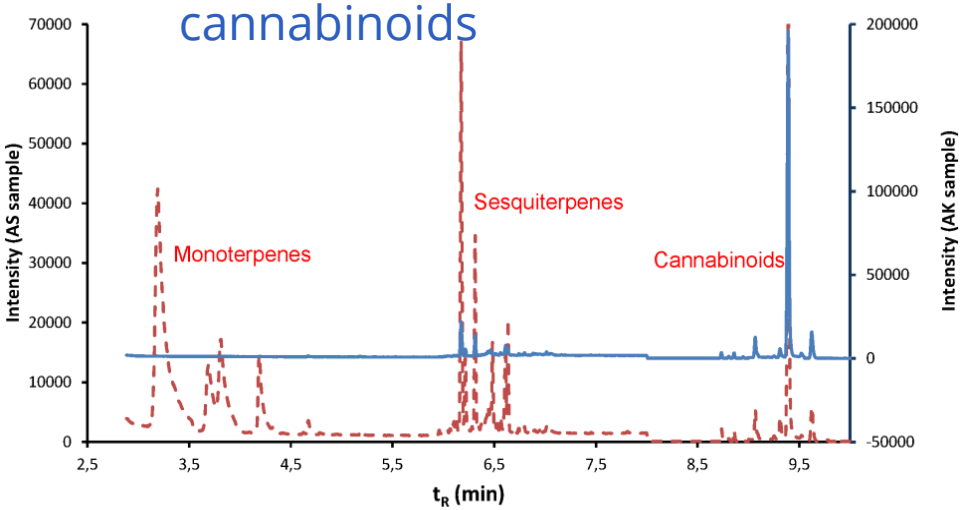
Develop & optimise a **deterpenation method** for extracting aromas & cannabinoids from cannabis by means of SFE or FUSE

1) Screening to see feasibility - FFD
2) Optimisation to get quantitative conditions - CCD



Highest amount = Value of interest

2 fractions: aromas & cannabinoids



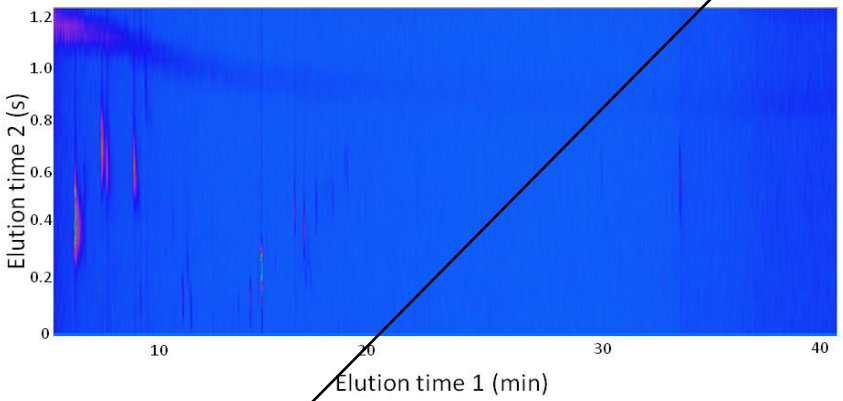
J.Omar, et al. Journal of Separation Science 36 (2013), 1397-1404, Optimisation and Characterisation of marihuana extracts obtained by SFE and FUSE and RTL-GC-MS

Example 4: deterpenation of cannabis

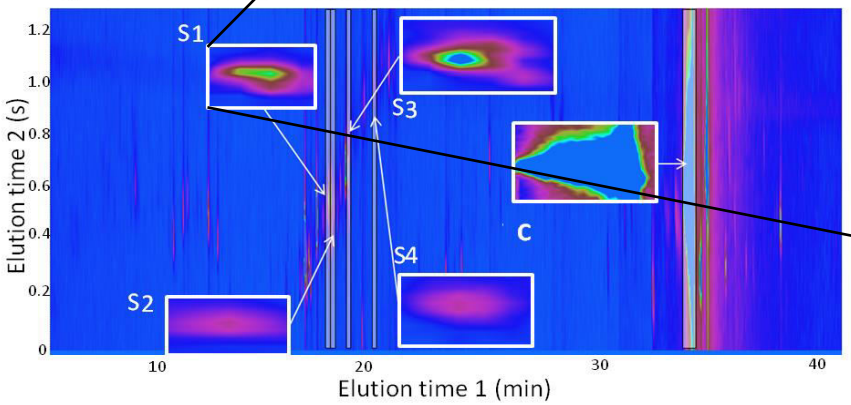
AIM

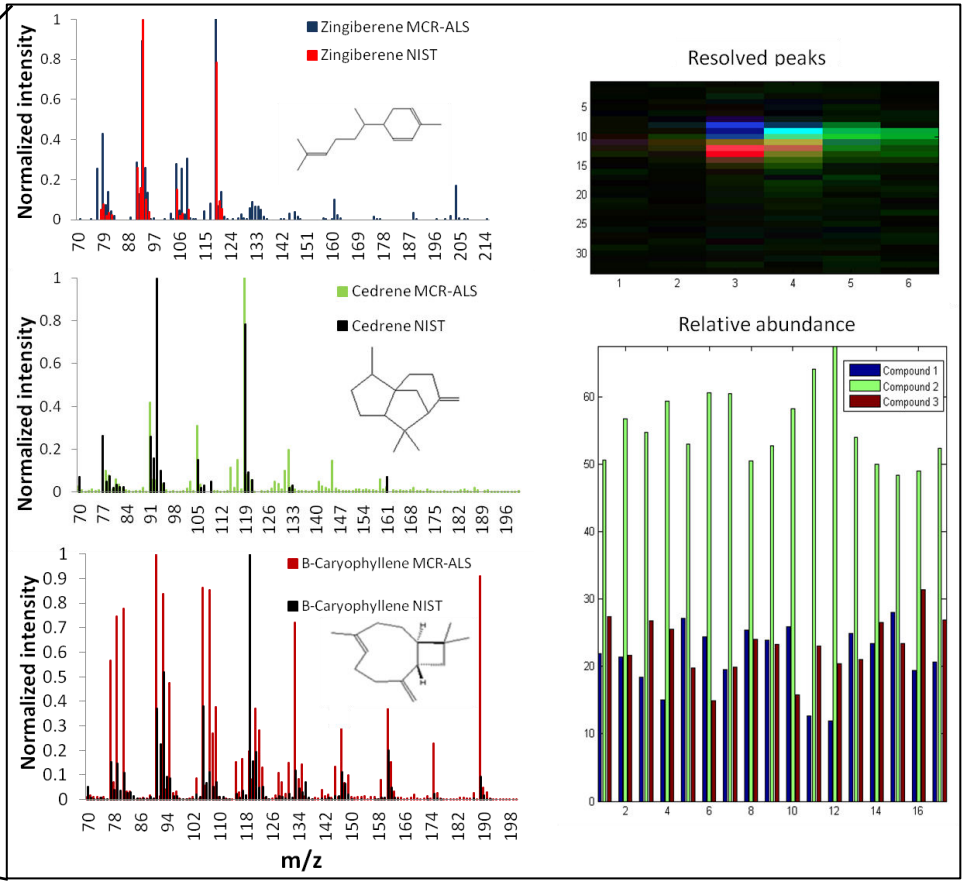
Deconvolute co-eluting sesquiterpenes and cannabinoids in GCxGC-MS

a) Monoterpene fraction



b) Cannabinoids and sesquiterpenes





MCR-ALS to deconvolute the co-elutions by means of MS information

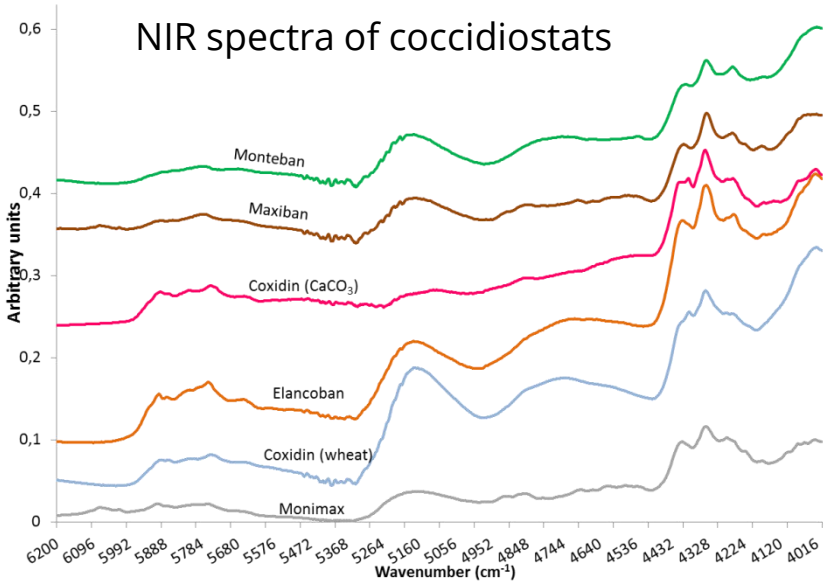
J.Omar, et al. Talanta, 121 (2014) 273-280, Resolution of co-eluting compounds of Cannabis Sativa in GCxGC-MS detection with Multivariate Curve Resolution-Alternating Least Squares

Example 5: authentication of coc

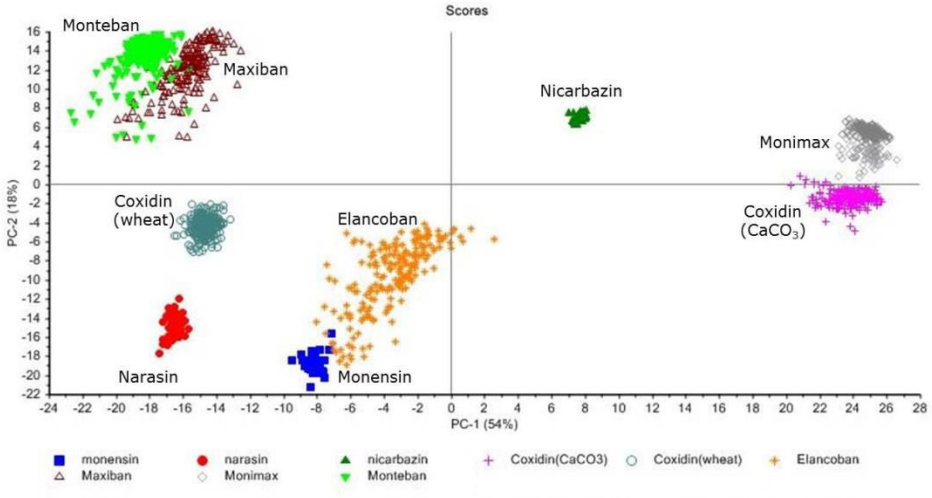
AIM

Develop a **model for authentication** of coccidiostats in NIR & MIR

NIR spectra of coccidiostats



Difficult to distinguish with the naked eye, model created by PCA and validated



J.Omar, et al. Journal of Food Additives and Contaminants, Part A, 32 (2015) 1464-1474, Differentiation of coccidiostats-containing feed additives by Mid and Near Infra-Red Microscopy

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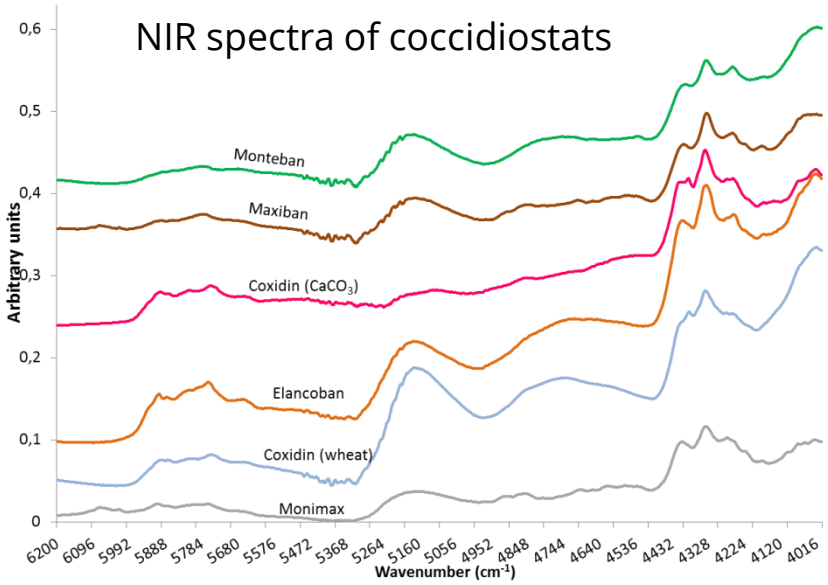
Example 5: authentication of coc

AIM

Develop a **model for authentication** of coccidiostats in NIR & MIR

NIR spectra of coccidiostats



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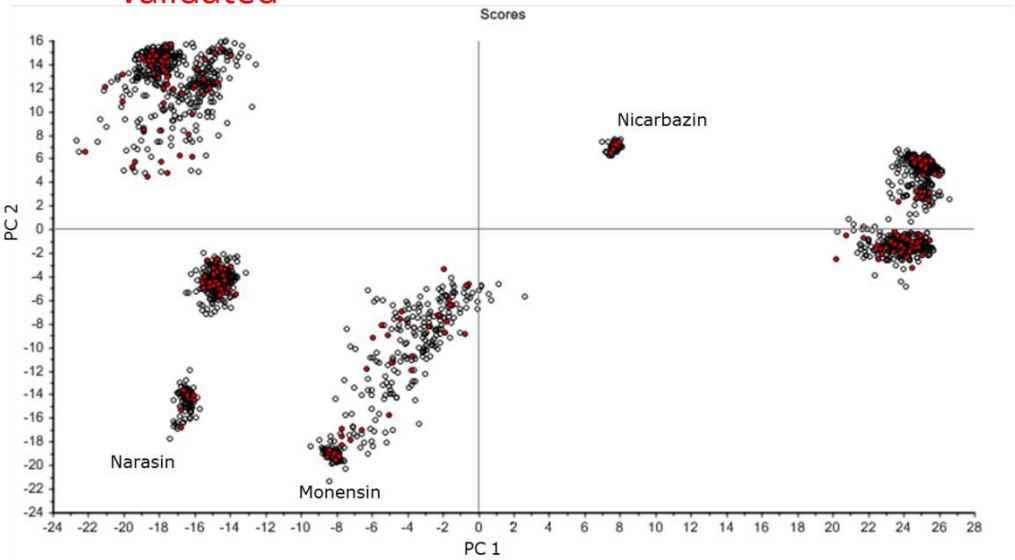
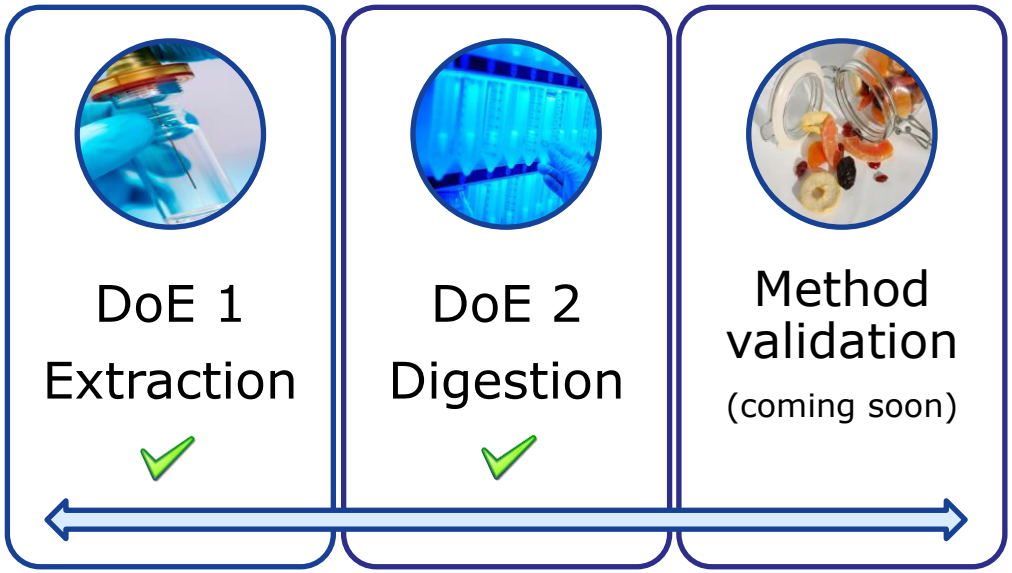


J.Omar, et al. Journal of Food Additives and Contaminants, Part A, 32 (2015) 1464-1474. Differentiation of coccidiostats-containing feed additives by Mid and Near Infra-Red Microscopy

Example 6: allergens in cookies

Develop & optimise an extraction + digestion method for MS based quantification of milk & egg allergens in food products.

Can one method suit all ?



18 peptides to monitor

compromise needed

Conclusions

-Time and money saving
-Interactions of parameters visible
-Applicability to many fields / matrixes
-Optimised methods will lead to better figures of merit

Acknowledgements

University of the Basque Country

Joint Research Centre

Standards for Food Bioscience

Stay in touch

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