FIA-ESI-MS FINGERPRINTING METHOD WITH CHEMOMETRICS FOR THE CHARACTERIZATION OF ADULTERATED COFFEE SAMPLES

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INTRODUCTION

Food products are very complex matrices, which makes the quality of these products an issue of great interest in our society. Considering the complexity of the food chain, the adulteration of food is increasing, causing food fraud cases. In this field, drinks are food products that can be very easily adulterated. This work will focus on the thematic of fraud detection in coffee, one of the most popular beverages in the world. Coffee contains an elevated number of bioactive substances (phenolic acids, polyphenols and alkaloids) that give place to its important antioxidant activity, known for its beneficial health effects. In addition, a growing tendency is the coffee adulteration with non coffee materials such as corn, barley, rice, brown sugar, soybean, among others, to reduce cost production and increase economic benefits. These practices are illegal and have not only economic consequences but could also imply a danger to the consumer health. Is for these reasons that food quality control of commercial coffee products to ensure coffee authenticity and to protect the consumers is very important.

OBJECTIVE

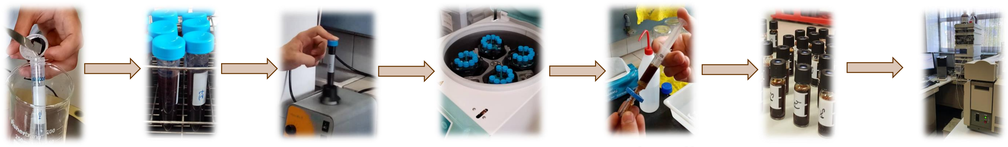
Development of rapid non-targeted FIA-ESI-MS fingerprinting method in combination with chemometrics to achieve the Characterization, Classification and Authentication of coffee samples, together with possible adulterants (barley, chicory and flours) using PLS-DA in order to try to prevent frauds in the future. Furthermore, PLS regression was employed to detect and quantify adulterant levels on adulterated Arabica and Robusta coffee samples.

EXPERIMENTAL PROCESS

SAMPLES

Sample Class	Sample Type	Number of Samples
Coffee	Vietnamese Arabica coffee	13
	Vietnamese Robusta coffee	26
	Vietnamese Arabica and Robusta mixture coffee	9
	Cambodian coffee (Unknown specie)	6
Chicory	Chicory	21
Barley	Barley	6
Flour	Wheat flour	7
	Rice flour	4
	Corneal flour	11
	Rye flour	15
	Oatmeal flour	5

Sample treatment



1 g of sample (15 mL tube PTFE) → 10 mL of methanol:water 50:50 *(v/v)* → The mixture was shaken vigorously for 2 min (Vortex) → The extracts were centrifuged at 3500 rpm for 5 min (Rotanta 460 RS centrifuge) → Transfer coffee extracts to injection vials filtering with 0.45 µm nylon filters → Analysis with the FIA-ESI-MS proposed method

INSTRUMENTATION AND CONDITIONS

Non-targeted FIA-ESI-MS fingerprinting method

Instrument	4000 QTrap mass spectrometer
Ionization source	Electrospray in negative mode
Adquisition	Full scan (m/z 100 - 550)
Scan time	1.5 minutes

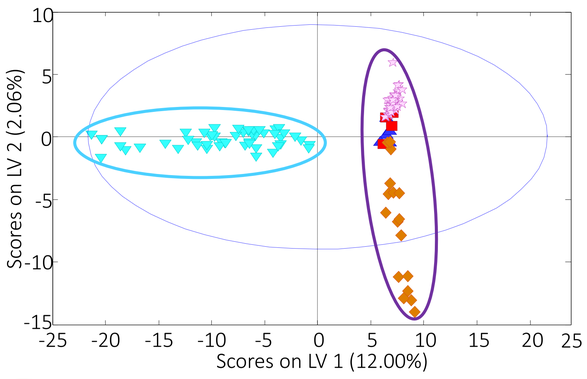
Optimised parameters of ESI source	
Curtain gas (psi)	10
Collisionally Activated Dissociation	-3
Nebulizing gas (psi)	50
Drying gas (psi)	50
Spray voltage (V)	-2500
Temperature (°C)	400
Declustering potencial (V)	-80
Collision Energy	-5

RESULTS

CHEMOMETRICS

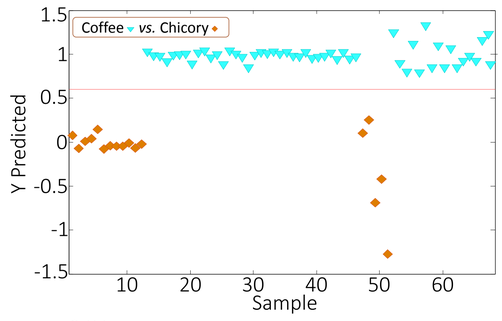
NEGATIVE MODE RESULTS

PLS-DA SCORES PLOT OF NON ADULTERATED SAMPLES

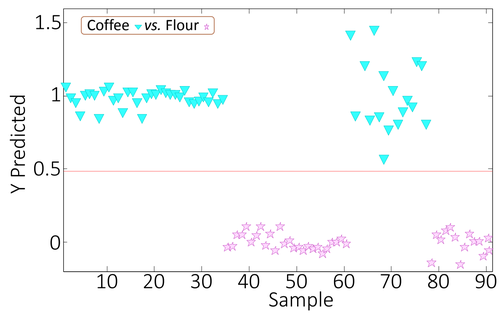


Clear discrimination between coffee samples and adulterants samples

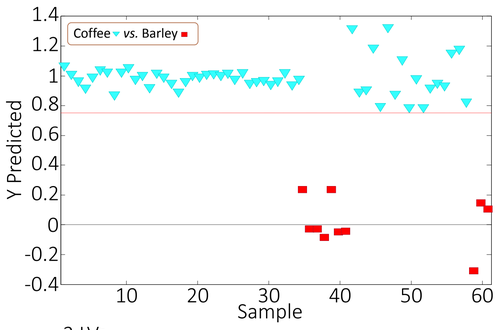
PLS-DA VALIDATION



2 LVs
Classification rate: 100%



3 LVs
Classification rate: 100%



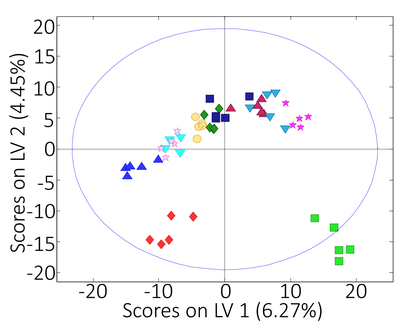
3 LVs
Classification rate: 100%

SCORES PLOTS OF ADULTERATED ARABICA AND ROBUSTA SAMPLES

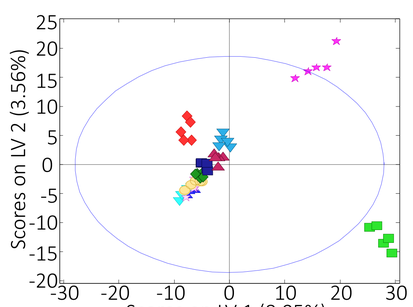
PLS-DA models
(In all of them, samples tend to be distributed according to the level of the adulterant coffee)

PLS models
(Dark and blue symbols correspond to calibration and validation sets)

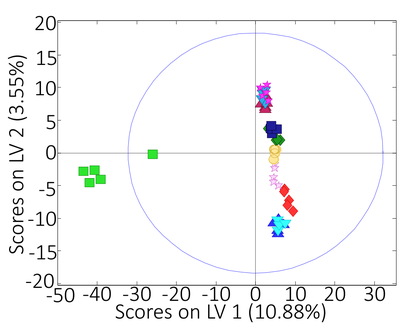
Arabica Coffee vs. Chicory



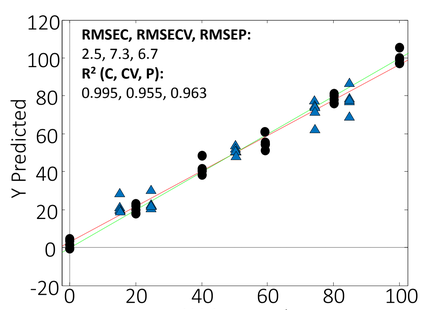
Arabica Coffee vs. Flour



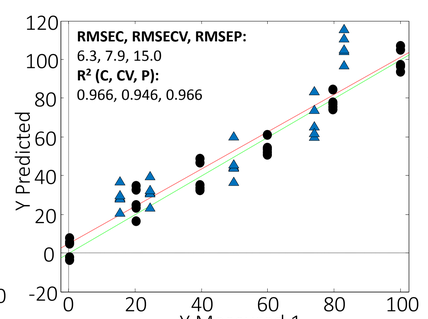
Arabica Coffee vs. Barley



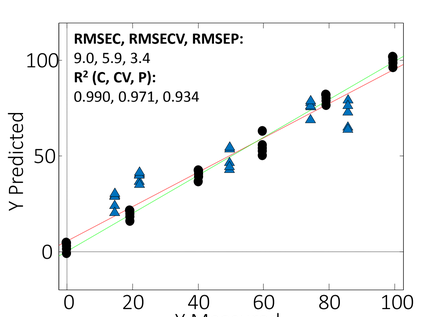
Arabica Coffee vs. Chicory



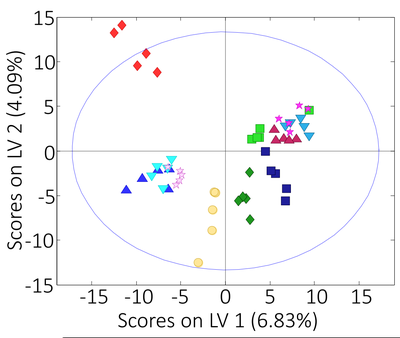
Arabica Coffee vs. Flour



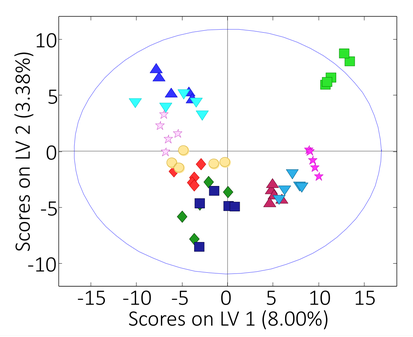
Arabica Coffee vs. Barley



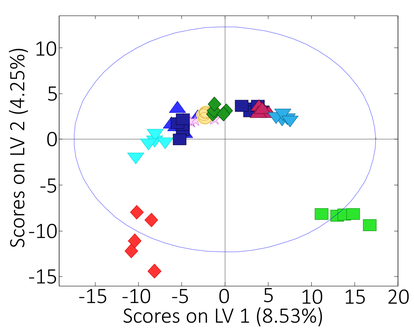
Robusta Coffee vs. Chicory



Robusta Coffee vs. Flour

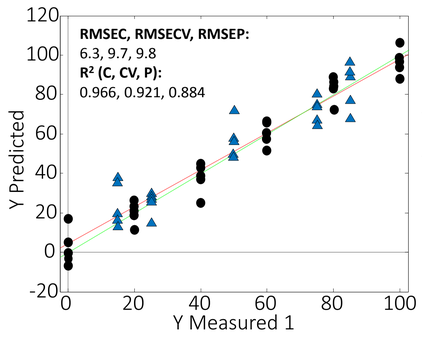


Robusta Coffee vs. Barley

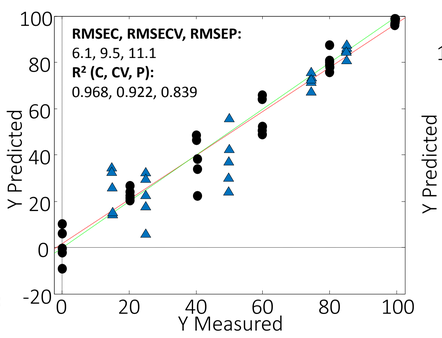


0% of adulterant ◆ 15% of adulterant ▲ 20% of adulterant ▼ 25% of adulterant ☆ 40% of adulterant ○ 50% of adulterant ◆
60% of adulterant ■ 75% of adulterant ▲ 80% of adulterant ▼ 85% of adulterant ★ 100% of adulterant ■

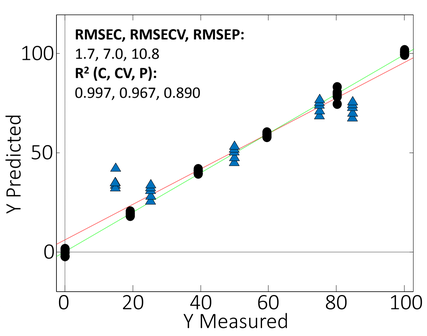
Robusta Coffee vs. Chicory



Robusta Coffee vs. Flour



Robusta Coffee vs. Barley



CONCLUSIONS

- FIA-ESI-MS fingerprinting method were developed for the classification of coffees and some adulterants.
- The proposed FIA-ESI-MS method provided suitable chemical descriptors to address the characterization, classification and authentication of coffee samples in front adulterants like chicory, flour and barley.
- Chemometric analysis of the obtained chemical descriptors allowed the classification of the analyzed coffee and adulterant samples.
- The proposed PLS-DA methods were validated for the authentication of Arabica and Robusta coffee samples obtaining classification rates of 100%.
- PLS-DA chemometric analysis for adulterated samples using the fingerprints provided by the proposed method revealed patterns that were perfectly correlated to the percentage of adulteration.
- Satisfactory errors of calibration, cross validation and prediction, as well as good linearity, were obtained for most of the studied cases with PLS models.
- The proposed method will be useful in the future in the field of coffee authentication for the prevention of frauds.

REFERENCES

- N. Núñez, J. Saurina, O. Núñez, Authenticity Assessment and Fraud Quantitation of Coffee Adulterated with Chicory, Barley, and Flours by Untargeted HPLC-UV-FLD Fingerprinting and Chemometrics, Foods (2021), 10, 840

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