Fuzzy algorithms applied in fruit spirits authentication

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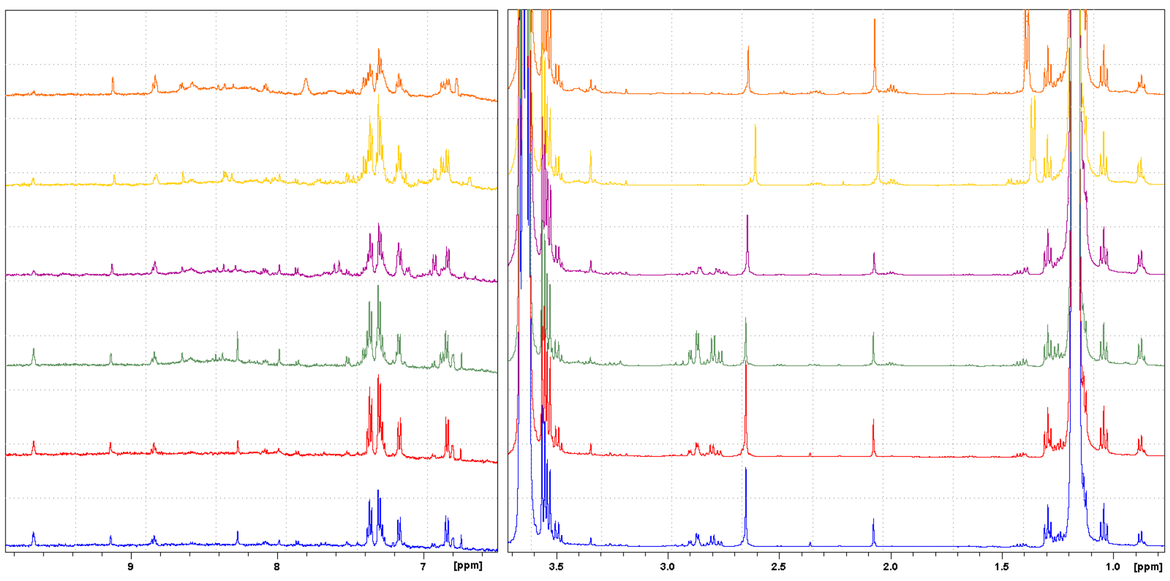
Abstract. The development of analytical approaches based on distinct types of spectroscopies in corroboration with either advanced chemometric models or artificial intelligence represents nowadays a priority for research and control laboratories, in the attempt to develop efficient tools for adulteration detection of food and beverages. The choose of the optimum data processing method, is important issue in the development of reliable models for alcoholic beverages differentiation. In order to prospect the efficiency of the application of ^{1}H-NMR spectroscopy in conjunction with Fuzzy algorithms, in this study a fruit spirits sample set were employed, for different classifications.

The ^{1}H-NMR measurements were recorded in buffered D_2O solution and all chemical shifts were measured relative to TSP (3-(trimethyl-silyl)-propionic acid sodium salt), added as internal standard referencing the chemical shift to 0 ppm, applying water suppression pulse program for irradiation of the water signal.



^{1}H NMR spectra of Romanian (first 3 samples from bottom up) vs. French vine samples

Sample

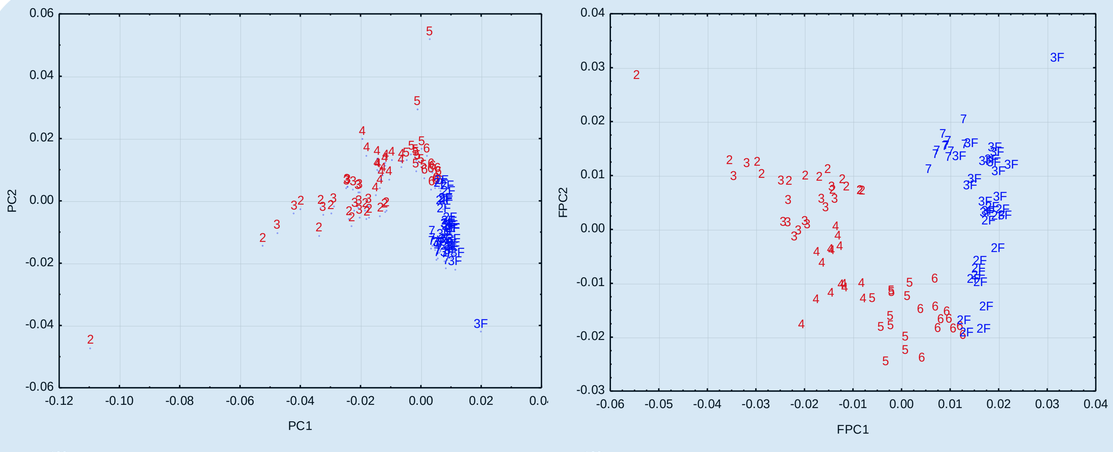
NMR Probehead

BRUKER AVANCE III 500 NMR spectrometer
Magnetic field: 11.7 Tesla

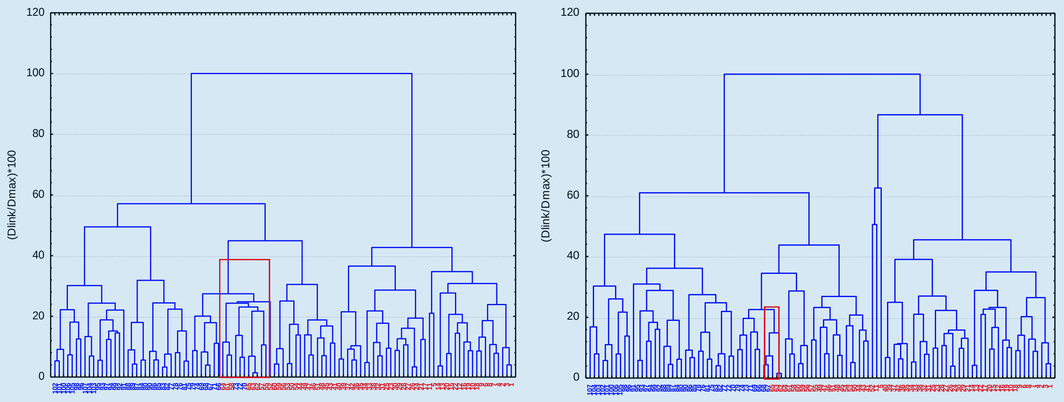
Principal Component Analysis (PCA) / Fuzzy Principal Component Analysis (FPCA)

After NMR spectra decomposition, a very large data was obtained and for an efficient and fast chemometrical processing, these two methods were applied. The resulted score matrix was used for further interpretation.

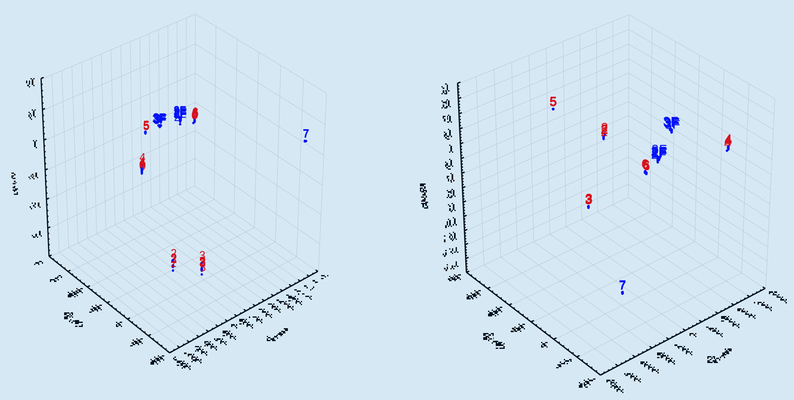
Wine's discrimination



Scores representation of 107 wine samples, produced in Romania – in red - vintages 2012- (2), 2013- (3), 2014- (4), 2015- (5) and 2016- (6) and France – in blue - 2012- (2), 2013- (3), 2017- (7), in the plan described by the first two main components: PCA (a), FPCA (b)

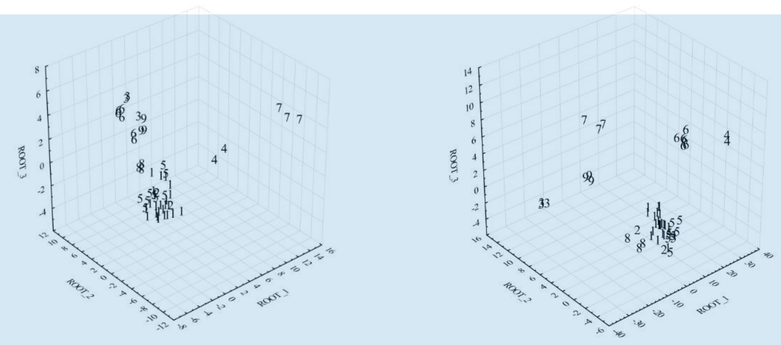


Dendrogram corresponding to the scores obtained with the classical method (a) and the fuzzy method (b), respectively of Romanian (red) and French (blue) wines spectra

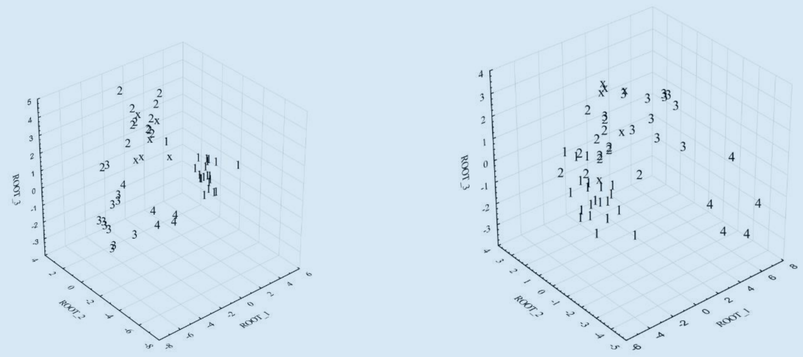


3D representation, of the canonical scores (corresponding to the vintage) obtained by applying the discriminant analysis on the scores from PCA (left) and to the fuzzy principal component analysis FPCA (right)

Fruit distillates discrimination



Fruit's distillates classification (2D and 3D) according to the fruit type, obtained with classical/PCA and fuzzy/FPCA (plums – 1; apricots - 2; cherries – 3; sour cherries – 4; apples -5; grapes – 6; quinces – 7; pears -8; blackberry – 9)



Fruit's distillates classification (2D and 3D) according obtained with classical/PCA and fuzzy/FPCA (plums – 1; apricots -2; cherries – 3; sour cherries – 4; apples -5; grapes – 6; quinces – 7; pears -8; blackberry – 9)

Conclusions

For both working matrices, the best results (complete separation of the samples according to the considered criteria) were obtained by applying **principal component analysis** based on the fuzzy sets theory and the **discriminant analysis** based on scores obtained with the latter method.

In the case of wine samples, a very good geographical differentiation was also obtained when **cluster analysis** was applied to the score matrix obtained after PCA and FPCA.

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