

ACTIVITY REPORT 2021

For the implementation of the Postdoctoral Project **PD 90/2020**

Advanced chemometric methods applied for authentication and traceability of Transylvanian agriproducts – *AGRICHEM*

Stage 2. Evaluation of the elemental and isotopic profile of natural juices, using ICP-MS and IRMS, and processing of experimental data using classical and advanced chemometric techniques (January-October 2021)

Summary of the stage

In this stage of the project, 108 juices samples were analyzed from isotopic and elemental content point of view. Among these, 35 samples were from freshly squeezed apples and 37 samples were from oranges. The rest of the samples (36 samples) were represented by juices obtained from other fruits (mango, berries, peaches, etc.). The obtained results were subjected to chemometric processing using classical methods (analysis of variance-ANOVA and linear discriminant analysis-LDA) and advanced methods (artificial neural networks-ANN). The best chemometric models were obtained for the differentiation of commercial apple juices vs. freshly squeezed. Thus, the LDA model was constructed based on K, Mn, Sr and Rb, while the ANN model was based on $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, K and Fe.

Content of the scientific and technical report (RST)

1. Samples juices collection, preparation and analysis using IRMS and ICP-MS techniques.
2. Experimental data set obtainment and application of chemometric methods
3. Results dissemination.

The experimental results obtained after the IRMS and ICP-MS analysis, were joined in a single data file, which constituted the working matrix for the subsequent chemometric processing. The initial processing of the matrix consisted in elimination of elements that were below the detection limit for more than half of the analyzed samples and otherwise could have led to erroneous statistical results.

For apple juices, a new data matrix was built, consisting of 54 samples, both commercial and freshly squeezed. Between the two groups, commercial and fresh, after the ANOVA analysis, all the variables were highlighted as differentiation markers, except Ca. In contrast, LDA highlighted only four markers, K, Mn, Sr and Rb. Mn and Sr are known to be very strong geographical markers, being closely related to the soil where the fruit trees grew. The freshly squeezed apple juices were prepared from local fruits, harvested from the Cluj area. Given that commercial juices were made from fruit from other parts of the country, or maybe even from other countries, so these elements can be considered geographical markers. For orange juices, a data matrix of 37 samples was constructed, using LDA analysis between juice and nectar, only

two differentiation markers were highlighted, namely As and Fe. As had higher average values in juice, while Fe had higher average concentrations in nectar.

By applying advanced chemometric methods (ANN), using the entire data matrix (108 samples) a total classification percentage of 67.6% was obtained for the training subset and 73.5% for the test subset of the obtained model. The variables with the most important contribution to these classifications are Sr, Cu, Pb and $\delta^{13}\text{C}$. For the set of commercial juices (73 samples), the classification percentages were slightly higher compared with the previous case, namely: 78.4% for the training subset, respectively 81.8% for the test subset. Among the most representative markers of the model were Zn, Mn, K and Ni. The last application of ANN was for the set of apple juices (54 samples), for which, as in the case of LDA, 100% percentages were obtained for both subsets. The markers in this case were: $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, K and Fe.

In conclusion, it is observed that the results obtained by applying ANN are complementary to those obtained by classical chemometric methods. It should be noted that ANN is much closer to real models, their results providing a much better accuracy compared to other prediction methods.

Results dissemination for this stage:

1. Project web page updating: <https://www.itim-cj.ro/PNCIDI/agrichem/#>
2. Experimental data set, with isotopic and elemental values, for commercial and freshly squeezed juice samples (108 juice samples).
3. Chemometric model developed based on specific markers to differentiate freshly squeezed apple juices and commercial ones.
4. Presentation at the 13th International Conference “Processes in Isotopes and Molecules”, September 22-24, 2021, Cluj-Napoca, Romania, with the paper “Mushroom's evaluation based on FT-IR fingerprint and chemometrics”, I. Feher, V. Floare-Avram, F. Covaciu, O. Marincas, DA Magdas, C. Sârbu
5. ISI article published: Ioana Feher, Cornelia Veronica Floare-Avram, Florina-Dorina Covaciu, Olivian Marincas, Romulus Puscas, Dana Alina Magdas, Costel Sarbu, Evaluation of mushrooms based on FT-IR spectra and chemometrics, Applied Sciences, 2021, 11, 9577-9587 (ISI= 2.679)
6. Phase report of the project
7. Participation in 2 training courses, Elements of Artificial Intelligence and Building Artificial Intelligence, University of Helsinki, 2021.

Data

08.11.2021

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