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Distilled beverages are important for both consumers, as well as for producers. Traditional methods and innovative technologies in fruit distillates production are focusing on their quality improvement. In recent years, the application of analytical methods for the quality assessment, classifying beverages according to origin or for the trademark specific fingerprinting has attracted increasing attention of researchers. Fifty fruit distillates ranging in alcoholic degree 40 and 80 from different regions of Transylvania were investigated from the elemental profile point of view using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The statistical analysis, based on the multielement content was applied in order to find which of the metals analyzed represents the best markers for: i) the geographical origin of samples; ii) the trademark specific fingerprinting; iii) the fruit varieties differentiation which were used for fruit distillates.

MATERIALS AND METHOD

FRUIT DISTILLATES SAMPLES: plum, pear, quince, sour cherry, blueberry, cherry, apple, grape, apricot
PROVIDER: Industrial Producer 1 (Ind. Prod 1), Industrial Producer 2 (Ind. Prod 2), Small Producers (Small Prod)

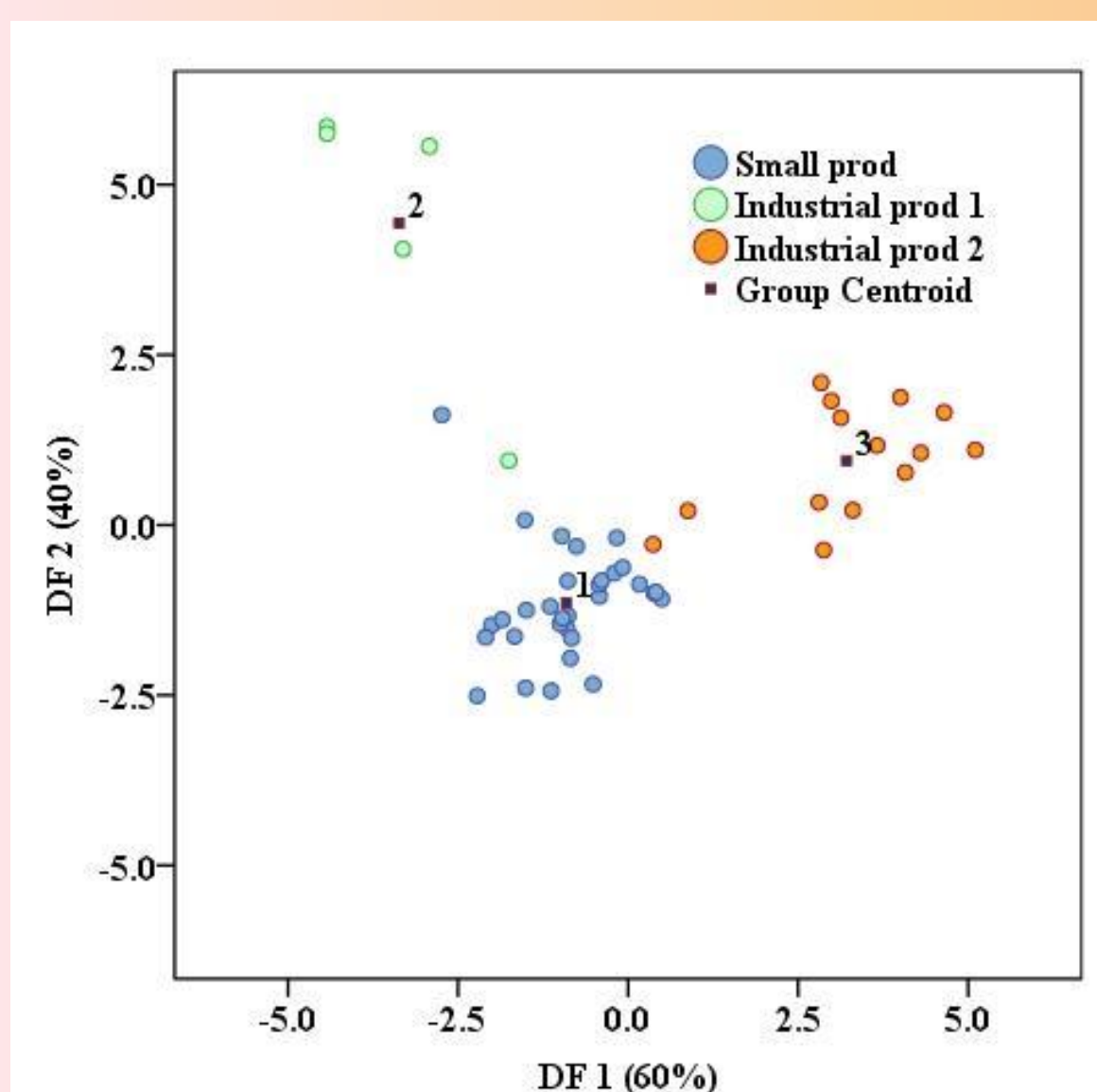
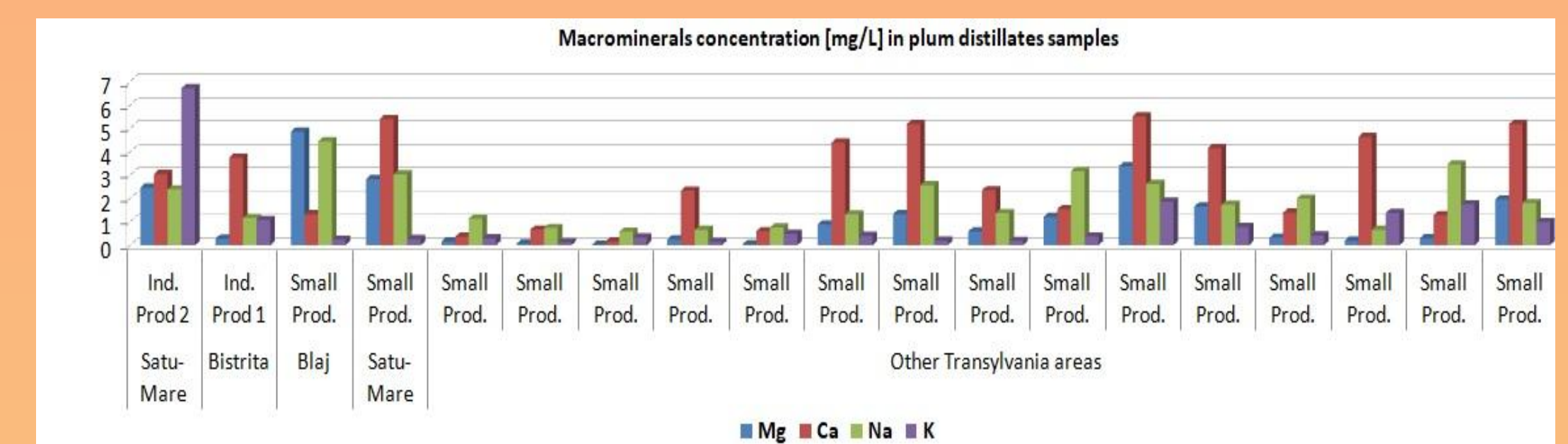
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) DETERMINATIONS

Prior ICP-MS analysis, each sample was prepared by 10 X dilution using 2 % nitric acid (v/v) (Suprapur[®], Merck) and 1 % hydrogen peroxide (v/v) (ChemPUR[®]ACS Reagent) prepared in ultrapure water (Simplicity[®]UV System, Millipore). Before accurate quantification, the concentrations of each element were analyzed by a TotalQuant approach using 10 µg/L Ba, Cd, Ce, Cu, In, Mg, Pb, Rh, U solution. By this method, as semi quantitative analysis was obtained the levels of concentration for each element. The standard multielement solutions of 10 µg/mL (ICP-MS Calibration Standard 2 containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Y and Yb and ICP-MS Calibration Standard 3 containing Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn and 10 mg/L (ICP-MS Calibration Standard 4 containing Au, Hf, Ir, Pd, Pt, Rh, Ru, Sb, Sn and Te) have been prepared by adding 4 % ethanol to all standard solutions, for quantitative analysis, taking into account of assessment of the semi quantitative method for each concentration level of analyte. ICP-MS was used for multi-element analysis of distilled beverages using an ELAN DRC (e) (Perkin Elmer) mass spectrometer with a Meinhardt nebulizer and silica cyclonic spray chamber.



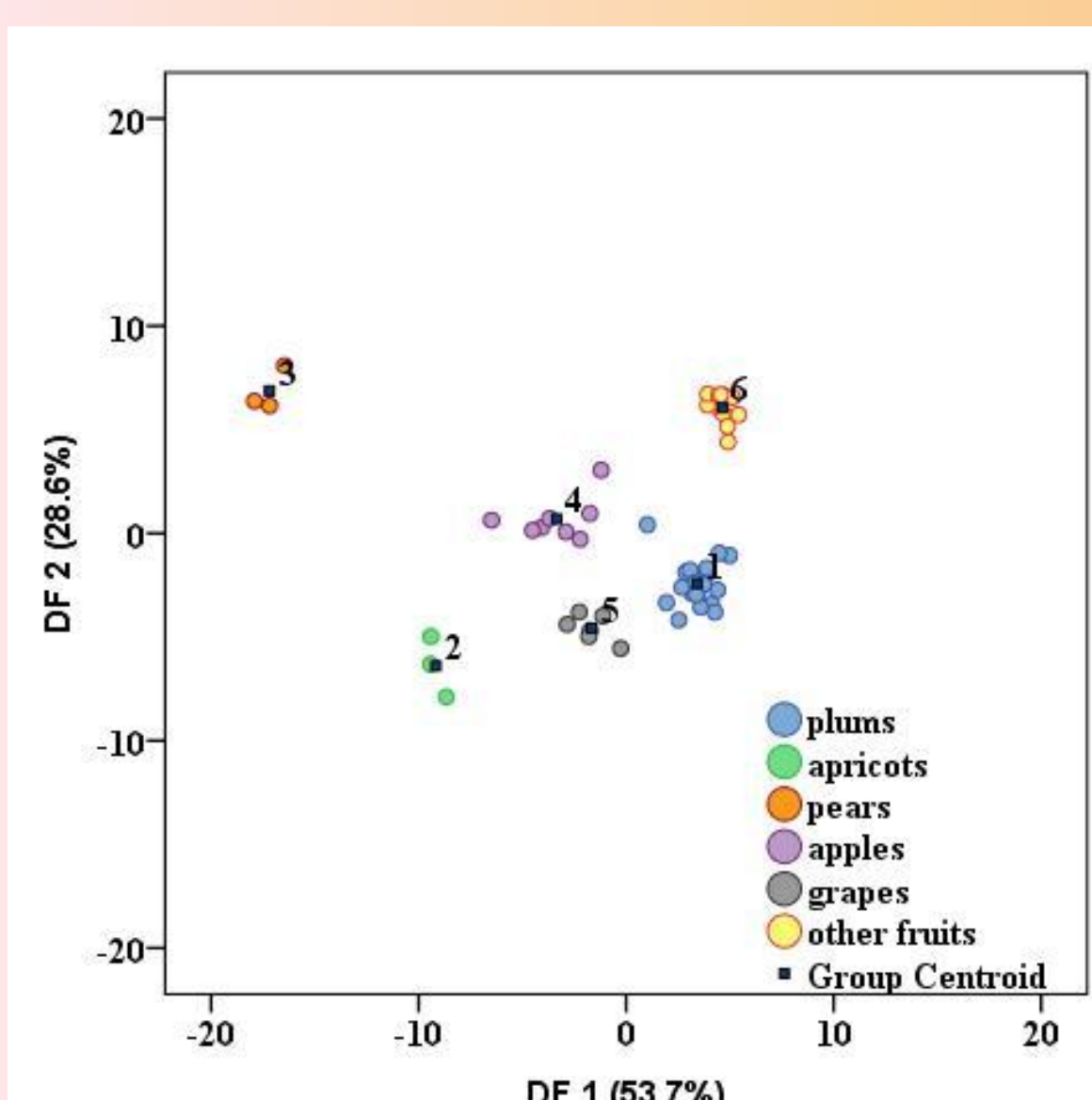
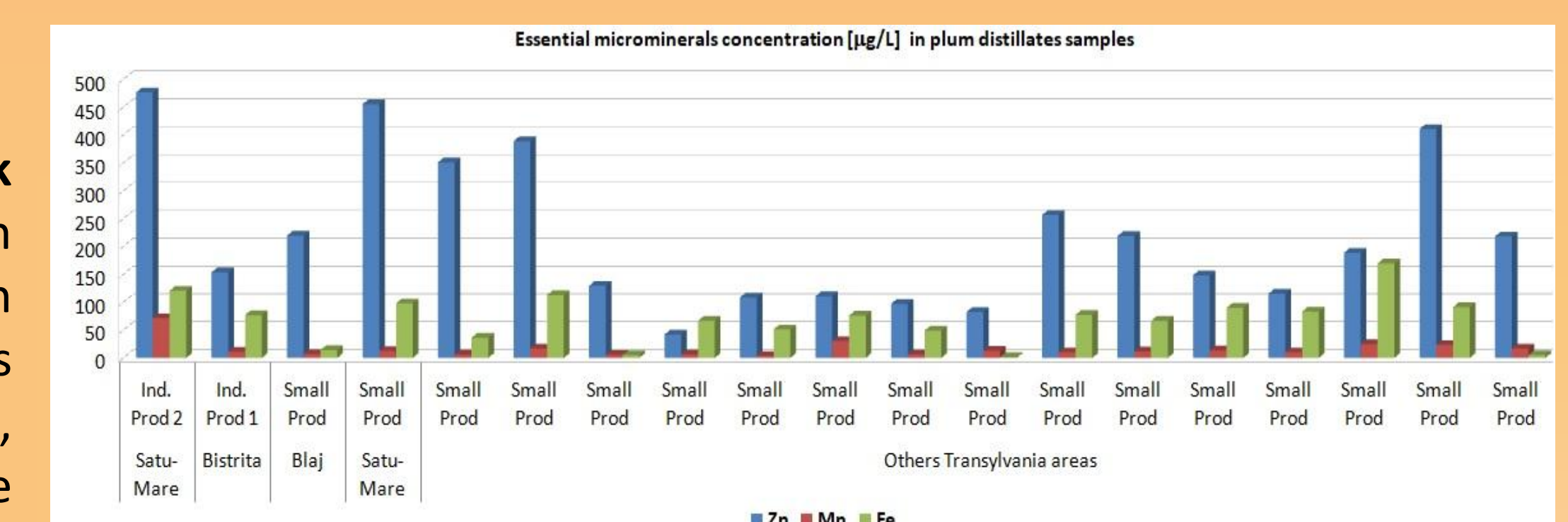
RESULTS AND DISCUSSION

LDA chemometric method is a supervised technique, which means that samples are coded from the beginning of the analysis, according to their label. Furthermore, the method tries to find the optimum parameters, which are able to maximize the distances between predefined groups and to minimize the distances within the same group. The obtained predictors are comprised in some linear function, called discriminant functions (DF). Based on these functions all the samples are classified and the result is expressed in percentage. Also, a cross-validation is made, which implies the testing of each sample using a model obtained from the rest of the samples. A higher value obtained from the cross-validation procedure suggests the robustness of the model.



DF1: 60 %: K, Ni, As, Pr, Tb
DF2: 40 %: Cu, B

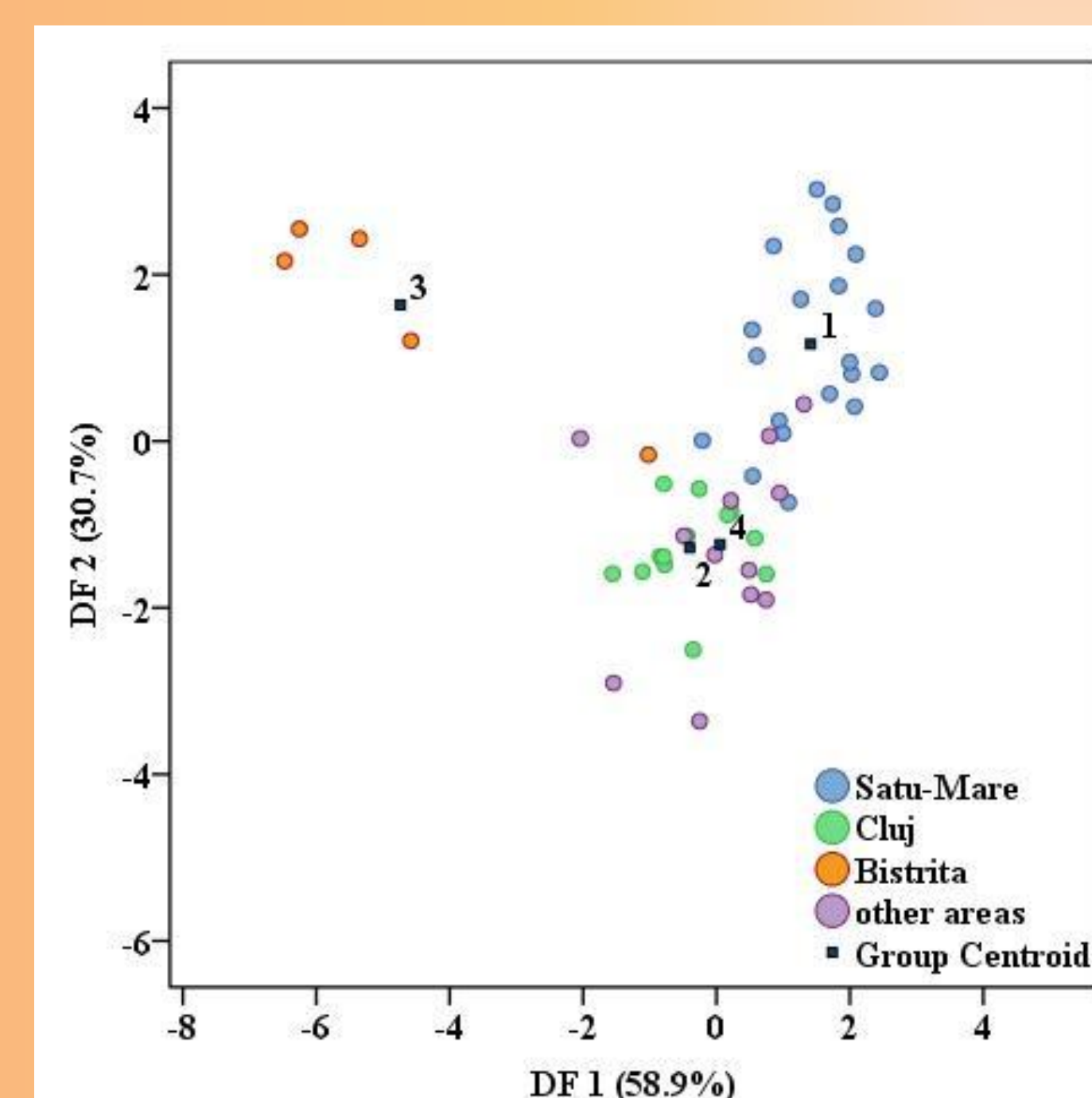
The effectiveness of this approach was mainly proved for the trademark fingerprint differentiation, where the distillates produced in two production units and one manufacture were discriminated in a percentage of 92 % in initial classification and 90 % in the cross-validation procedure. This classification was mainly based on the following elements: K, Ni, As, Pr, Tb, Cu and B. Three of these discriminators (K, Cu and B) were also among the most powerful for the geographical origin differentiation, the explanation for this consisting in the fact that the distillates producers used for the distillates elaboration mainly raw materials from their specific areas from Transylvania.



DF1: 53 %: Mg, Na, K, Mn, Rb, Eu, Pr
DF2: 28.6 %: Ca, Fe, Zn

The individual fingerprint of each distillate type, with regard to its fruit variety, was identified by performing the classifications between two groups i.e., the investigated fruit spirit versus all the rest. Based on this approach, it was possible to assess the main predictors which differentiate a certain distillate variety type by the rest.

The discrimination of fruit distillates with respect to fruit variety was achieved in a percentage of 100 % in initial and cross-validation procedure for apricot and pears distillates. On opposite side were placed quinces distillates where a modest differentiation was obtained (76.5 % in initial classification followed by 70.4 % in cross-validation).



The distillates set was split in three groups, corresponding to 3 geographic regions namely, Satu-Mare, Bistrita and Cluj and another group containing samples from other Transylvanian areas.

The first function (DF1) explains the classification in a percentage of 58.9 % and comprises the following predictors: Na, K, Ni, As and B. The second function (DF2) explains the rest of 30.7 % and has as main discriminators Al and Pr
DF3: 10.5 %: Tm, as main predictor

CONCLUSIONS

This work confirmed the potential of the association between elemental content corroborated with supervised statistical methods, namely linear discriminant analysis (LDA), for fruit varieties differentiation of raw materials which were used for fruit distillates and trademark specific fingerprinting. Based on the promising results obtained in the frame of this pilot study, further research in which a higher number of samples will be involved is ongoing.

Acknowledgments:

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