Studies regarding speciation and chemical fingerprinting as fruit products quality markers

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Abstract This paper presents an experimental research carried out on apples and grapes, using flame atomic absorption spectroscopy as a method for the analysis of mineral content and the thermo gravimetric analysis as a method for determining free water content. Speciation and Chemical Fingerprinting was realized taking into account the content in Ca, K, Na, Mn, Mg, Cu, Zn and Pb using FAAS method and statistical analysis program MVSP 3.1. Combined use of trace metals fingerprints and humidity may recommend this method as identification method for content composition and / or declared origin of fruits.

Key words

trace metals, thermo gravimetric analysis, fingerprinting, speciation

The surface of the apple crop is on all continents and also in temperate areas, both in the Northern and Southern hemisphere [4]. In Europe, apple juice is a highly-consumed product, in second place after orange juice [5, 9]. Apples are by far the most cultivated and consumed fruits in Romania. Almost every Romanian orchard grows at least an apple tree and apple fruits are eaten all year long. Two major problems in modern societies are cardiovascular diseases (CVD) and cancer. An increased consumption of fruits and vegetables may help to reduce the risk of CVD [2, 3] and some types of cancers [7, 8, 1, 9]. However, the data on cancer hazards and fruit and vegetable consumption are still ambiguous [10, 9].

Golden Apples of the variety known as "Golden Delicious" are large and almost round in shape. Golden apple peel is yellow rust points, rare. They are sweet, juicy, and slightly crunchy and have a pleasant aroma. Fuji variety apples were delicious flavor, texture them to store more than the other apples, that are perfect for meals, salads or snacks. Fuji apples present red color with green and yellow stripes, having sweet flavor, ideal for different preparation [12].

Grapes contain 73% water and 23% monosaccharide sugars, cellulose, pectin, free tartaric acid, mineral matter. In addition, the remaining 4%, contain B vitamins, C, A, PP and K, and minerals: potassium, phosphorus, magnesium, iron, calcium, silicon. They all have a diuretic effect and are beneficial for the treatment of diseases such as rheumatism, gout, skin diseases [11].

Material and Method

For the studies have been used two varieties of apples (Golden, Fuji) and two of grapes (Pinot Noir and Cabernet – Sauvignon), both available on the local market.

Samples collection and preparation

All the collected samples of various fruits were washed with double distilled water to remove airborne and pollutants. After washing, fruits samples were oven dried at 90°C to constant weight. The dried samples were ground, passed through a 2 mm sieve and stored at room temperature before analysis.

The trace metals contents in edible parts of fruits were carried out in HNO₃ solution resulted by ash digestion [6]. Each sample solution was made up with dilute HNO₃ (0.5N) to a final volume of 50 mL and analyzed by flame atomic absorption spectrometry (FAAS) in University Environmental Research Test Laboratory. The concentrations of the metals in the filtrate were determined by using flame atomic absorption spectrophotometer with high resolution continuum source (Model ContrAA 300, Analytik Jena, Germany), using appropriate drift blanks. Solutions of varying concentrations were prepared for all the metals by diluting the standards. Double distilled water (spectroscopic pure) was used for the preparation of reagents and standards. All chemicals were trace metal grade (Suprapur). Concentrate nitric acid (HNO3 65%), and concentrate HCl (30%), were obtained from Merck Germany.

Determination of free water was made by Sartorius MA50 moisture analyzer, aiming mass

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variation while increasing and maintaining the samples temperature to 105 degrees C.

Statistical analysis

The data were statistically analyzed using a statistical package MVSP 3.1.

We are grateful to WEBOMATIK RO SRL for permission to use statistical package MVSP 3.1. and technical assistance.

Results and Discussions

Speciation and chemical Fingerprinting was realized taking into account the content of calcium, potassium, sodium, manganese, magnesium, copper, zinc, lead using FAAS method and statistical analysis program MVSP 3.1. The mineral composition of the studied samples is presented in table 1.

Table 1

FAAS Mineral composition (ppm Metal/ mg dry matter)

Samples	Ca	K	Na	Mn	Mg	Cu	Zn	Pb
Pinot Noir Grapes	19.07	81.21	2.99	0.67	12.95	0.01	0.01	0.00
Cabernet – Sauvignon Grapes	6.02	41.81	2.95	0.00	3.52	0.01	0.01	0.00
Apple Golden	3.53	63.99	1.00	0.01	7.07	0.01	0.01	0.02
Apple Fuji	7.03	68.78	1.00	0.00	3.29	0.01	0.01	0.00

Principal Components Analysis (PCA) allows an assessment of mineralogical content data corresponding to the samples of grapes and apples, using the square root of their transposed matrix (figure 1).

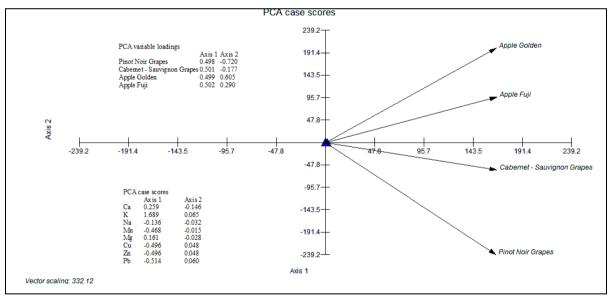


Fig. 1. PCA joint-plot graphical reprezentation

The join-plot representation of the calculated case scores permits the identification of the types of fruits that are used in different fruit products like jam, liquers, alcoholic drinks etc. In quarter I, we can observe the vectors for apples varieties and in quarter

IV, the vectors for the grapes varieties, the vectors are represented taking in consideration the trace metal composition of the studied samples (figure 1). In figure 2 we can identify the graphical fingerprints of the trace metals.

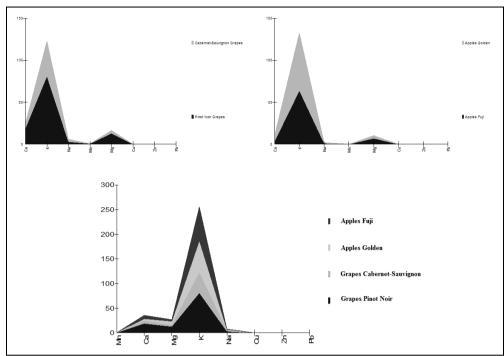


Fig. 2. Trace metals Fingerprints of studied Fruits

The determination of free water was made by Sartorius MA50 moisture analyzer, aiming mass variation while increasing and maintaining the samples temperature to 105 degrees C. Analysis of changes in humidity studied clusters, permits to identify specific fingerprints using as parameter free water content of various types of fruit (figure.3). It is noted that for

apples dissimilitude distance is 43.188 while for the grapes is 315,270. The difference between Euclidean distances show that this parameter allows fingerprinting and can be used as a marker to proof the processing said content (figure 3) Shannon diversity index can be used for the same purpose. (figure 4).

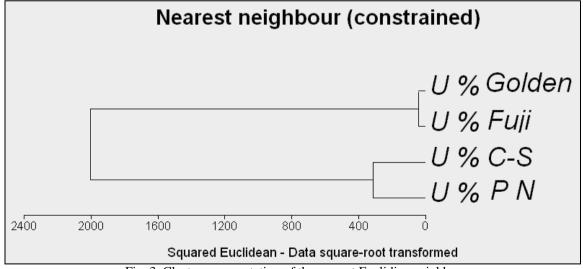


Fig. 3. Cluster representation of the nearest Euclidian neighbor

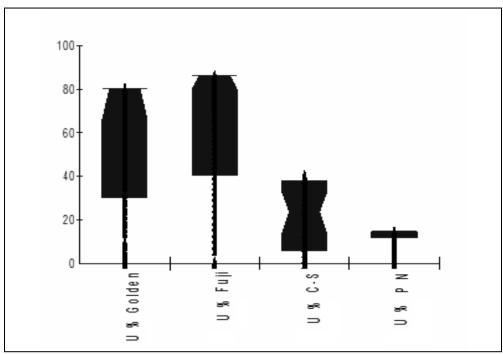


Fig. 4. Determination of diversity indices

Figure 5 is presenting the graphical representation for fingerprint factor, a marker that

permits the identification of the declared composition or origin of a fruit product.

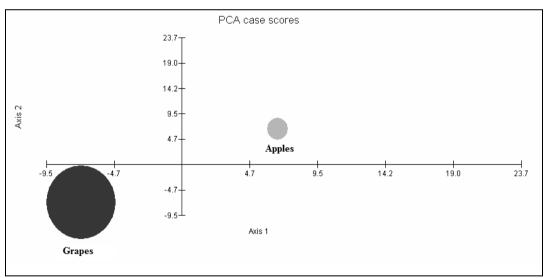


Fig. 5. PCA graphical representation for fingerprint factor identification

Conclusions

Mineral composition as well as moisture determination can be used as fruit quality markers for the cultivators as well as for the processing food industries.

CA correlation analysis (figure 5) allows highlighting mineralogical components specific to each variety separately. The potassium content is a characteristic of all the samples studied and may be considered major fingerprint identification form.

Specific fingerprint of overlapping bands is given for the following minerals: manganese, magnesium, copper and zinc.

Determination of free water can be a specific parameter, used as marker, because water is a key component that supports and activates biochemical processes that occur in all plant material from its formation until the total depreciation.

Analysis of changes in humidity clusters permit the identification of specific fingerprints while using the parameter, free water content of various kinds

of fruit. The big difference between Euclidean distances allows the use of this parameter as a factor that is able to indicate the authenticity of the content and to identify the company said processor.

References

- 1.Barth, S. W., Fahndrich, C., Bub, A., Dietrich, H., Watzl, B., Will, F., Briviba, K. and Rechkemmer, G. 2005 Cloudy apple juice decreases DNA damage, hyperproliferation and aberrant crypt foci development in the distal colon of DMHinitiated rats. Carcinogenesis, 26, 1414–1421;
- 2.Bazzano, L. A., He, J., Ogden, L. G., Loria, C. M. and Whelton, P. K. 2003 Dietary fiber intake and reduced risk of coronary heart disease in US men and women: the National, Health and Nutrition Examination Survey. I. Epidemiologic Follow-up Study. Archives of International Medicine, 8, 1897–904;
- 3.Boyer, J. and Liu, R.H 2004 Apple phytochemicals and their health benefits, Nutrition Journal, 3, 5–19;
- 4.Campeanu Gh., Neata Gabriela , Darjanschi Gina 2009 Chemical Composition of the Fruits of Several Apple Cultivars Growth as Biological Crop, Not. Bot. Hort. Agrobot. Cluj 37 (2), Print ISSN 0255-965X; Electronic ISSN 1842-4309, 161-164;
- 5.Kay-Shuttleworth, R. 2008 The World and Europe Fruit Juice, Industry in Data, AIJN 50th

- Anniversary Symposium, Brussels, Belgium, http://www.aijn.org/documents/4265.p;
- 6.Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG 2008 Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ Pollut.;152:686–692. doi: 10.1016/j.envpol.2007.06.056;
- 7.Knekt, P., Kumpulainen, J., Järvinen, R., Rissanen, H., Heliövaara, M., Reunanen, A. and Hakulinen, T. 2002 -. Flavonoid intake and risk of chronic diseases. American Journal of Clinical Nutrition, 76, 560–568; 8.Lambert, J. D., Hong, J., Yang, G., Liao, J. and Yang, C. S. 2005 Inhibition of carcinogenesis by polyphenols: evidence from laboratory investigations. American Journal of Clinical Nutrition, 81, S284–
- 9.Markowski J., Baron A., Mieszczakowska M.and Plocharski W., 2009 -, Chemical composition of French and Polish cloudy apple juices, Journal of Horticultural Science & Biotechnology, ISAFRUIT Special Issue, 68–74, http://www.jhortscib.com/isafruit/isa_pp068_074.pdf; 10.Williamson, G. and Manach, C. 2005 Bioavailability and bioefficacy of polyphenols in humans. II. Review of 93 intervention studies. American Journal of Clinical Nutrition, 81, 243S–255S;

http://dieta.ele.ro/Dieta_cu_struguri_pentru_sanatate_si _frumusete_--a205.html;

http://www.gradinamea.ro/Fuji 3485 598 1.html;