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Quality assessment of commercial apple juices

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Abstract

This study presents the use of carbohydrate chromatography, refractometry and pH-metry for obtaining the profiles of fructose, glucose, sucrose together with pH and Brix as indicators of apple juice quality. Commercial apple juices originating from the Romanian market were analysed; using a minimum sample workup, this approach is low time-consuming, enabling also the detection of common sweetening practices. Principal component analysis (PCA) of the obtained data revealed a data structure with three classes: I - unsweetened apple juices; II - apple juices sweetened with glucose-fructose syrup; III - apple juices sweetened with saccharose. A final cluster analysis was accomplished with Ward's method, leading to the classification of the analyzed juices according to their established carbohydrates composition, the resulted three main clusters confirming the class structure obtained using PCA.

Keywords: HPLC, carbohydrates, chromatography, food analysis, apple juice, PCA

1. Introduction

Apple juice has a strong position in the world consumption ranking, being appreciated not only for its taste and nutritional properties but also for its health effects [1]. However, these features are related with a proper juice quality; evaluation of the apple juice quality requires determination of the chemical composition, sensory attributes as well as of the presence of undesired substances such as preliminary fermentation products, patulin or heavy metals. The main components of apple juices include fructose, glucose, saccharose, as well as organic acids, mineral salts, vitamins, dyes, and phenolic compounds [3,5]; hence, complex analytical methods are necessary. Of the different techniques available for carbohydrate analysis, enzymatic and high performance liquid chromatography procedures are the most commonly used; techniques such as capillary electrophoresis, Fourier transform infrared spectroscopy or near-infrared transflectance spectroscopy are growingly cited [4,6,10,11].

Gas – chromatography, despite its sensitivity, was almost abandoned in routine analysis because the labor-intensive sample preparation, requiring derivatization [7]. From many different analytical techniques which were used for carbohydrate analysis, high performance liquid chromatography (HPLC) is commonly used to check the juices' quality by analyzing their oligosaccharide fingerprint profile, as a tool for quality control and for checking adulterations.

Among other compounds form the apple juices, sugars are important not only for their nutritive value; meanwhile, their pressence can be assesed for adulteration detection carried out by adding sucrose, high fructose corn syrup, cane medium invert syrup or beet medium invert syrup to apple juice [9]. These types of adulterations can be detected knowing that a genuine apple juice should contain a minimum fructose/glucose ratio of 1.6 and a maximum sucrose content of 3.5% [2,5,12].

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The present study investigates the use of carbohydrate chromatography, pH – metry and refractometry in order to establish the apple juice quality. The proposed approach has the advantage of a minimum sample workup for HPLC analysis (consisting in dilution followed by filtration), being low time-consuming and also enabling the detection of common sweetening practices. A final cluster analysis of the obtained data lead to the classification of the analyzed juices according to their established carbohydrates composition.

2. Materials and methods

Glucose, fructose, saccharose and maltose were all reagent-grades (Merck); HPLC grade acetonitrile (Merck) was used for mobile phase preparation, together with ultrapure water with a specific resistance of 18.2 MΩ/ cm, produced with a Millipore Direct Q 3UV Smart.HPLC mobile phase was filtered through 0.45 μm membrane (Millipore) then degassed under vacuum using an Elmasonic S30 H ultrasonic bath.

Commercial apple juices were obtained from supermarkets; juice samples (table 1) were analyzed in triplicates, using 10 mL apple juice from each brand, which were brought to a volume of 100 mL with ultrapure water. Aliquots from the diluted samples were filtered through 0.45 □m membrane filter (Millipore), being then injected to HPLC. One reference apple juice was obtained from Starkinson apples using a centrifugal juice-extractor, being then processed as mentioned earlier.

HPLC analyses were performed on a Shimadzu system, consisting from a Prominence LC-20AP solvent delivery module, a Prominence DGU 20As online degasser, an automatic sample injector SIL-10AF, a EC 250/ 4 Nucleodur 100 – 5 NH_2 RP column (250 x 4.6 mm – Macherey Nagel) protected with an appropriate guard column, a RID-10A differential refractive index detector, a Prominence CTO-20A column oven and a Prominence CBM-20A system controller. Instrument control, data acquisition and data analysis were accomplished by „LCsolution" ver.1.2. software. Isocratic separations were accomplished using 77 : 23 v/ v % acetonitrile in water as mobile phase at the flow rate of 1.0 mL/ min and 40^0C [8], injection sample volumes being of 10 μl; the external standard method was used for quantifications.

pH measurements were accomplished on undiluted samples using a HI 223 Hanna instrument, while refraction indexes were measured with a 96811 digital Brix Hanna refractometer.

Principal component analysis and cluster analysis were accomplished using Matlab (The Mathworks Inc., USA).

Table 1. Analyzed apple juice samples – label information

Samples ID's	Commercial brands & label information
Cap	Capy Premium 100% Apple juice - apple juice made from concentrated apple juice 100%, no added sugar
Ciao	Ciao Green Apple - apple juice made from apple puree and concentrated apple juice (17%) sweetened with sugar and/ or glucose – fructose syrup, sodium cyclamate and acesulfame K
Cool	Tymbark Cool green apple - apple juice made from apple puree and concentrated apple juice (5%) sweetened with sugar and/ or glucose – fructose syrup, sodium cyclamate and acesulfame K
Fru	Fruttia 100% Apple Juice - apple juice made from concentrated apple juice (100%), no added sugar
Gra	Granini apple - apple juice made from concentrated apple juice 100%, no added sugar
Jab1	Jablko – Mieta Napoj - Concentrated apple juice (20%) sweetened with glucose – fructose syrup
Jab2	Jablko sok 100% - apple juice 100%, no added sugar
Mal	Natural apple juice Mălâncrav - pressed apple juice 100%, no added sugar
Pfa	Pfanner Apple 100% - apple juice 100% made from concentrated apple juice, no added sugar
Pfag	Pfanner Green Apple with smooth apple puree - Apple juice (17%) made from concentrated apple juice, apple puree (20%) - fruit content min.40%, sweetened with saccharose
Rau	100% Natural apple juice – Râureni - apple juice made from concentrated natural apple juice, no added sugar
Rauch	Rauch Bravo Apple – apple juice made from concentrated apple juice (min 12% fruit content), sweetened with sugar and glucose – fructose syrup
Real	Apple – fruit juice 100% - apple juice 100% made from concentrated apple juice, no added sugar
San	Santal 100% mela - apple juice made from concentrated apple juice, no added sugar
Sio	Sio Apple - apple juice made from concentrated apple juice (12%), sweetened with saccharose (97 g/ L) and glucose-fructose syrup
Stark	Freshly pressed apple juice - 100% Starkinson apple juice obtained by lab-scale extraction

3. Results and discussion

A synthetic view of the mean values obtained for the analyzed apple juice brands is presented in table 2, data being sorted in a descending manner with respect to the fructose/ glucose ratio; figure 1 reveals the chromatographic profiles of some representative apple juice samples.

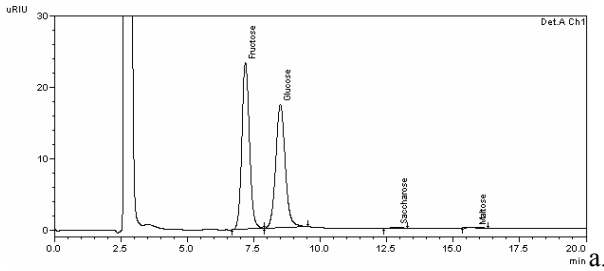
Table 2. Mean values obtained for analyzed samples ± standard deviations

Sample ID	Fructose [g / L]	Glucose [g / L]	Saccharose [g / L]	Fructose/ glucose	Brix	pH
Cap	59.37 ± 2.41	23.43 ± 1.02	20.49 ± 0.84	2.53	11.41 ± 0.48	3.39 ± 0.17
Real	61.48 ± 2.47	26.02 ± 1.05	13.12 ± 0.59	2.36	11.02 ± 0.41	3.45 ± 0.20
San	67.51 ± 2.70	29.90 ± 1.24	10.75 ± 0.45	2.26	10.93 ± 0.47	3.32 ± 0.15
Pfa	65.86 ± 2.66	29.41 ± 1.19	13.42 ± 0.63	2.24	10.89 ± 0.43	3.25 ± 0.16
Jab2	62.93 ± 2.52	28.33 ± 1.15	12.49 ± 0.57	2.22	11.23 ± 0.54	3.39 ± 0.18
Rau	61.32 ± 2.46	29.84 ± 1.23	11.42 ± 0.48	2.05	11.21 ± 0.46	3.66 ± 0.23
Stark	64.38 ± 2.62	31.80 ± 1.36	7.43 ± 0.34	2.02	11.20 ± 0.48	3.47 ± 0.21
Gra	58.23 ± 2.41	29.76 ± 1.19	10.37 ± 0.42	1.96	11.02 ± 0.50	3.41 ± 0.16
Mal	58.09 ± 2.34	31.31 ± 1.21	9.55 ± 0.41	1.86	11.16 ± 0.53	3.61 ± 0.21
Fru	60.79 ± 2.49	33.96 ± 1.38	12.92 ± 0.54	1.79	10.54 ± 0.47	3.52 ± 0.19
Pfag	40.12 ± 1.65	29.05 ± 1.22	38.46 ± 1.51	1.38	10.68 ± 0.45	2.91 ± 0.17
Jab1	27.23 ± 1.17	20.84 ± 0.91	35.55 ± 1.53	1.31	8.26 ± 0.39	2.95 ± 0.15
Sio	53.16 ± 2.18	45.45 ± 1.87	10.37 ± 0.42	1.17	10.94 ± 0.46	2.74 ± 0.12
Rauch	46.13 ± 1.84	42.13 ± 1.79	14.56 ± 0.59	1.09	10.81 ± 0.51	2.75 ± 0.17
Cool	41.67 ± 1.69	46.46 ± 1.92	25.89 ± 1.04	0.9	11.23 ± 0.48	2.71 ± 0.14
Ciao	58.21 ± 2.40	71.13 ± 2.83	1.33 ± 0.06	0.82	12.10 ± 0.52	2.78 ± 0.12

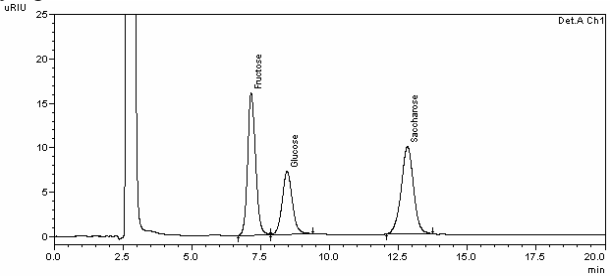
As mentioned in the introductory section, authentic apple juices are characterized by a minimum fructose/glucose ratio of 1.6 and a maximum sucrose content of 3.5 %. The first nine samples agrees with these criteria, the determined values also agreeing with the label information; the small differences between the total carbohydrates concentrations from the labels and the determined ones can be due to the heterogeneity of the raw materials, as the carbohydrates' fingerprints of apple juices depends of the maturation degree, cultivar's feature and effect from growing places.

Principal component analysis (PCA) was performed on the autoscaled data, using three variables: the concentrations of fructose, glucose and saccharose. This leads to a model with two principal components, accounting for 64.56% and 32.24% of the total variability (figure 2).

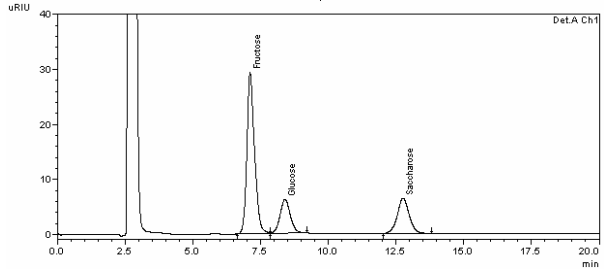
The score plot and the biplot from figure 2 reveal a data structure with three clusters: I – corresponding to unsweetened apple juices (those with fructose / glucose ratio higher than 1.6), II – corresponding to apple juices sweetened with glucose-fructose syrup and III including apple juices sweetened with saccharose. For the 95% confidence of this model, Ciao sample is an outlier.



a. Ciao green apple - sweetened with glucose – fructose syrup



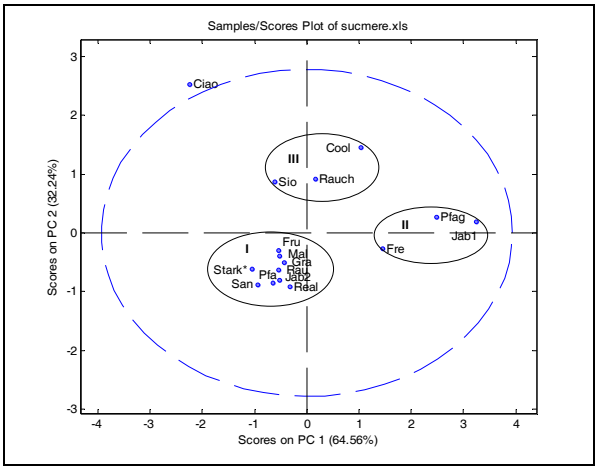
b. Pfanner green apple - sweetened with saccharose



c. freshly pressed apple juice

Figure 1. HPLC chromatograms obtained for some representative apple juices

Cluster analysis was accomplished with Ward's method, using principal component analysis with 2 PC's, the obtained dendrogram being presented in figure 3; the resulted three main clusters agrees with PCA's results.



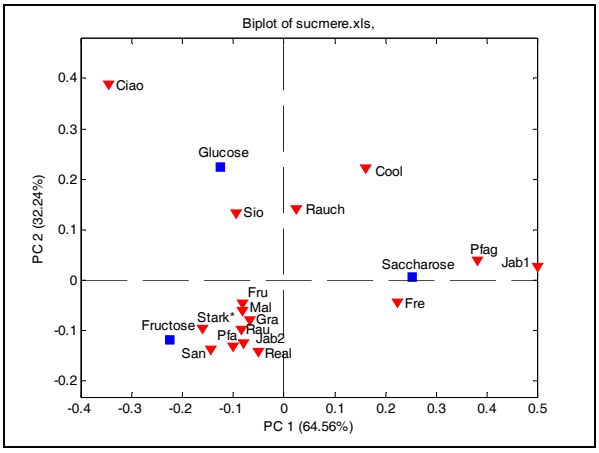


Figure 2. Scores plot and PCA biplot obtained for a three variables model

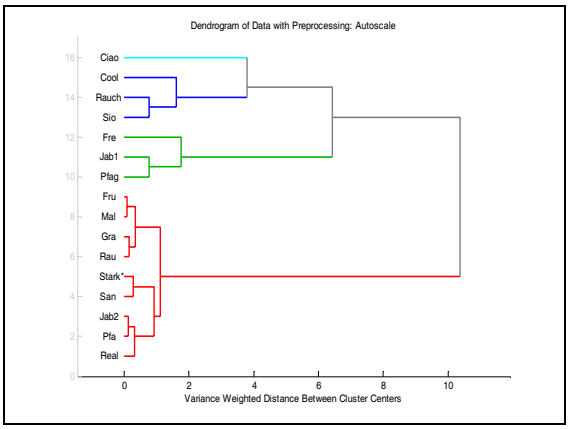


Figure 3: Dendrogram obtained with Ward's method, using principal component analysis with 2 PC's

4. Conclusion

Using a minimal sample workup, in less than 30 minutes analysis time the proposed approach can reveal the fingerprints for four carbohydrates (fructose, glucose, saccharose and maltose), pH and Brix, being thus a fast tool for assessing the apple juice quality. The subsequent principal component analysis revealed three major apple juice types, with respect to carbohydrate content, these being in good agreement with the composition declared on the products' labels.

Acknowledgements

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