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Electronic Nose and sensorial characterization - discrimination for seven apple types stored, 7 months, in refrigeration and controlled atmosphere conditions

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Abstract

The apple storage by refrigeration and controlled atmosphere is a technique for quality fruit preservation involving careful control of temperature, oxygen, carbon dioxide and humidity. During storage in controlled atmosphere storing rooms for a long period fruits lose their freshness and some of their characteristics depreciate but market differences appears in refrigeration conditions. In this article we characterized seven types of apples stored in these conditions through instrumental and sensory methods concerning their sensorial attributes, respective their smell. The objective evaluation of the quality of fruits is a difficult task, mainly due to the fact that every single person is not necessarily influenced by the same attributes and that the quality scale may vary strongly from one person to another. The perception of volatile compounds by the human nose is of great importance in evaluating quality of foods; therefore, similar principle as the human nose, the electronic nose, was used.

The resulting E-nose intensities were analyzed by PCA, DFA and SQC. All the samples were analyzed using the E-nose FOX 4000 with 18 metal oxide coated or uncoated sensors. The resulting E-nose intensities were analyzed by Principal Component Analysis (PCA), Discriminant Factor Analysis (DFA) and Statistical Quality Control (SQC), which resulted in grouping the used varieties of apples or in grouping the types of samples (peel, homogenate or diluted homogenate from the same apple). The obtained results indicated that E-nose could discriminate successfully among varieties of apples (% of variance >> 90; percentage of recognition ≈ 100 %).

Keywords: quality of apples, sensorial analysis, volatiles, E-nose, multivariate statistics (PCA, DFA, SQC)

1. Introduction

Romania is a leading producer of fresh fruits and vegetables, topping the 6th place among the biggest European producers of fruit, after France, Spain, Poland, Italy and Germany, which limits export opportunities in this country, according to a release of the Ministry of Agriculture, Forestry and Rural Development. Apple flavors and essences are food ingredients that emit a vast array of aromatic volatile gases, which contribute to the sensorial quality of foods in which they are incorporated.

Apples are the most widely consumed fruits in Romania. After the apples are harvested, they are commercialized. Today, the extended availability of seasonal fruit in the market place is common due to both post-harvest technologies and fruit varieties that allow for longer periods of storage. The apples which are not sold yet are stored in cold storage warehouses, consisting of large refrigerated rooms where the temperature and air humidity are maintained at optimal conditions.

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During storage, fruits lose their properties, although low temperatures slow the ripening process. In the controlled atmosphere storage, temperatures are kept constant according to apple variety, fruits chemical composition and fruit ripening level. Long time cooling may lead to losses in fruits quality caused by differential or inexistent activity of some enzymes [1,2]. Refrigeration warehouses with controlled atmosphere, although need supplementary costs, are widely used for fruit storage because of possibility to store the fruits for longer periods of time. Using these storage conditions, the fruit quality loses are lower and fruits have a better quality as it will be observed in this paper [3,4]. In this article, we followed the variation sensorial characteristics for apples stored under controlled atmosphere and, respectively, under refrigeration conditions, because of the importance of these analysis for apples quality and perception of the volatile compounds. The quality of fruits is an extremely complex matter, difficult to describe objectively. The consumer does not judge the nutritional quality of a certain fruit but he can make statements about sensory aspects such as shape, color, texture, juiciness, firmness, taste and aroma.

Volatile (often aroma) compounds are analyzed with sensory panel but, a major challenge for the fruits and vegetables industry is to replace time-consuming laboratory analyses, used in process and control quality monitoring, with new application techniques that are fast, precise and accurate. E-nose technology represents a possible alternative to volatile measurement, at least in some applications [11]. These are multi-sensor arrays designed to measure headspace volatiles. Each sensor type has a greater or lesser affinity for a particular chemical class or group of compounds. Using chemometric techniques and multivariate statistical analysis, it is possible to distinguish among groups of samples, and possibly identify individual sample components. Several studies have investigated the use of E-nose type sensors for apple quality evaluation. A non-destructive evaluation of apple maturity has been measured by means of E-nose by Pathange et al.[14]. Evaluation of the feasibility of detecting differences between volatile gases from intact apples and apple juice extracts from different cultivars using E-nose was studied by Marrazzo et al. [12,13].

Xiaobo and Jiewen [15] realized a comparative analysis of apple aroma by a tin-oxide gas sensor array device. Other researchers like Li and Heinemann [10] developed a multisensor data fusion model to integrate two volatile detection instruments (Enose and zNose) for apple defect detection, a new method throw which they could differentiate undamaged from deteriorated apples using Enose and zNose and an ANN-integrated Enose and zNose system for apple quality evaluation [8,9].

The objective of this study was to develop a methodology for discriminating Romanian apples from different regions of Romania. In order to achieve this goal we focused our efforts on chemical and sensory (instrumental) analysis. As far as the sensory approach is concerned, were elaborated “fingerprints” (↔ E-nose intensities) of the apples analyzed using an E-nose FOX 4000, that were further used for mutivariate statistics analysis (PCA, DFA and SQC).

2. Materials and methods

Four varieties of apples: Jonathan, Starkimson, Gala and Golden were harvested from Reghin territory and three varieties of apples: Golden, Pinova and Fuji were harvested from Insuratei. They were stored in four different cells of the storehouse placed in Reghin and in warehouses placed in Insuratei and they were used in the following experiments. The temperature and air humidity in the storage room were continuously recorded during storage and they were specific for each apple variety. The apples were tested using sensorial analysis every month. The sensory panel was formed by students from The Food Science and Engineering Faculty, „Dunarea de Jos’’ University, Galati, Romania.

The student’s panelists were selected for food sensorial analysis using specific methods for panel selection. The subjects were asked to rate the following sensory attributes: odor, aroma, sweetness, acidity, firmness, juiciness and to give marks for the overall appreciation. The panel rated the different parameters on a 1 to 1o scale (eg. 1 – very weak aroma intensity and 1o – very strong aroma intensity).

Panelists received water and bread as neutralizing agents between samples testing.The sensory analysis was carried out in the standard sensory laboratory under well controlled conditions.

Volatile compounds of the apples harvested and stored at Reghin territory (Jonathan, Starkimson and Golden) were analyzed with electronic nose, α-Prometheus (FOX 4000, Alpha.Mos, France), to The Institute of Food Bioresources, Bucharest .

Prior to testing, all the samples were kept at room air temperature (23°C) for about 12 hours to reach ambient air temperature. Average samples from each of the analyzed varieties were made.

Three types of samples were analyzed using an E-nose FOX4000: pare of apples, homogenized pare and pulp of apples and diluted homogenates to 25%. 2 grams of each sample were weighted into 10 ml vials (to ensure the repetability 3 vials for each kind of sample were used). The samples were heated to 50°C for about 3 minutes. 1500 µl of headspace was injected at 2000 µl/s. The signal aquisition lasted 2 minutes.

3. Results and Discussion

The sensorial characteristics of the apples were determinate using ten panelists, monthly, at the same data, from December until May. The evaluated characteristics were: smell intensity, acid smell, grass smell, honey smell, fruit smell, chemical smell, almond smell, aroma intensity, fresh acid aroma, grass aroma, honey aroma, fruit aroma, acid aroma, sweet aroma, bitter aroma, chemical aroma, almond aroma, firmness, masticability, hardness, mealiness, juiciness, aftertaste.

Applying ANOVA analysis method to the obtained results, we can conclude that the differences between panelists are low concerning the grades given for each characteristic of every apple variety, so average of the grades given by panelists can be used for apples sensorial characterization. Spider sensorial profiles were realized for each variety of apples, but in this article, the varieties of apples stored in CA are representative for analyzing the aroma intensity until May month (figures 1 to 4).

So it can be seen that during storage, apples loose their quality characteristics. Smell and aroma intensity, aftertaste, juiciness, mealiness, hardness, masticability and firmness are, generally, better expressed in December than in February. Also, acid aroma, fruity aroma and sweet aroma had higher scores in December than in February.

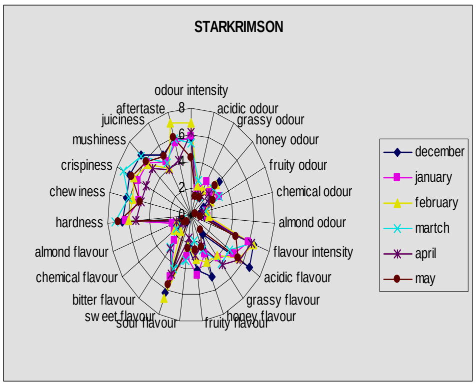

Figure 1. Sensorial analyse-Starkrimson

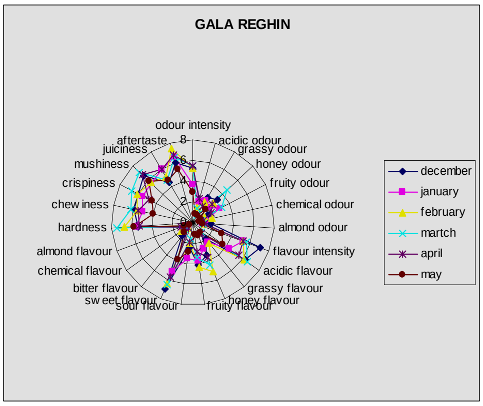

Figure 2. Sensorial analyse-Gala

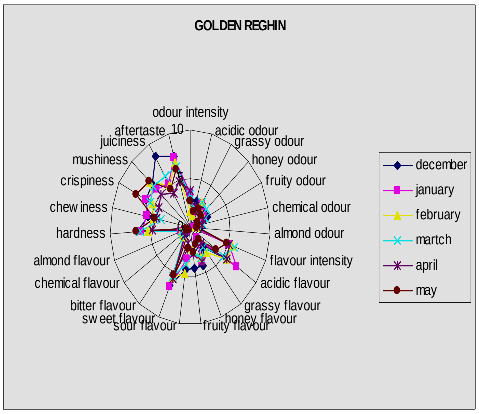

Figure 3. Sensorial analyse-Golden

The aroma profile can change dramatically during the post-harvest life of fresh produce, particularly in climacteric fruits in which the dominant volatile may be quite different in the unripe fruit, the ripe fruit and the over-ripe or senescing fruit. Refrigeration also tends to limit the development of aroma volatiles in ripening fruits [1].

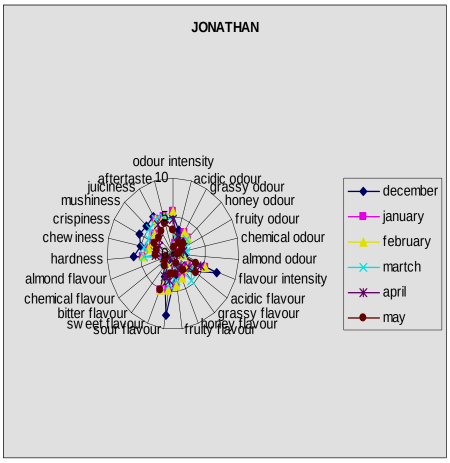

Figure 4. Sensorial analyse-Jonathan

The storage of apples under low temperature and controlled atmosphere conditions inhibited the synthesis of volatiles compounds (apples aroma had a lower level) but in inadequate conditions of gaseous composition, grain alcohol and formaldehyde will be accumulated. Volatiles accumulation will be accelerated by the ripen process [4,5]. The apples type storage in atmosphere with normal composition (Pinova, Fuji and Golden) synthesized ethylene and other volatiles faster that why these types of apples were analyzed concerning sensorial until March. Sensorial analysis indicated that the attributes of Golden and Starkimson apples maintained in time, but Jonathan less and Gala more less identical figure 2 [6,7].

Aroma can be an important factor in the storage and shelf-life of fresh products. Jonathan, Starkrimson and Golden, due to their physiology-are compatible for storage under controlled atmosphere as it can be seen in figure 2. Concerning aroma, Golden apples are highly aromatic products because the volatile compounds were synthesized more lately. These apples were harvested immature with higher content of starch, so the intensity of aroma increased in March.

Discriminate odors have been tested with "electronic nose". The obtained diagrams, which represent the answer of the sensors in analyzing the volatiles compounds from the samples, are presented below (fig5: left –apple sample from Starkimson; right: apple sample from Golden). Analyzing the two diagrams it seems that no concrete differentiation is visible between the two varieties of apples.

The answer of the sensors is similar, which means that no important differences are between the headspace of the Starkimson samples and the headspace of the Golden samples.

Statistical methods PCA (Principal Component Analysis) and DFA (Discriminant Factor Analyis) were used further in order to differentiate the results between the three analyzed varieties. The figure 6 presents the graphic of PCA analysis. PCA method is the best method of visualizing a complex, multivariate data set.

The aim of this method is to find a "structure" or proximities within the samples - and not to identify samples. It gives a representative map of the different areas (olfactive, concentration area ...).

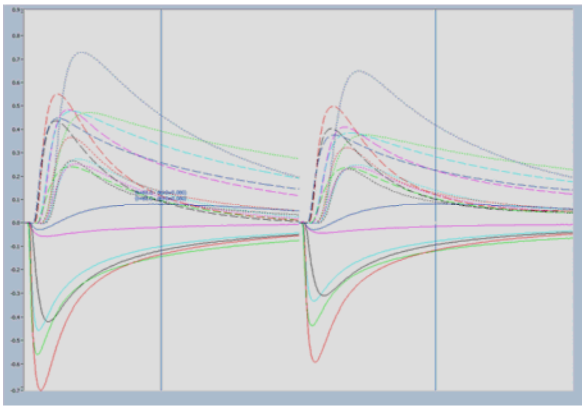

Figure 5. The response of the sensors (left: apple sample from Starkimson right: apple sample from Golden

On the PCA graph, the percentage reported on each axis (C1, C2 …Cn) gives the amount of information given by sensors on each axis (also called components). This percentage is also called the % of variance. The sum of the percentage of variance on all the axes (C1, C2 …Cn) is 100%. A PCA is valid if: the discrimination index is as closest to 100. If the discrimination index is negative the analysis is not valid.

As we have obtained a low discriminant index, the samples couldn't be clearly differentiated, probably because the samples suffered damages in their quality during the preservation. If the discrimination through PCA is valid, we can then perform the DFA to classify the samples in distinct groups. The DFA method represents a qualitative analysis for discrimination and identification (prediction of belonging to a group of an unknown sample). DFA allows the user to construct a model which enables to identify a new sample.

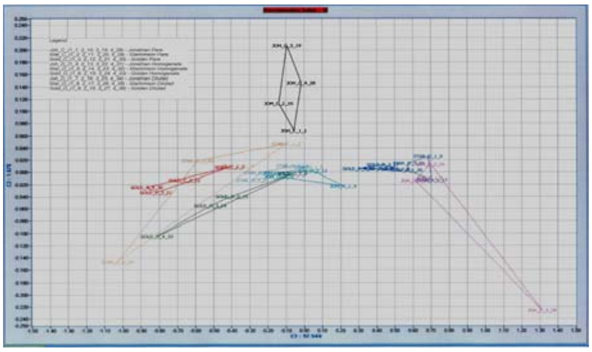

Figure 6. PCA analysis of all the apple samples (legend attached)

A DFA is valid if: there are enough samples per group and if the percentage of recognition > 90%. Figure7 presents the DFA diagram; DFA analysis proved to be successful in performing overall correct classification (86%) of the nine samples of apples used in these experiments. The pares samples and homogenate samples are located in the right part of the graphic and the diluted samples are more oriented on the left part. With sensor and mass optimization we have a better discrimination -The second series of measurements gave a very astonishing result**.** It is very surprising that the kind of sample for same apple can also be discriminated.

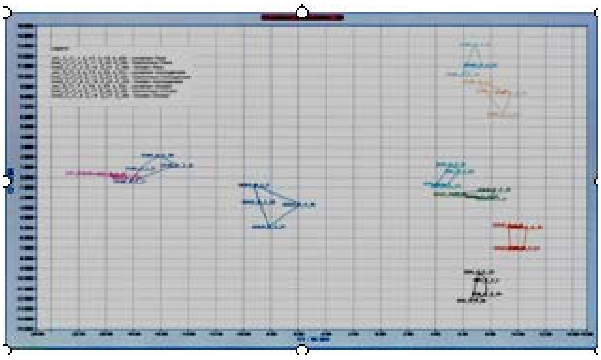

Figure 7. DFA - sensors show discrimination between various samples of the same group

Figure 8 gives the SQC chart which generally presents the acceptability region, defined according to the reference samples (grey area)- as it can be seen, in generally the obtained result is good, for apples from Reghin which are not situated in the area of the reference.

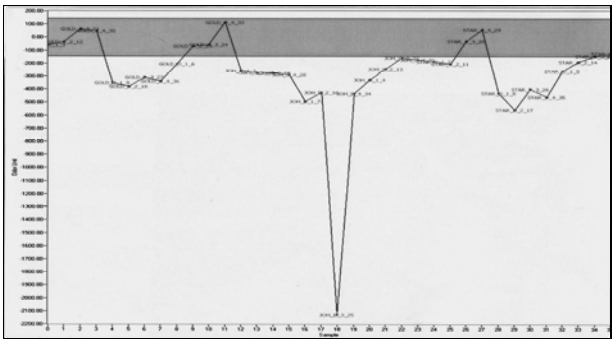

Figure 8. SQC of diluted homogenate of apples

4. Conclusions

Results indicate that electronic nose may be successfully applied as rapid method for discriminating Romanian apples. Rapid methods usually refer to methods that take minutes to get a result. In our study, under the mentioned experimental conditions, the E-nose intensities were available for statistics after approximately 20 minutes of analysis.

Compared to traditional methods, multivariate analysis combined with modern instrumental techniques (eg, E-Nose) often give new and better insight into complex problems by measuring a greater number of chemical compounds at once. These methods are attractive due to their inherent features of versatility, flexibility, effectiveness, and richness of information.

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