ELECTRONIC NOSE FAST METHOD FOR APPLES DISCRIMINATION TO DETERMINE OPTIMUM HARVEST MOMENT

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Abstract: *Appes should harvested before it is fully ripe, but after it has time to mature. This varies according to cultivar and different apples varieties will often ripen at different times over a three-month period. Sugars are major soluble solid in fruit juice and therefore soluble solids are often used as an estimate of sugar content. As the fruit mature, the starch changes to sugar and the aroma and flavors develops, when is generating volatile compounds. 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. An electronic nose (E-nose) was used to classify apple samples based on their smell. Seven varieties of apples from Romania, Golden, Starkrimson, Jonathan, Gala were from Reghin region and Pinova, Fuji, Golden,too, from Insuratei area, were used. 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 %). Choosing proper harvest moment for apples give us posibility of long term preservation in good quality conditions.*

Key words: *Multivariate statistics (PCA, DFA, SQC), correlating maturity indices, response surface.*

Introduction

Apples are the most widely consumed fruits in Romania. 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.
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. The headspace atmosphere of different flavors and essences are distinct both qualitatively and quantitatively. [1]

Volatile (often aroma) compounds are traditionally analyzed by gas chromatography (GC), GC analysis with flame ionisation (FID), GC mass spectrometry (GC-MS), and GC olfactory (GCO) methods (Lebrun et al., 2008), which involve very expensive equipment, time- and labor intensive steps, methods development, sample preparation, separation of specific volatile compounds using appropiate chromatographic columns, and chromathogram interpretation; 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. [3,4] 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. [5]

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. [6] 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.[7] Were realized a comparative analysis of apple aroma by a tin-oxide gas sensor array device. [8] Other researchers like 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. [9,10,11]

The objective of this study was to develop a methodology for discriminating apples from two regions of Romania, regarding optimal harvesting period determination. In order to achieve this goal we focused our efforts on fizico-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).

Materials and methods

1. *Experimental set-up*

Golden, Starkrimson, Jonathan, and Gala varieties are the most in Romania while Pinova, Fuji are varieties less cultivated by growers across the country.

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.

The resulting E-nose intensities were analyzed by PCA, DFA and SQC.

2. Optimum harvest moment choosing

This important stage for horti field was done by three maturity indices correlating: firmness (F), soluble solids(S.S.) and starch iodine index (SI). Firmness of the apples was evaluated using a electronic penetrometer Penefel DFT 14, with a plunger of 11 mm. Soluble solids were determined using an Abbe refractometer model 2 WAJ Optika and starch iodine index was determinated with o solution of iodine. Fruits testings for maturity were starts three weeks before harvesting period expectations. Maturity indices was fallowed in dynamics once at every five days in preharvest period.

Correlating those three indices help us to accomplish specific charts for each apples type offering us oportunity to deduce optimal harvesting moment for each apples variety.

Results and discussion

In order to evaluate the capability of a commercial electronic nose to discriminate varieties of apples from different regions of Romania, the resulting E-nose intensities of the analyzed apples were grouped on varieties of apples and types of sample (pare of apples, homogenized pare and pulp of apples and diluted homogenates to 25%). Best results was obtained for pare sample. Because of the big number of figures obtained from multivariate statistics (PCA, DFA and SQC; ≈ 12 for each group) only two of them are shown below. For the others are presented in Table 1, the % of variance and the percentages of recognition obtained.

Table 1
% of variance and the percentage of recognition for some of the groups mentioned at the begining of the discussion

Group	% of variance			percentage of recognition		
	pare	homogenate	Diluted homogenate	pare	homogenate	Diluted homogenate
1	91	89	87	-	-	-
2	91	89	-	100	100	-
3	97	94	92	100	100	-
4	98	96	94	100	100	100
5	98	88	-	100	100	100
6	97	95	-	-	100	100
7	92	-	-	100	-	-

The obtained results indicated that E-nose could discriminate successfully among varieties of apples:

- 12 of 16 PCA ploted graphs were having a % of variance >> 90;
- 13 of 13 DFA ploted graphs were having a percentage of recognition = 100 %.

In Figure 1 and Figure 2 are presented the graph and the chart of Principal Component Analysis and respectively Statistical Quality Control analysis for toate grupurile (pare samples).
The PC on X-axis (Figure 1), represents 99,15% of the global information given by the instrument analysis, with an discrimination index of 91 % of variance. It can be easily observed that the Golden pare samples have well distinct profiles. The Golden samples from Insuratei and Reghin, are located on the same axis but on different positions meaning that Golden from Reghin should be harvested before Golden from Insuratei. On the same chart for Pinova variety (on the right) we can observed that harvesting period was delayed; for Jonathan is the optimal period. Starkrimson and Fuji varieties are closer like positions and harvesting period is more delayed comparing with the others apples varieties (on the left) in comparison with Gala which is in climacteric stage, already (consumption maturity). All those were confirmed by SQC. Green field is acceptability area where Fuji variety was considered sample references by the equipment (Figure 2).

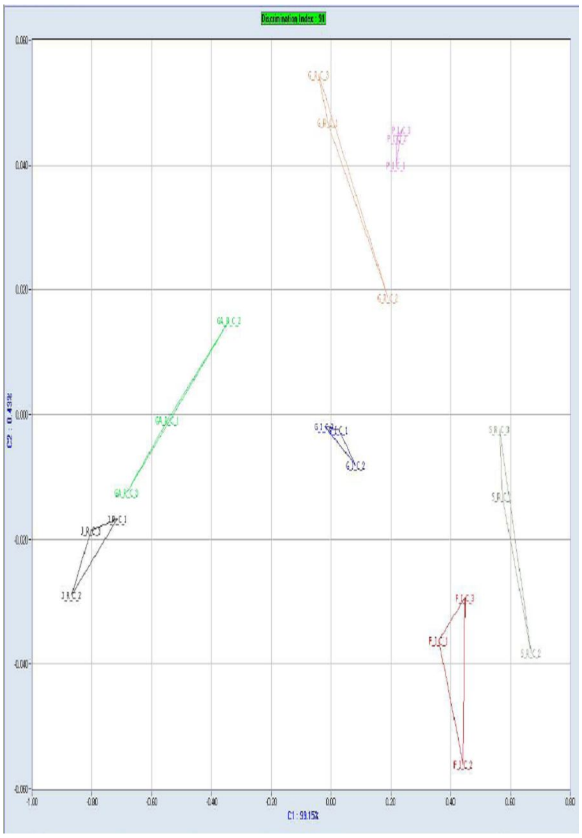

Figure 1: PCA analyse for pare sample in september

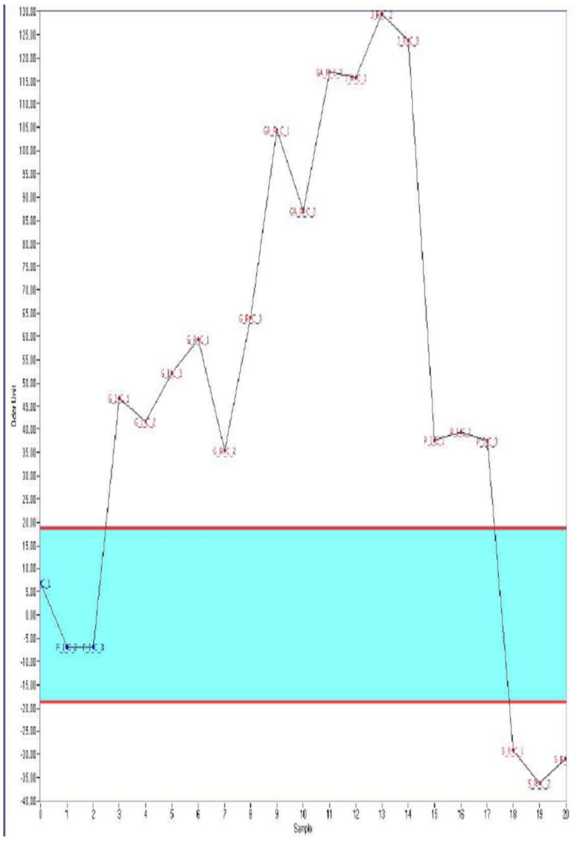

Figure 2: SQC analyse for pare sample in september

Each country has developed its own standard procedure to determine the right time to pick apples. Various indices have been devised, but because there are considerable variations in a wide number of quality parameters each year, considerable practical experience is needed when determining best harvest data. In our determinations were correlate firmness, soluble solids and grade hydrolysis(SI) of the starch for obtaining optimum harvest moment. Because of the big size of figures obtained from representing this point only one of them are shown below (Figure 3). For the others are presented in table 2, the co-ordinates of the optimum harvest moment.

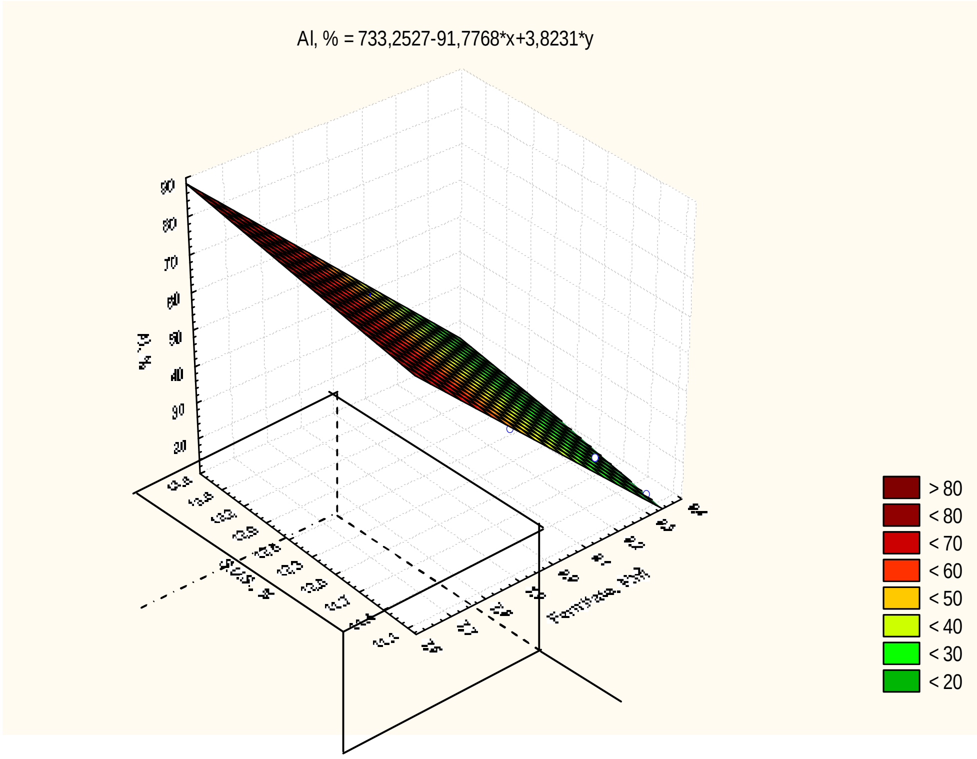

Fig.3-Graphic of correlate for Jonathan apples

Table 1

Typical values to determine optimum harvest moment

Variety of apple	M(optimum harvest moment)		
	Fimness, N/cm2	**Soluble solids, %**	**Grade hydrolysis of the starch, % of surface transverse section of the apple**
Gala	9.425	14.375	35%
Starkrimson	9.568	13.160	40%
Fuji	8.795	15.320	45%
Pinova	8.500	12.075	40%
Golden Reghin	8.878	13.230	35%
Golden Insuratei	8.626	13.875	35%

Conclusions

We used response surface metodology to establish independent variable efect (firmness, soluble solids) against optimum harvest moment considered to be dependent variable. Results indicate that electronic nose may be successfully applied as rapid method for discriminating apples, regarding optimum harvest moment. 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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