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Fast GC as a useful tool for authenticity assessment of kiwifruit

Paweł Michalczuk[1,*], Joanna Myszka[1], Martyna Lubinska[2], Anna Różańska[2], Jacek Namieśnik[2]

[1]Scientific Students Circle at Gdansk University of Technology
11/12 Gabriela Narutowicza Str., Gdansk, Poland

[2]Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology,
11/12 Gabriela Narutowicza Str., Gdansk, Poland

*E-mail address: pamichalczuk@gmail.com

ABSTRACT

Kiwifruit is one of the healthiest fruits due to its high content of biologically active substances and nutrients. The most popular species of *Actinidia* (kiwifruit) are the *Actinidia deliciosa* fruits called kiwi and *Actinidia chinensis* commonly called golden kiwi, while the lesser known species is *Actinidia arguta* known as mini kiwi. Bioactivities and nutrients of *Actinidia* are influenced by species and cultivars. It is very important to find a way to distinguish kiwifruit samples from botanical and geographical origin. For this purpose, the possibility of application of electronic nose based on ultra-fast gas chromatography for differentiation three types of kiwifruit was investigated. A set of 18 samples of kiwifruits were analyzed by fast GC e-nose. This device contains two parallel chromatography columns with different polarity connected with two flame ionization detectors (μ-FIDs). Four data analysis methods were used: discriminant function analysis (DFA), principal component analysis (PCA), soft independent modeling of class analogies (SIMCA), and statistical quality control (SQC). Application of e-nose based on fast GC system allows to effective and rapid compare of aroma profiles of three types of kiwifruits. PCA, DFA and SIMCA data analysis method were for visualization the discrimination between groups of kiwifruit species. The SQC method allowed to assess the quality of the samples. All of used chemometric methods allows for full discrimination of all groups of samples. In summary, the use of ultra-fast GC with four statistical methods can be used to discrimination of kiwifruit samples due to their botanical and geographical origins.

***Keywords*:** kiwifruit, food analysis, gas chromatography, electronic nose, botanical origin, chemometric analysis, DFA, PCA, SIMCA, SQC

1. INTRODUCTION

Actinidia is one of about 55 species of kiwifruit from Central China. *Actinidia* species are long-lived and grow on woody vines. Their fruits are spherical or oblong berries, varying in shape and color [1]. *Actinidia deliciosa* is the most commonly cultivated and consumed species in southern China. Yang Tao is the Chinese name, meaning strawberry peach. This name has been replaced by Europeans as a Chinese gooseberry. Europeans thought this name reflects the taste and color of the fruit. In 1962, growers from New Zealand began to call it "kiwi", similar to the national kiwi bird. *Actinidia deliciosa* fruits have the largest size of the three presented species. Their skin is brown and covered with short, stiff brown hair. The flesh is juicy and green. Its taste is usually sweet and sour, resembling the taste of strawberry or gooseberry [1-3]. *Actinidia chinensis* otherwise called golden kiwifruit is another popular variety of kiwi from China. The fruits of *Actinidia chinensis* have smooth, brown skin and a sweeter and more aromatic flavor than *Actinidia deliciosa*. The color of the fruit can range from light green to intense yellow. However, the most sought after and attractive variety is the so-called "red iris", when its center the flesh is red and the outside yellow [4-6]. *Actinidia arguta* is one of the lesser known kiwi species. The fruits of this variety look like large grapes. On the other hand, the skin is not covered with hair so it is edible. The other names of *Actinidia arguta* are kiwiberry, kiwai, mini kiwi, baby kiwi or kiwibes [7,8].

Incorporating kiwi fruit into daily diet can have a positive effect on the human body. This is due to the fact that these fruits are characterized by health benefits [9,10]. Kiwifruit contains a large amount of vitamin C, up to 50% more than citrus [11,12]. They are also an excellent source of vitamin E, folic acid or minerals: potassium, calcium, magnesium and phosphorus. *Actinidia* also has high antioxidant capacity [13,14]. There are a number of carotenoids in the fruit of this species, namely β-carotene, lutein and cellulite, which counteract free radicals, protecting the body from many chronic diseases. Other antioxidants such as tocopherol, caffeine, α-sitosterol, chlorogenic acid, flavones and flavonoids have also been detected. These fruits also have high levels of lutein and actinidin (an enzyme regulating the digestive system) [3,10].

However, different varieties of fruits can differ not only from taste and smell, but also from the content of many chemicals for example the nutrient content. And consequently it may affect on properties and antioxidant action.

Authentication of fruits is therefore very important from the point of view of both health impact and commercial value. There are many references methods to evaluate the authenticity of food samples. Many of them, such as dry matter measurement, water content and nutrient or mineral content, are associated with a very complicated and laborious preparation process [6]. This step can be simplified by applying techniques in which volatile fractions are analyzed, e.g. gas chromatography, olfactometry [15-17]. However, these techniques are often characterized by long analysis times. Therefore, devices are sought to make it possible to quickly and easily distinguish the botanical origin of fruit. Such an analysis is possible thanks to the use of the electronic nose.

An electronic nose is a device whose use is convergent to the function performed by the human sense of smell. Its use makes it possible to detect and distinguish complex mixtures of fragrances. For its construction most often a group of chemical sensors is used [18]. In the presence of fragrances a characteristic sensor response signal profile i.e., "fingerprint". In the last years, there has been an intensive development of sensor technology. At the same time the development of electronic noses, which used the technique of spectrometry mass or ultrafast gas chromatography has been observed [19].

The aim of this work was to verification of the usefulness the application of electronic nose based on fast GC for the authenticity assessment of three types of kiwifruit: *Actinidia deliciosa*, *Actinidia chinensis* and *Actinidia arguta*. Another objectives in this work were determination of the similarities and possibility of differentiation of the aroma profiles of these three species of kiwifruit by applying four statistical methods of data analysis, i.e., PCA, DFA, SIMCA, and SQC.

2. EXPERIMENTAL

2. 1. Materials

Three species of kiwifruit were taken to conduct the anaysis: golden kiwi (*Actinidia chinensis),* kiwi Hayward *(Actinidia deliciosa)* and mini kiwi *(Actinidia arguta).* For each type of kiwifruit, 6 samples were prepared. Each sample was taken from another fruit. All kiwi fruits were bought at local distribution points in Gdańsk, to where they had been imported from New Zeeland, Italy and Germany respectively.

2. 2. Sample preparation

The fruits were washed with cold running water and then rinsed with Millipore deionized water. Later they were cut into smaller pieces and homogenized using a blender. In this form the fruit was put in beforehand prepared vials.

5 gram of each kind of fruit was weighted. After weighing the appropriate weight of fruit 1 m of Millipore deionized water was added. The vials were tightly closed using aluminum caps with silicone-teflon membrane.

2. 3. Electronic nose analysis

To carry out the analysis, the electronic nose with ultra-fast gas chromatography Alpha M.O.S., Heracles II was used. Scheme of the construction of the Heracles II is shown in Figure 1.

During measurement, 2.5 mL of gaseous sample is introduced into the system using autosampler HS 100. Analytes are transferred in the carrier gas stream (hydrogen) to the sorption trap, filled with 10 mg of sorbent Tenax TA. Then they are desorbed and put into two parallel linked chromatographic columns, whose stationary phases are characterized by different polarity (non-polar MXT-5 and medium polar MXT-1701) with a length of 10 m and an internal diameter of 0.18 mm.

After elution of the analytes from the chromatographic columns, they are transferred to the measuring cells of μFID detectors, which can work at temperatures up to 300 °C.

During the measurement, the injector worked in splitless mode. Incubation was carried out in 80 °C for 300 s. Samples were stirred at 300 rpm in agitator.

The volumetric intensity of the carrier gas flow was equal to 250 µL/s. The injector worked at 250 °C and the pressures of carried gas at the level of 250 kPa. Desorption time was 20s at the initial temperature of the trap sorption of 40 °C and the pressure of 80 kPa. The temperature of FID detectors was 270 °C.

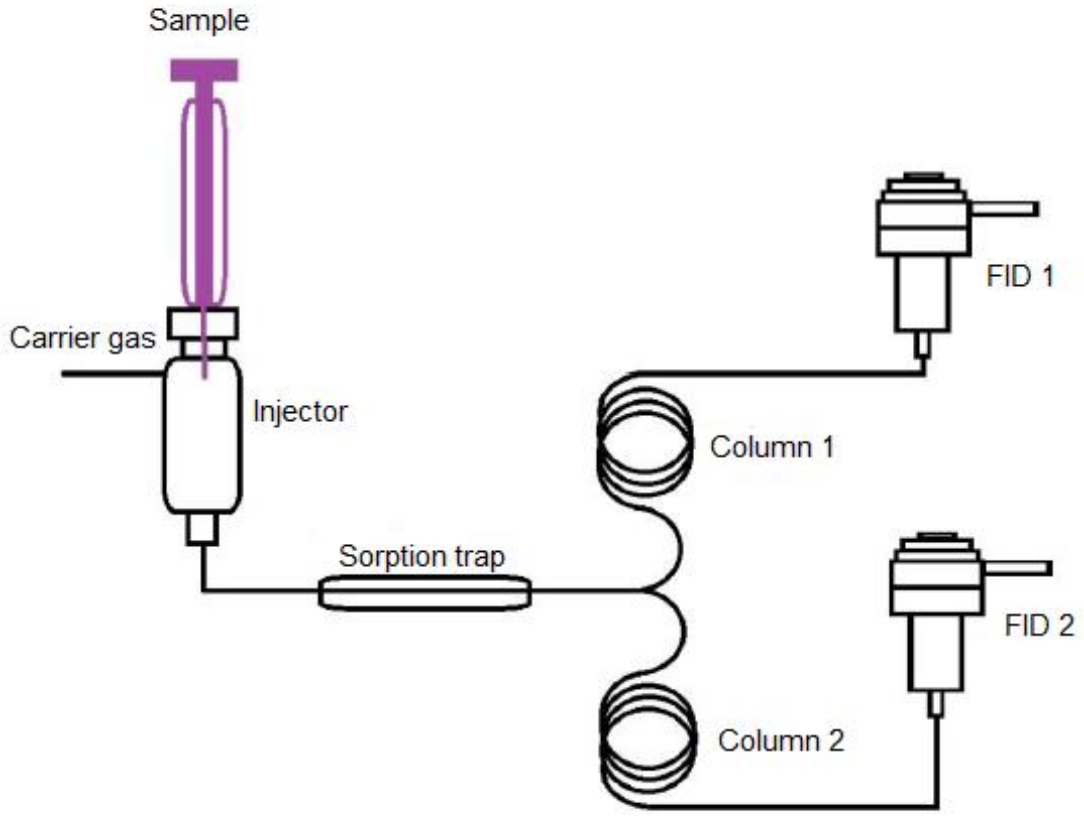

Figure 1. Scheme of ultrafast gas chromatography based electronic nose

3. RESULTS

3. 1. Discriminant function analysis

Discriminant function analysis is an chemometric method that is used to determine which variables discriminate between two or more groups that occur naturally [20]. In case of this research DFA was employed in to determine if an electronic nose is an useful tool to distinguish the botanical origin of three species of kiwifruit. The results of DFA analysis are shown on Figure 2.

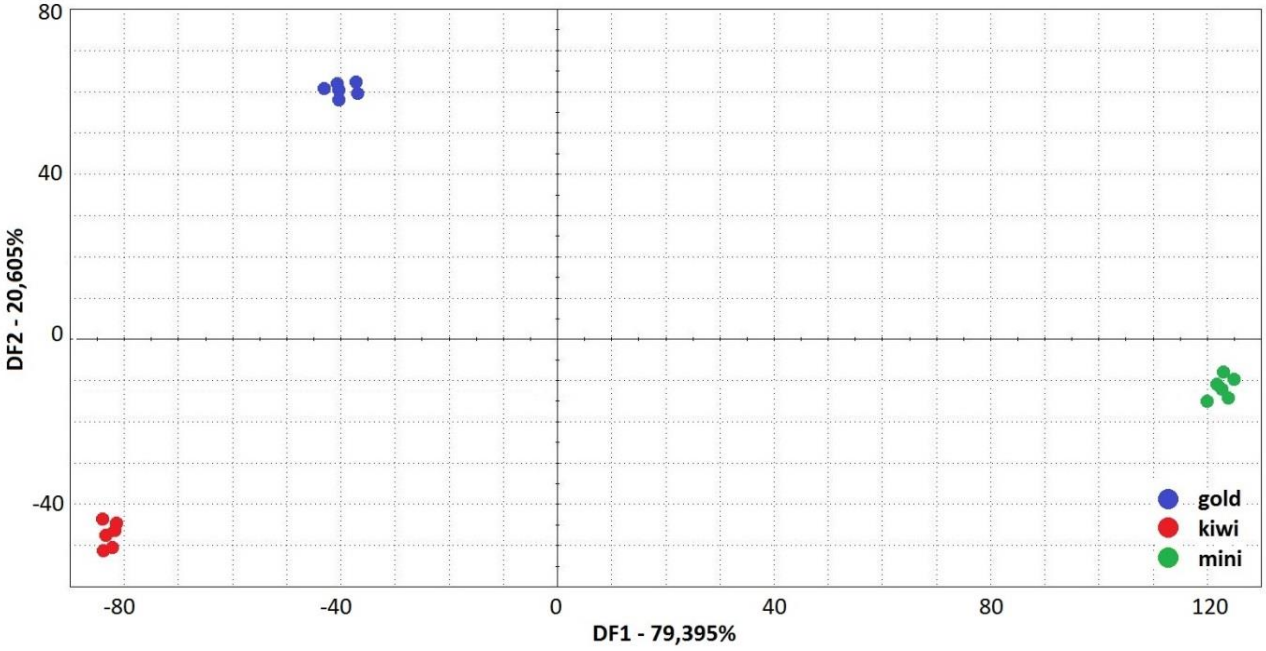

Figure 2. DFA results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit

DF1 accounted for 79,935% and DF2 accounted for 20,605%. It was possible to distinguish between all samples very well. The points of all species are also located in different quadrant of the plot. Moreover the point create more concise groups than in case of PCA. The results are also more unequivocal to interoperate. The distances between the groups of samples are also large, which shows a good distinction. The DFA results also confirm that samples of kiwi gold and kiwi mini show more similarity among themselves.

3. 2. Principal component analysis

Principal component analysis (PCA) is one of the most commonly applied chemometric techniques that allows to analyze a data table described by several dependent variables, which are intercorrelated. It is used to display patterns in multivariate data. As it can be seen at Figure 3, it was possible to distinguish three species of kiwi fruit by using PCA.

PC1 accounted for 69,2% and PC2 accounted for 30,6%.So the sum of the first and second principal components accounted for 99,8% of data variance. This means that the first two components explain almost 100% of the total volatility. It can be observed that points representing each species of fruits are relatively distant from each other. The point belonging to different species of fruits are in the different quadrant of the plot. There is the biggest distance between kiwi gold points and other groups. It suggests that this group differ the most from groups of mini and kiwi fruit. The proximity of points of other fruits, corresponding to the composition of the volatile fraction of these fruits, close together on the graph confirms similarity of the composition of the volatile fractions of fruit.

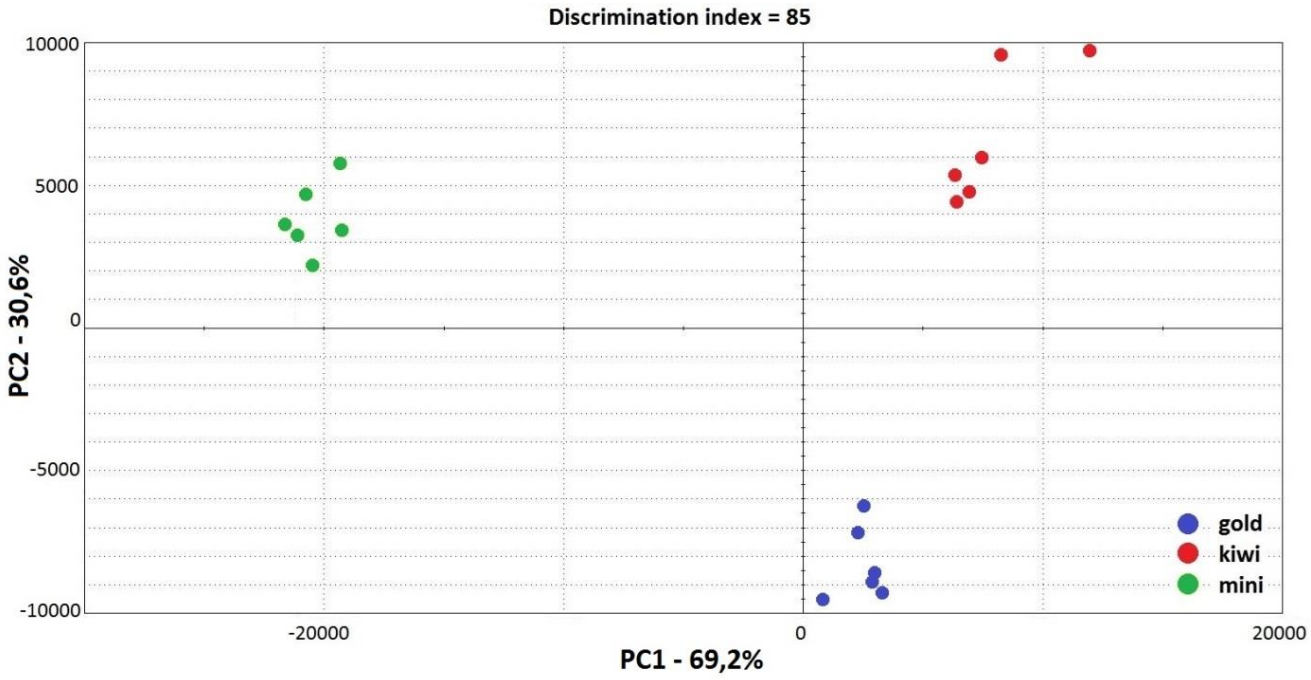

Figure 3. PCA results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit

3. 3. Soft Independent Modeling of Class Analogies

SIMCA, which stands for Soft Independent Modeling of Class Analogies, is a very useful method for classifying observations [21]. This classification is based on a disjoint PCA modeling created for each class [22,23]. Then a multidimensional field (i.e., a certain volume or plane), the so-called "confidence envelope" is constructed for each group [24]. All elements belonging to this class should be included in this field. The SIMCA method was used for classification samples into 3 groups. The SIMCA analysis was performed for each of the reference groups: gold (Figure 4a), kiwi (Figure 4b), mini (Figure 4c).

In all cases, all points belonging to the reference group were located in the confidence envelope (light blue area). It means that all of the samples were classified appropriately. SIMCA analysis is similar to PCA and DFA, but its purpose is not just to classify samples into groups but also to get information about particular group structures such as relevance of the different variables and measures of separation [21].

For this reason, the distinction between different groups is more apparent. Due to the creation of multidimensional fields with clearly defined group boundaries, the classification of unknown samples into existing groups is unequivocal.

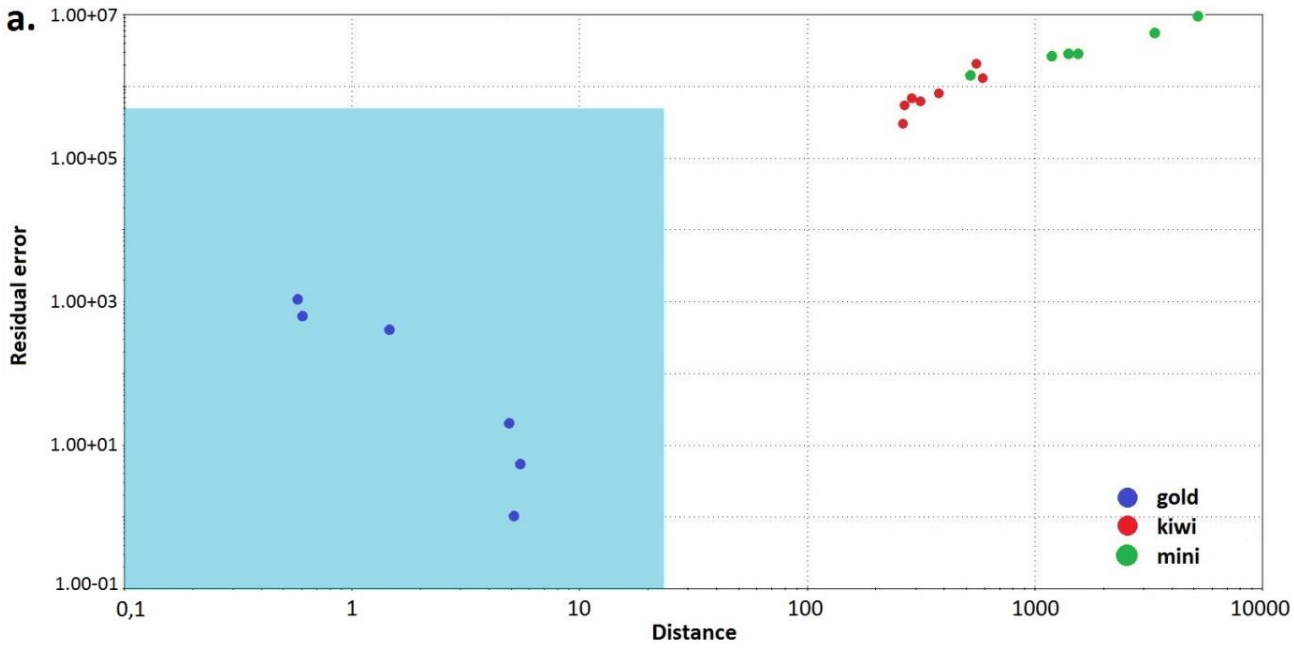

Figure 4a. SIMCA results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit; reference group: gold kiwi

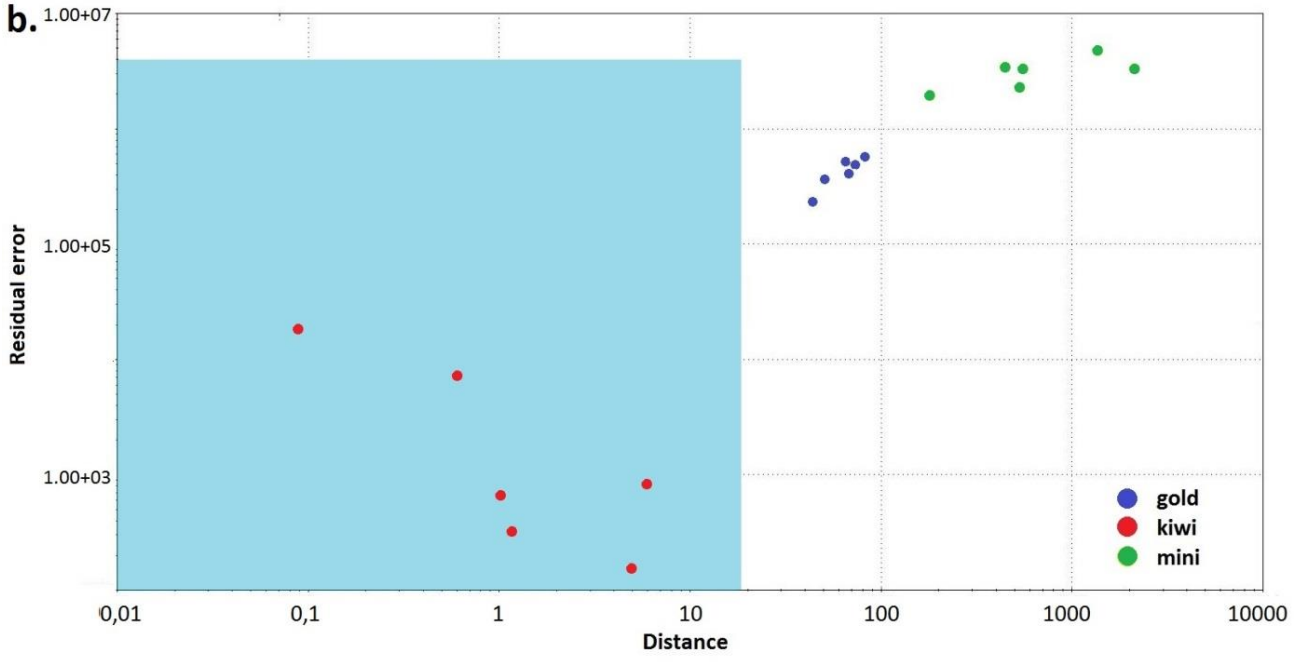

Figure 4b. SIMCA results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit; reference group: kiwi

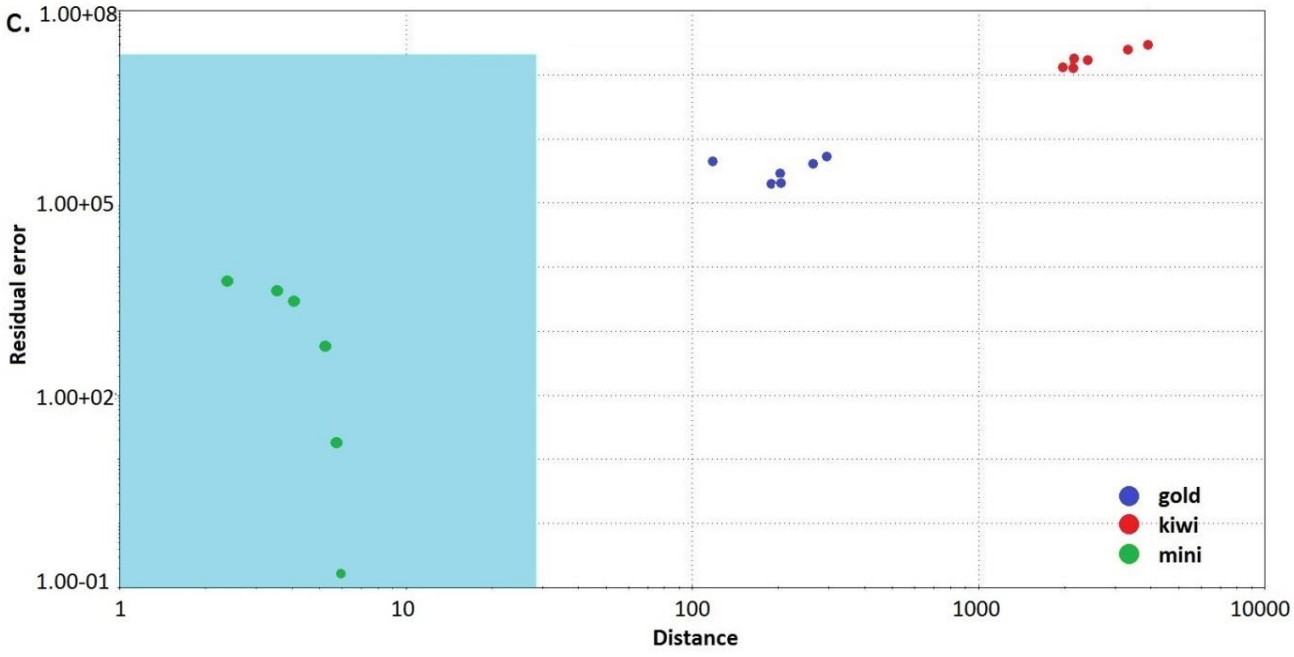

Figure 4c. SIMCA results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit; reference group: mini kiwi

3. 4. Statistical Quality Control

SQC which stands for statistical quality control, is a set of statistical techniques used for surveillance. This is a useful method for controlling the quality of actual samples, e.g. on production lines, to control the quality of process. Samples belonging to a defined class should be located in the area defined in the chart by appropriate parameters [25]. An acceptability areas (grey areas) on the SQC charts are define through the upper and lower limits (horizontal lines).

The upper and lower control limits are set at plus or minus 3 standard errors from the mean. The SQC method was used to control the quality of 3 groups of kiwi samples. The SQC analysis was performed three times, taking as a reference group each of the 3 classes: gold (Figure 5a), kiwi (Figure 5b) and mini (Figure 5c).

In all cases samples from different classes of kiwi have been discriminated. Using the SQC analysis, it is possible to discern differences between samples belonging to one group. For this reason, this method allows finding and excluding a statistically different sample from the certain class.

The range of the reference area depends on the deviations between points in a certain group. When the deviation values between samples in the group is increasing, the tolerance range is increasing too. In the Figure 5a it can be seen that the differences between the points belonging to the gold kiwifruit group are the smallest. And the differences between samples of kiwi and kiwi mini (Figure 5b, Figure 5c) are more noticeable and the tolerance range is bigger.

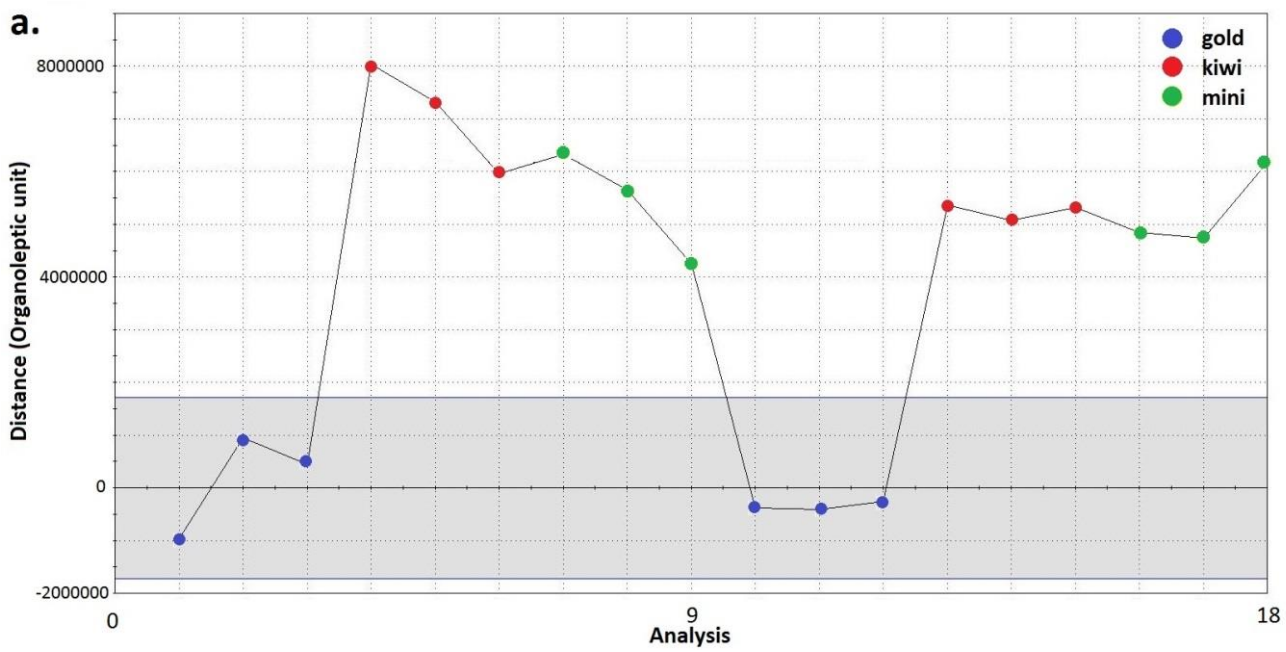

Figure 5a. SQC results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit; reference group: gold kiwi

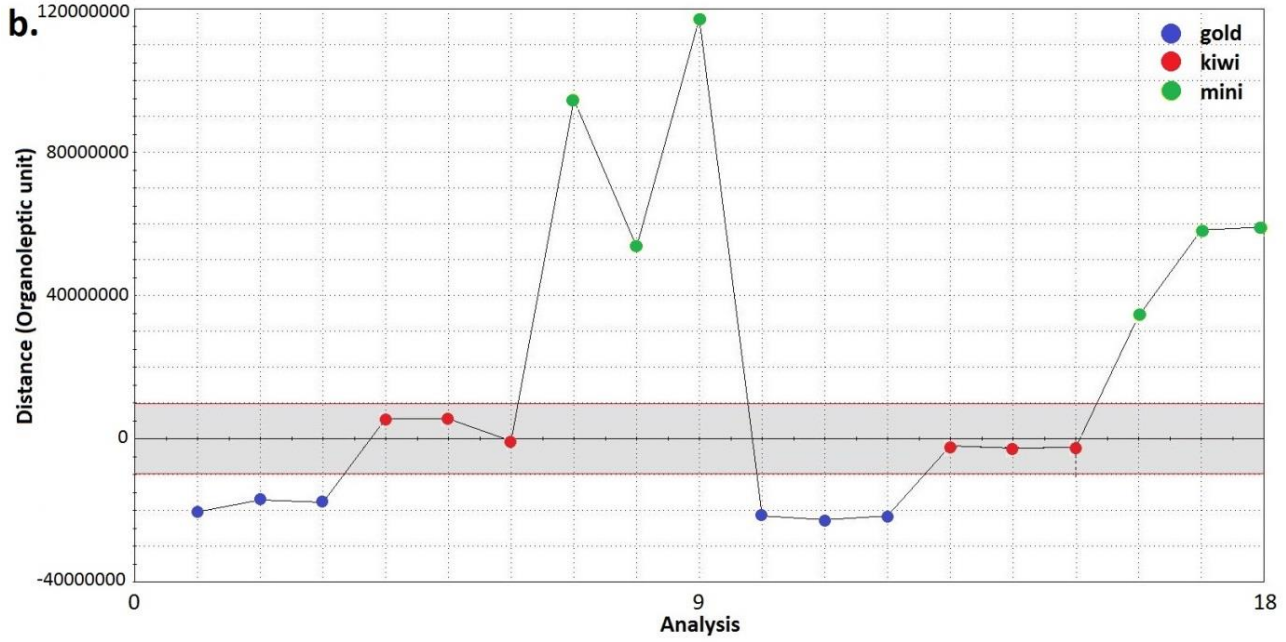

Figure 5b. SQC results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit; reference group: kiwi

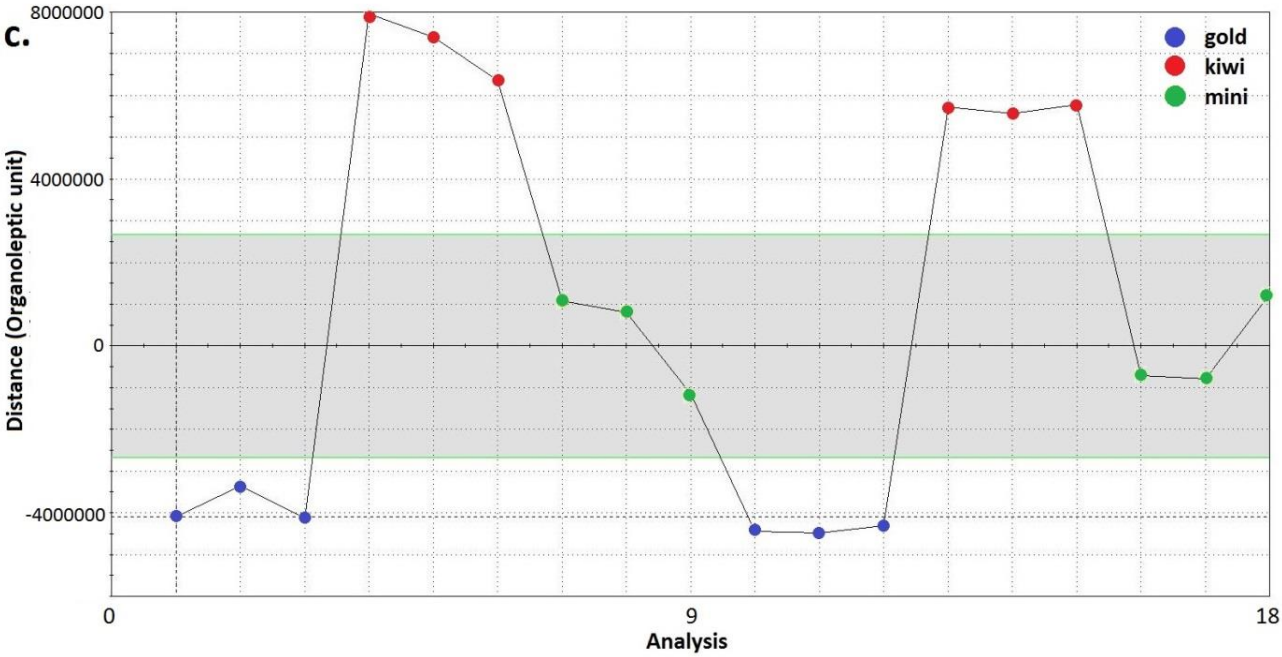

Figure 5c. SQC results for gold (blue points), normal (red point) and mini (green points) samples of kiwifruit; reference group: mini kiwi

3. 5. Radar plot

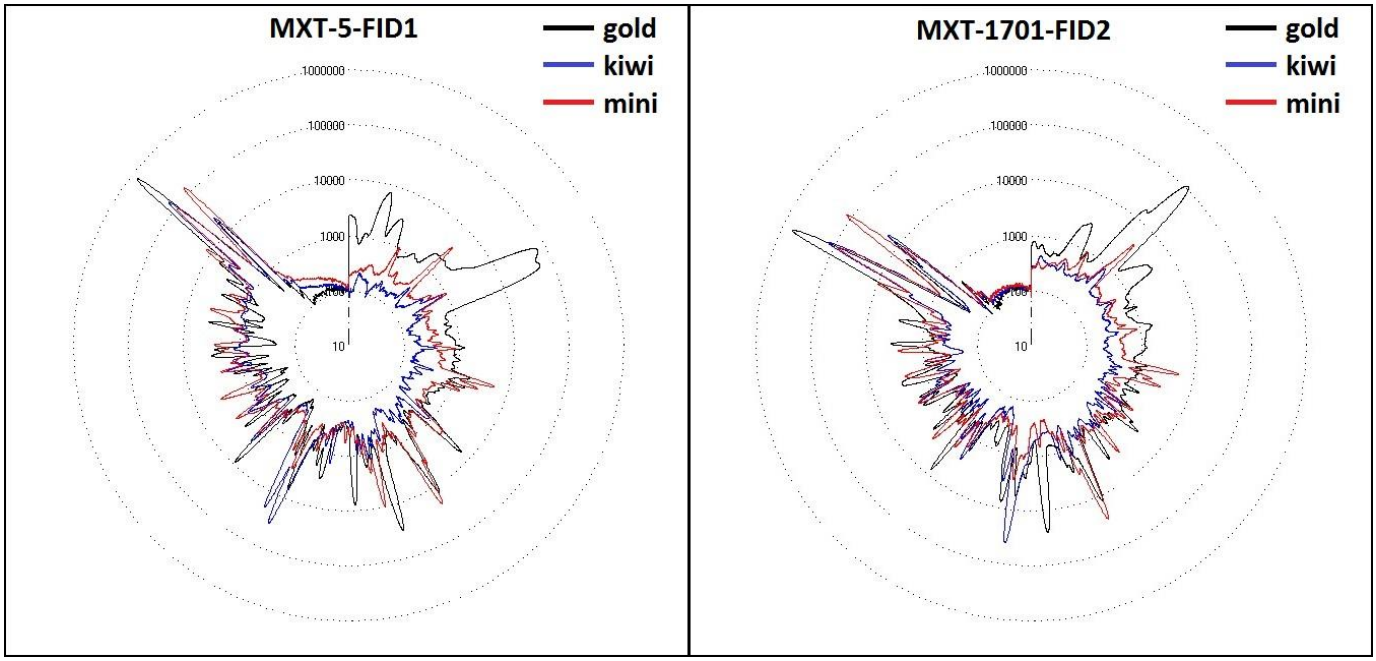

Figure 6. Radar plot obtained by conducting analysis of gold (black lines), normal (blue lines) and mini (red lines) samples of kiwifruit

The Figure 6 shows the radar maps for different groups of kiwifruit species. These radar maps was obtained of electronic nose based on fast GC (for two column: MTX-5 and MTX-1701).

The comparison of radar maps showed significant differences in volatile compounds profile of three groups of kiwifruit. The number of peaks collected for all sample groups was comparable, but the peaks heights were different. Radar maps show that gold kiwifruit specie have the most intensive aroma profile than other types of kiwifruit species. Samples of Hayward kiwifruit species were characterized by the least intensive aroma. Based on this situation it can be seen that the electronic nose based on fast GC is useful tool to very rapidly indicate that aroma profiles of three groups of kiwifruit species are different.

4. CONCLUSIONS

In this paper the usefulness of ultra-fast GC based electronic nose for the determination of botanical origin of three species of kiwifruit was presented. It was possible to determine the differences between species by using of four data analysis methods. The PCA was used for the visualization of dataset, observation of the variation inside groups of samples of kiwifruits. The SQC method was applied to assess the quality of the samples. Both the DFA and SIMCA data analysis methods were used for discrimination of kiwifruit samples. By using of two chromatographic columns of different polarity it would also be possible to conduct a qualitative analysis that allows to find differences between aroma of kiwifruit of three species. By the presence of chemical compounds library it is also possible to attribute to the smell which has been previously described in the literature. It is planned to conduct such research in the future. To sum up, e-nose seems to be a good tool to the assess the authenticity of fruits. It allows for quick and cheap measurements. Designing a device for assessing the botanical origin of fruit, which is based on the principle of electronic nose operation, would be a great facility in the fruit and vegetable and fruit industries.

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