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**SPME-GC and sensors as rapid methods for monitoring the lipid oxidation in nuts**

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Food Types:	Dried fruit

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Manuscripts

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6 2 **Solid phase micro-extraction (SPME-GC) and sensors as rapid**  
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9 3 **methods for monitoring lipid oxidation in nuts**  
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49 21 **Abstract**

50  
51 22 Dry foods with high fat content are susceptible to lipid oxidation, which involves a  
52 23 quality deterioration of the product, since this process is responsible for the generation  
53 24 of off-flavours. Hexanal is considered to be a good shelf-life indicator of such oxidation  
54 25 products. In addition, due to its high volatility, hexanal can be easily determined by fast  
55 26 headspace analytical techniques. For this reason an electronic nose comprising 10 metal

1 oxide semiconductors (MOS) and a solid-phase microextraction (SPME) coupled with  
2 gas chromatography and flame ionization detector (GC-FID) method were compared in  
3 order to determine hexanal formed in hazelnuts during storage under different  
4 conditions (room temperature, 40°C, UV light, with and without oxygen scavenger).  
5 The results obtained by the two methods showed a good correlation, confirming the  
6 possibility of using a multi-sensor system as a screening tool for the monitoring of  
7 shelf-life and oxidation state of nuts.

8  
9 **Keywords:** Multi-sensor system, electronic nose, SPME, hexanal, lipid oxidation,  
10 oxygen scavengers, shelf-life

## 1 Introduction

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1 Foods with high fat content like nuts are very good model products for shelf-life studies  
2 (Del Nobile 2001). These products are susceptible to rancidity because of the lipid  
3 oxidation (Brunton et al. 2000; Goodridge et al. 2003; Lee and Krochta 2002; Stashenko  
4 et al. 2002). Different storage variables such as light and temperature can influence the  
5 off-flavours development from the products generated by lipid oxidation (Jensen et al.  
6 2005).

7  
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9  
10 Hexanal is the main aldehyde formed during the oxidation of unsaturated fats (Shahidi  
11 2001). For this reason hexanal is a representative marker of the oxidative rancidity.

12 The purpose of the present paper was the development of a simple, efficient and fast  
13 method to determine hexanal and to monitor its presence in hazelnuts samples stored  
14 under controlled conditions.

15  
16 A multi-sensor system (electronic nose) and solid phase micro extraction (SPME) were  
17 compared in order to evaluate the effect of storage conditions on packaged food.

18 According to the Gardner and Bartlett's definition (Gardner and Bartlett 1994), an  
19 electronic nose is "an instrument, which comprises an array of electronic chemical  
20 sensors with partial specificity and an appropriate pattern-recognition system, capable  
21 of recognising simple or complex odours". Different kinds of gas sensors have been  
22 developed and in function of their ability, the e-nose can be fit for various applications  
23 in food industry (Schaller et al. 1998). It was shown to be suitable both to evaluate the  
24 odour of packaging materials such as paper (Holmberg et al. 1995), paperboard (Willing

1 et al. 1998) and plastic films (Frank et al. 2001; Van Deventer and Mallikarjunan 2002)  
2 and to determine the sensory contamination of packaged foodstuffs (Heiniö et al. 2002).  
3 The aroma evaluation of foods can be performed in different steps of production from  
4 the raw material stage right to the final product in order to monitor the quality and  
5 freshness (Bartlett et al. 1997). In the last years, the use of an e-nose was tested both on  
6 different foods such as olive oil (Ulmer et al. 1997; Gonzáles Martín et al. 1999; García-  
7 Gonzáles et al. 2004), tomato (Berna et al. 2004), tea (Dutta et al. 2003), coffee (Ulmer  
8 et al. 1997; Singh et al. 1996), fruits (Di Natale et al. 2001; Saevels et al. 2003), bakery  
9 products (Needham et al. 2005) and on animal foods, e.g. meat (Berdagué and Talou  
10 1993), poultry (Rajamäki et al. 2006), fish (Di Natale et al. 2001) and milk (Capone et  
11 al. 2001; Labreche et al. 2005). Moreover, the correlation of the sensor data with  
12 classical analytical techniques was investigated by various authors (Frank et al. 2001;  
13 Annor-Frempong et al. 1998; Bleibaum et al. 2002; Aishima 2004; Strathmann et al.  
14 2005).

15  
16 Solid phase micro extraction was selected as sampling technique to compare to e-nose  
17 data because it has been proven to be a simple, fast, solventless technique and it does  
18 not require sample preparation. Volatile profiles in different foodstuffs have been  
19 successfully characterised by SPME. Many SPME applications can be found in the  
20 literature for fruit (Augusto et al. 2000; De Lourdes-Cardéal et al. 2005), meat (Ramirez  
21 et al. 2004), vinegar (Natera-Marin et al. 2002), olive oil (García-Gonzáles et al. 2004),  
22 soybean (Boué et al. 2003), truffle (Diaz et al. 2002). The analysis of hexanal in several  
23 matrices has also been performed by SPME in turkey (Brunton et al. 2000), powder

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4 1 infant milk formula (Fenaille et al. 2003) and freeze-dried chicken (Goodridge et al.  
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6 2003).  
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10  
11 4 Due to the fact that both e-nose and SMPE has been successfully applied in food  
12  
13 5 analysis, in the present work specific methods for hexanal determination in nuts have  
14  
15 6 been carried out. The experimental design included also the use of oxygen scavengers.  
16  
17 7 Commercial pouches for food active packaging were tested for their efficiency and the  
18  
19 8 eventuality of an undesirable absorption of flavours generated from the food spoilage  
20  
21 9 was also investigated.  
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## 25 26 27 28 11 **Materials and methods**

### 29 30 12 *Samples*

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33 13 Powdered hazelnuts purchased from a local supermarket were packed in transparent  
34  
35 14 plastic pouches with high oxygen barrier properties. For each time-storage condition 3  
36  
37 15 different sachets were prepared: pouch with oxygen scavenger, pouch with 7 g of nuts,  
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39 16 pouch with 7 g of nuts and an oxygen scavenger.  
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45 18 Samples were then stored at room temperature, at 40°C and under UV light. After each  
46  
47 19 exposure period (0, 2, 5, 16, 31 days), pouches were opened and 6 head space vials (20  
48  
49 20 mL) were prepared for each package containing hazelnuts: 3 vials with 2 g of hazelnuts  
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51 21 for e-nose evaluation and 3 vials with 0.1 g of hazelnuts for SPME analysis.  
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56 23 In the same way the oxygen scavenger powder was removed from the pouches,  
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58 24 transferred in a 20 mL headspace vials and analysed by SPME/GC-FID technique.  
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1

2 *Reagents and Analytical Standards*

3 Hexanal with purity of 98% and triacetin for standard solutions preparation were  
4 purchased from Sigma-Aldrich (Steinheim, Germany).

6 *E-Nose*

7 A commercial portable electronic nose (PEN 2 model) from WMA Airsense Analytix  
8 Inc. was used. The sensor array system comprises 10 metal oxide semiconductors  
9 (MOS) of different chemical composition and thickness to provide selectivity towards  
10 volatile compound classes as indicated by the instrument supplier even if typically the  
11 sensors react broadband-like on organic and inorganic gases (Table 1). These devices,  
12 also called oxide or ceramic gas sensors, rely on changes of conductivity induced by the  
13 adsorption of odour molecules. The elevated operative temperature (200-500°C) allows  
14 avoiding interference from water and to aid rapid response and recovery times (Kohl  
15 1992). The detection limit of hot sensors was in the range of 1 mg kg<sup>-1</sup>.

16  
17 [Table 1, please insert here]

18  
19 For e-nose evaluations, 2 g of nut powder was placed in a 20 mL glass vial, sealed with  
20 a PTFE/silicone septum and a crimp top, stored at 25°C for 1 hour to equilibrate and  
21 analysed at the same temperature.

22  
23 The measurement system permitted suction of the gaseous compounds from the  
24 headspace of sample through the sensor array at 400 ml/min for 180 secs. Then a



1 second pump transported the filtered reference air to the sensor array (the flow rate was  
2 600 ml/min) for 400 secs to rinse the system between two following samples. The  
3 dimensionless ratio between the conductivity change induced by the volatile compounds  
4 from the headspace sample and the conductivity variation due to the interaction between  
5 the reference air and the metal oxide semiconductor (analysing air sample the ratio for  
6 each gas sensor is equal to 1) has been considered as response furnished by the single  
7 gas sensors.

### 9 *SPME-GC-FID-MS*

10 Details concerning the development of the method and the analytical conditions are  
11 reported in a previous paper (Pastorelli et al. 2006).

## 13 **Results and discussion**

15 E-nose and SPME have been used in this experimental work in order to monitor the  
16 shelf-life and oxidation state of hazelnuts during different storage conditions. Both  
17 techniques are rapid, convenient and solventless methods for the determination of  
18 volatiles compounds from sample materials.

20 The possibility of using an electronic nose with 10 metal oxide semiconductor sensors  
21 to evaluate the quality of nuts stored under different conditions was explored and  
22 compared with the SPME-GC-FID results. Figure 1 shows the principal component  
23 analysis (PCA) visualization of sensor array measurement performed on hazelnuts  
24 stored at room temperature, at 40°C and under UV light.

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[Figure 1, please insert here]

The two first principal components (PCs) accounted 89% of the total variability (71% and 18% respectively). The dominant effect was given by the first principal component (PC1) and a minor part by the second (PC2). The biplot (a scatter plot for scores and factor loadings) illustrated the mutual relationships between samples and sensors (Figure 1). In fact, the position of the samples in a part of the graph was determined by the influence of the response of the sensors collocated in the same area of the plot. In particular, in the left part of the graph the samples that have induced a higher interaction between volatile compounds and some metal oxide semiconductors (W5S, W6S, W1S, W1W, W2S, W2W, W3S) are shown. On the contrary, the position of the samples in the right part of the biplot was determined by a lower response of the above cited sensors. Moreover, the raw data used to perform the PCA (data not shown) indicated that the sensors coded as W1C, W3C and W5C provided the lowest electronic signals for all samples, similar to those obtained analysing the reference air. Therefore the samples resulted distributed along the PC1 (from positive to negative values) according to their increasing emission of volatile compounds.

An examination of the sensor correlation matrix and the overlapping of the W1C, W3C and W5C sensors revealed that those sensors were strongly correlated and so contributed little to the discrimination process. In order to evaluate the usefulness of these three sensors in data exploration, a PCA excluding them was performed.

[Figure 2, please insert here]

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The new score plot (Figure 2) did not show significant differences in distribution of samples in comparison with previous results obtained considering all 10 sensors (Figure 1). On the basis of that, it is possible to affirm that the W1C, W3C and W5C sensors did not provide any essential information to discriminate nuts, because probably nut degradation did not produce aromatic compounds able to react with these metal oxide semiconductors (Table 1). In other words, satisfactory results could be achieved performing analysis with only the seven selected sensors (W5S, W6S, W1S, W1W, W2S, W2W, W3S).

PCA data could be used to differentiate sample degradation as function of different storage conditions (Figure 2). As can be seen, nuts stored under UV light and without oxygen scavenger in the pack were well separated from the others. The action of UV light associated with the presence of oxygen represented the worst storage condition that favoured the highest production and accumulation of volatile compounds in nuts, as demonstrated by the position of these samples in the part of score plot that reveals the highest quantity of volatile compounds detected from the electronic nose.

With regard to the storage temperature differences were not observed among samples stored at 40°C and at room temperature. In fact the response of the array of the 7 sensors did not permit separation of nuts into two groups as function of the storage temperature, on the contrary the samples were grouped in only one cluster.

1 In figure 2, it was also possible to appreciate a minor detection of volatile compounds in  
2 hazelnuts packed with oxygen scavenger (empty symbol) with respect to ones packed  
3 without the active device (full symbol) at the same storage time and condition. In fact,  
4 in all cases, the samples with oxygen scavenger were positioned in the plot more to the  
5 right than the nuts without oxygen scavenger.

6  
7 For the development of a fast screening method the systems would need to calibrate  
8 more samples and a greater variety of conditions but the discrimination appeared to be  
9 feasible. The multi-sensor system provided a good differentiation among samples  
10 stored at different time-conditions. Anyway e-nose did not permit an identification of  
11 odour compounds responsible for the shelf-life state of the product. For this reason we  
12 used a SPME/GC-FID method for the identification of hexanal as indicator of hazelnuts  
13 oxidation state.

14  
15 The results obtained with the SPME/GC-FID confirmed the findings of the investigation  
16 with the e-nose. The different hexanal content obtained in the SPME/GC-FID analysis  
17 was correlated to the results of the sensor array measurements. The hexanal content  
18 profile of the mean results out of triplicate measurements of different samples is  
19 described in the figure 3.

20  
21 [Figures 3, please insert here]

22  
23 UV radiation seems to be the most critical factor for product oxidation. In fact, samples  
24 stored under UV light showed a higher hexanal content compared with the ones stored

1 at room temperature and at 40°C. However no big differences have been detected  
2 among samples stored at room temperature and at 40°C so that temperature seemed to  
3 have a minor effect on oxidation process.

4  
5 With samples stored under UV radiation hexanal content increased during storage time  
6 while in all the other hazelnuts without oxygen scavenger the hexanal content remained  
7 mostly constant or slightly decreased along exposure time. In the samples with oxygen  
8 scavenger it was possible to observe a clearly reduction of hexanal content compared to  
9 hazelnuts without active packaging under the same storage conditions. These results of  
10 samples stored under UV showed the efficiency of oxygen scavenger in reducing  
11 hazelnuts oxidation during storage.

12  
13 In the case of samples stored at room temperature and at 40°C the hexanal content in the  
14 hazelnuts with an oxygen scavenger decreased progressively with time. Due to the fact  
15 that in hazelnuts without oxygen scavenger under these storage conditions there was no  
16 increase in hexanal content during exposure, the data obtained seemed to indicate that  
17 active packaging could have absorbed hexanal from package headspace. In order to  
18 check this phenomenon the oxygen scavenger content was analysed by SPME.

19  
20 Hexanal was always found in the powder content in oxygen scavenger pouches and,  
21 with the exception of 40°C, hexanal concentration increased along storage time (figure  
22 4 shows the mean results out of triplicate measurements).

23  
24 [Figures 4, please insert here]

## 1 **Conclusion**

2 An e-nose has been used as a screening tool to monitor the state of rancidity and  
3 therefore the shelf-life of the hazelnuts stored under controlled conditions. The portable  
4 electronic nose equipped with 10 metal oxide semiconductors provided a satisfactory  
5 differentiation among samples stored under diverse conditions. The identification of  
6 hexanal as hazelnut shelf-life marker was performed by solid phase micro extraction  
7 coupled to a GC-FID and confirmed by GC-MS.

8  
9 E-nose measurement results and data obtained by SPME showed a good correlation  
10 between off-flavours evaluation and hexanal content during storage. Both techniques  
11 are complementary and could be used for monitoring the lipid oxidation in dry fat food.

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1 Table 1. Codes and selectivity of e-nose gas sensors.  
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Sensor code	General description
W1C	aromatic compounds
W5S	broad range compounds, polar compounds, nitrogen oxides and ozone
W3C	ammonia, aromatic compounds, aldeides, chetons
W6S	hydrogen
W5C	alkanes, aromatic compounds, less polar compounds
W1S	methane, broad range compounds
W1W	sulphur compounds, terpenes and sulphur organic compounds
W2S	alcohols, partially aromatic compounds, chetons
W2W	aromatic compounds, sulphur organic compounds
W3S	methane

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1 **Figure legends**

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3 Figure 1. PCA of the response of 10 sensors to the headspace of samples (N=Nuts, NS=  
4 Nuts+Scavenger) stored under different conditions (RT=Room Temperature, 40=40°C,  
5 UV= UV light) at different storage times (t=0, 2, 5, 16, 31 days).

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7 Figure 2. Score plot from the PCA analysis of samples (N=Nuts, NS= Nuts+Scavenger)  
8 stored under different conditions (RT=Room Temperature, 40=40°C, UV= UV light) at  
9 different storage times (t=0, 2, 5, 16, 31 days).

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11 Figure 3. Hexanal content of samples stored with and without oxygen scavenger at  
12 room temperature, 40°C and under UV light

13 Figure 4. Hexanal content in scavenger powder at room temperature, 40°C and under  
14 UV light

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Figure 1.

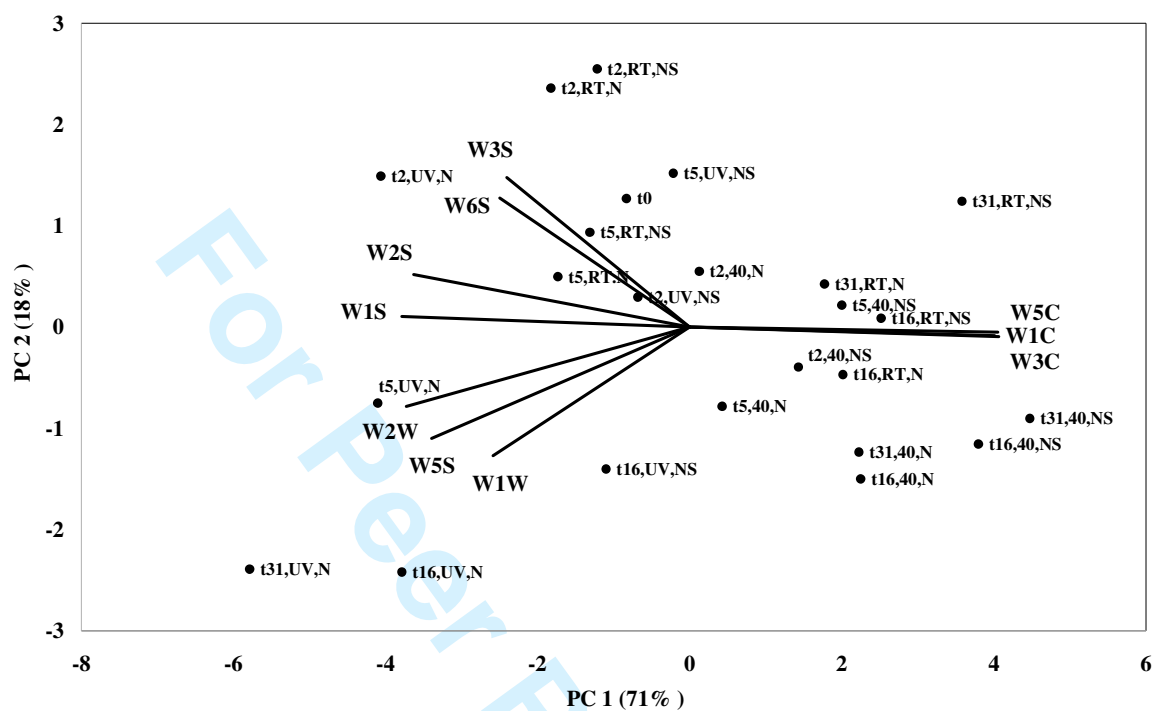
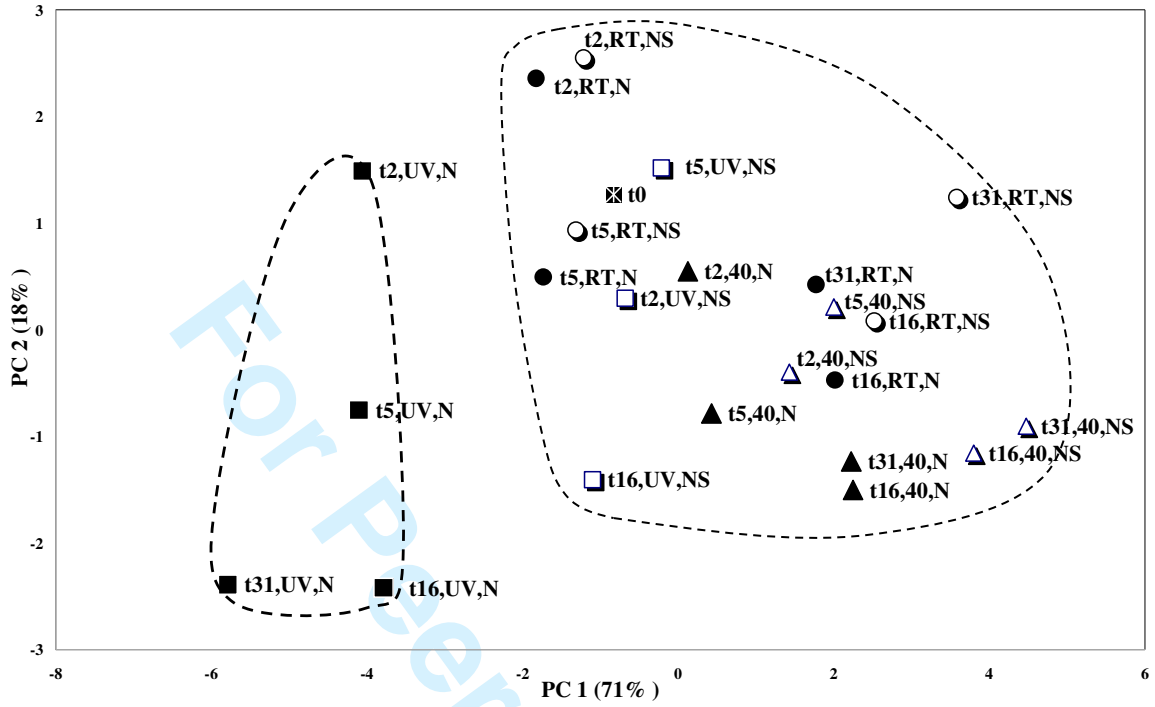
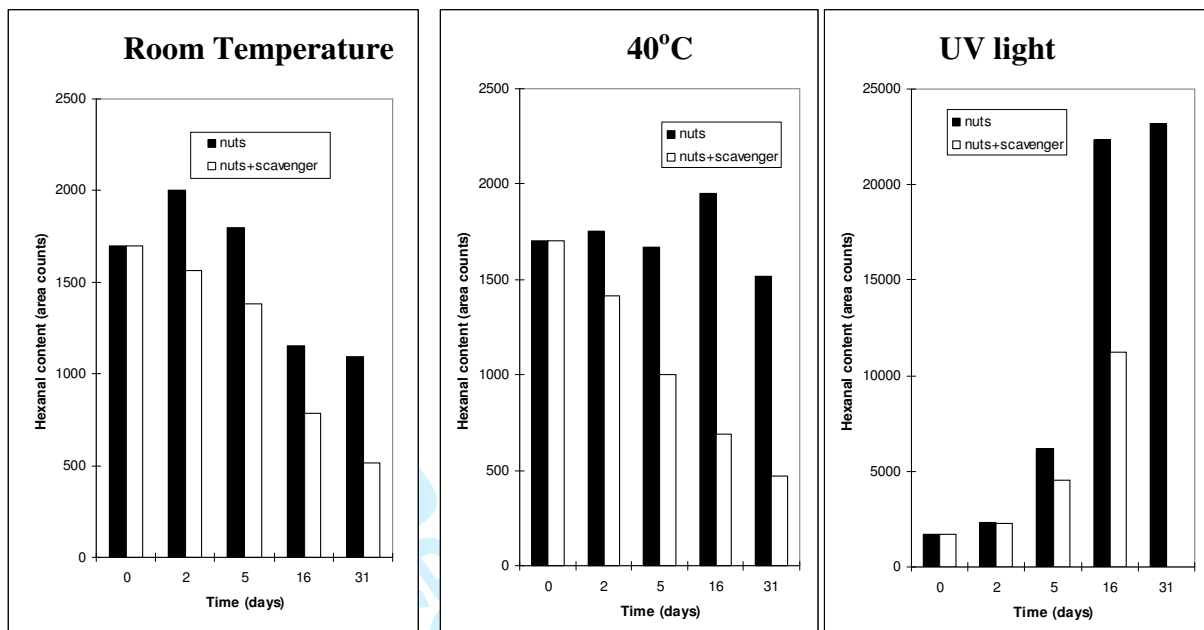


Figure 2.



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1 Figure 3.





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1 Figure 4.

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