# A COMPARISON OF HUMAN AND ELECTRONIC NOSE RESPONSES TO FLAVOUR OF VARIOUS FOOD PRODUCTS OF DIFFERENT DEGREE OF LIPIDS OXIDATION

Sylwia Mildner-Szkudlarz, Renata Zawirska-Wojtasiak, Józef Korczak, Henryk H. Jeleń

Department of Food Science and Nutrition, The August Cieszkowski Agricultural University of Poznań, Poznań

Key words: electronic nose, sensory profile analysis, principal component analysis, partial least squares analysis

This paper investigates the effectiveness of electronic nose with subsequent principal component analysis (PCA) treatment of data for differentiation of food samples of varied odour quality caused by lipid oxidation. Samples were evaluated for off-flavours with an electronic nose and a sensory analysis and for Totox value. Volatile compounds of fresh samples and samples subjected to storage test at 60°C were isolated with a static headspace technique. The results suggest that the electronic nose could help to supplement the sensory analysis. Models based on partial least-squares analysis were able to predict the oxidized flavour attribute of samples, with correlation coefficients ranging from 0.66 to 0.99. Based on elaborated methods and data treatment with PCA it was possible to distinguish between different food samples and monitor the formation of off-flavours associated with lipid oxidation.

## **INTRODUCTION**

Food products, which contain polyunsaturated fatty acids, are highly susceptible to lipid oxidation. Edible fats, oils and fatty food slowly oxidize during storage and various oxidation products formed cause rancidity and deterioration of sensory properties of food [Wąsowicz *et al.*, 2004].

Various methods, such as peroxide value, anisidine value, TBARS (thiobarbituric acid reactive substances), conjugated dienes and trienes have been developed to determine the lipid oxidation of food. According to Broadbent & Pike [2003], sensory analysis can detect flavours caused by oxidative and non--oxidative degradation processes. The human sense of smell is the ultimate discriminator of food aroma and flavour quality [Lawless, 1991]. Sensory evaluation is therefore one of the important parameters for quality assessment of food. Typically sensory evaluation of food and beverages odours is performed by a panel of well-trained professionals based on their sense of smell, taste and expertise. Sensory analyses provide sometimes a useful approach to identify flavour or odour defect in the processing of food and beverages that cannot be detected by either instrumental or chemical methods. The main limitations of sensory analyses however, are the poor reproducibility of data, time-consuming analyses and requirement for trained personnel to carry out assessment.

Chromatographic methods used in aroma research, which have developed rapidly since the introduction of capillary columns, cannot sometimes detect some volatile compounds present in ultra low concentrations and detectable by human nose [Gardner & Bartlett, 1994]. Moreover, gas chromatography measures particular volatile compounds – not flavour, which is a sensory perception of humans and animals.

For these reasons, alternative methods have been developed aimed at mimicking the human sense of smell. The concept of an "electronic nose" was formed in 1982 at the University of Warwick by Persand and Dodd. The "electronic nose" also called an "artificial-nose" is defined as an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate patternrecognition system, capable of recognising simple or complex odours [Gardner & Bartlett, 1994]. Their advantage is that they measure volatile compounds in a similar mode to human olfaction system. Of the electronic noses present on a market two main types can be distinguished: sensor based electronic noses and mass spectrometer based ones. Lots of various sensors are available on the market, which utilize three dominating modes of action: a change of resistance (MOS - metal oxide semiconductors and CP - conducting organic polymers), change of potential (MOSFET - metal oxide semiconductors field effect transistors), and change of resonance frequency (piezoelectric crystals, BAW - bulk acoustic wave and SAW - surface acoustic wave). The metal oxide semiconductors sensor is the most frequently used in studies on food products [Schaller & Bosset, 1998]. This new technology has been successfully used to classify off-odours of numerous products such as: dairy products, beer, coffee, meat, grains, and quality control of wine.

The purpose of this work was to evaluate usefulness of the electronic nose for discrimination of food samples of different odour quality related to lipid oxidation, and to compare results obtained by the electronic nose measurements to those of sensory profile analysis. Products chosen for experiments represented various types of foods with different fat contents: plant oils, oat and corn flakes and meatballs.

Author's address for correspondence: Henryk H. Jeleń, Department of Food Science and Nutrition, The August Cieszkowski Agricultural University of Poznań, Wojska Polskiego 31, 60-624 Poznań, Poland; tel.: (48 61) 848 72 73; fax: (48 61) 848 73 14; e-mail: henrykj@au.poznan.pl

<sup>©</sup> Copyright by Institute of Animal Reproduction and Food Research of the Polish Academy of Sciences

## **MATERIALS AND METHODS**

Materials. Various plant oils (rapeseed, soybean, peanut, sunflower, and extra virgin olive oil, purchased at a local grocery store), corn flakes and two different rolled oats, fresh and after storage, fresh and frozen meatballs with and without addition of antioxidants were used for this study. Table 1 shows peroxide value, anisidine value and total oxidation value of analyzed samples before and after storage. For storage test a total of 100 mL of oils and 100 g of corn flakes and oats was put into a 1000 mL flat-bottom flask with a glass cap and stored at 60°C for 5 days (oils) and 20 days (corn flakes and oats). The following antioxidants were added to meat product: butylated hydroxytoluene (BHT, Sigma, Poznań, Poland) (0.02%), rosemary ethanolic extract (0.02%) and green tea ethanolic extract (0.02%). A total of 50 g of ground meat (pork) with and without addition of antioxidants were steam-cooked for 30 min at 105°C. Then meatballs were packed in LDPE foil and stored for 6 months at -20°C.

HS-E nose. An Alpha M.O.S. Electronic nose system, Fox 4000 (Alpha M.O.S., France) was used. The instrument was equipped with three chambers, each containing six MOS sensors. Sampling was done automatically using CTC Combipal autosampler (HS-100). Volatile compounds (500  $\mu$ L) were sampled from 10 mL vials containing 2 mL of oil, 1 g of flakes and 1 g of meatballs in various experiments using a gas tight syringe. After heating at 35°C for 30 min samples headspace was transferred to electronic nose. Pure (5.0) synthetic air (150 mL/min) was used to sweep samples through the electronic nose chambers. Sensor resistance was measured for 120 sec at the rate of one acquisition every 0.5 sec. All samples were run at least in triplicates. The principle of detection is based on conductivity measurements, in the presence of a combustible gas, oxygen species that are adsorbed on the metal oxide react and are removed from the surface. As a result, the conductivity of the metal oxide film changes. The values obtained from the gas sensors are summarized in the library. Data acquired by sensors were processed by Alpha Soft 8.0 software package. Operation on the raw signals included signal pre-processing, selection of sensors providing the highest degree of sample differentiation and principal component analysis (PCA) of data obtained.

**Sensory analysis.** A 10-member panel experienced in descriptive analysis did the odour profiling of samples in three sessions. The samples were kept in 100 mL closed glass vessels at  $35^{\circ}$ C for 30 min to liberate volatile compounds. After that time, the samples were sniffed by the panel members.

The odour attributes were chosen according to the "Basic Flavour Descriptive Language" from Givaudan Roure Flavor Ltd [Stampanoni, 1998] for each kind of the tested product. The following odour descriptors were offered for the examined samples: six odour attributes for oils, corn flakes and rolled oats - acidic (ac), sweet (sw), green (gr), floral (fl), oxidized (ox) and hay (hy) and five odour attributes for meatballs: meaty (me), fatty/oily (fa), herbal (he), chemical (ch), oxidized (ox). Panel members assigned the intensity of each odour descriptor on a 0-10 scale. Results from linear scales were converted into numerical values for data analysis. Mean, variance, and standard deviations were calculated for all attributes of each sample, for each session separately, and across all three sessions. The data obtained were calculated from 30 replicates and after statistical interpretation by multivariate procedure presented as a graphic projection of Principal Component Analysis (PCA) [Baryłko-Piekielna et al., 1992].

**Oxidation measurements.** Peroxide value (miliequivalent O<sub>2</sub>/kg lipids) was determined by the International Norm ISO 3960-1977(E). Anisidine value and total oxidation value (Totox) were determined according to the ISO International Norm [ISO 6885:1988]. All the analyses were performed in duplicate.

TABLE 1. Peroxide value, anisidine value and total oxidation value of plant oils, flakes and meatballs lipids before and after storage.

| Samples   | Peroxide value (PV)<br>(meqO <sub>2</sub> kg <sup>-1</sup> lipids) | Anisidine value<br>(p-AV) | Total oxidation value (Totox)<br>(2x PV+ p-AV) |
|---|--|---------------------------|--|
|   | Fresh / stored oils for 5 days at                                  | 60°C                      |  |
| Rapeseed oil (RS)                               | 1.12 / 8.19  | 3.07 / 11.42              | 5.31 / 27.80                                   |
| Soybean oil (SB)                                | 3.36 / 11.75   | 2.19 / 4.07               | 8.91 / 27.57                                   |
| Peanut oil (PN)                                 | 2.23 / 6.35  | 2.16 / 3.44               | 6.62 / 16.14                                   |
| Sunflower oil (SF)                              | 1.10 / 11.36   | 4.00 / 6.59               | 6.20 / 29.31                                   |
| Olive oil (OO)                                  | 3.90 / 4.36  | 5.28 / 6.30               | 13.08 / 15.02                                  |
| Fresh / stor                                    | ed corn flakes and rolled oats fo                                  | r 20 days at 60°C         |  |
| Rolled oats (OA)                                | 2.10 / 8.22  | 1.59 / 3.25               | 5.79 / 19.69                                   |
| Rolled oats (OB)                                | 2.30 / 8.63  | 2.03 / 2.83               | 6.63 / 20.09                                   |
| Corn flakes (F)                                 | 2.70 / 16.97   | 2.15 / 9.34               | 7.55 / 43.28                                   |
| Fres  | h / frozen meatballs for 6 month                                   | ns at -20°C               |  |
| Meatballs without antioxidants (MC)             | 1.96 / 9.56  | 0.0 / 7.92                | 3.92 / 27.04                                   |
| Meatballs with BHT (MB)                         | 1.27 / 1.24  | 0.0 / 0.0                 | 2.54 / 2.48                                    |
| Meatballs with rosemary ethanolic extract (MR)  | 3.75 / 4.01  | 0.0 / 4.48                | 7.50 / 12.50                                   |
| Meatballs with green tea ethanolic extract (MT) | 5.73 / 7.09  | 0.0 / 7.86                | 11.46 / 22.04                                  |

**Statistical analysis.** Two-dimensional principal component analysis score plots (PCA) were created on the data. The PCA analysis gives a representative map of the different olfactive area. The principal components were orthogonal and linear combinations of the original variables. The principal components were classified depending on the level of information they produced. The PC1 was the axis, which contained the largest possible load of information and PC2 was perpendicular to PC1. The two main aims of PCA were reduction of the number of variables and elimination of redundancy. All models were validated using "leave-one-out" method.

The discrimination index used in electronic nose shows the discrimination quality through an indication of the surfaces between groups. When groups are distinct, the discrimination index is positive and defined as:  $D_i = 100 \text{ x} [1 - (\text{surface (A)} + \text{surface (B)} + ... + \text{surface (n)} / \text{total surface)}].$ When groups overlap each other, the discrimination index is negative and defined as:  $D_i = -(\Sigma \text{ intersection surface} / \text{total surface}) \times 100 \text{ (Alpha M.O.S., 2002a)}$ 

Partial least squares analysis (PLS) was used to build a model that was able to predict the quantitative information. PLS algorithm was based on linear regression method. The objective was getting a better linear correlation between the sensors response and the sensory panel score.

#### **RESULTS AND DISCUSSION**

For evaluation of electronic noses responses in comparison with sensory profile analysis the following food products were used: plant oils, corn flakes, rolled oats and meatballs. They differed in the degree of oxidation. Oils, rolled oats and corn flakes were analysed fresh and subjected to accelerated storage tests, meatballs were analyzed fresh and after storage at -20°C. Table 1 provides information on the degree of oxidation measured using peroxide value and anisidine value. After accelerated storage tests all samples subjected to it showed several folds higher PV and anisidine values. The differences in PV and anisidine values were the smallest in the case of olive oil. For meatballs the effectiveness of various antioxidants is reflected in Table 1.

#### Fresh and stored plant oils

Figure 1 shows the comparison of PCA plots of sensory data (Graph I) with PCA treatment of electronic nose data (Graph II) of plant oils fresh and stored for 5 days at 60°C to accelerate oxidation. Both methods indicated a similar grouping, and clearly showed the differences between the oils. Graph I presents the PCA score plot based on odour profiling analysis of fresh and stored oils. The dominating descriptors in the sensory analysis were oxidized (ox), green (gr), acidic (ac) and hay (hy) with the oxidized-like being the main. Panellists were able to differentiate between samples, grouping samples of oils into three distinctive clusters. Samples of fresh oils RS (rapeseed), SF (sunflower), SB (soybean) and PN (peanut), perceived as odourless, were grouped into one cluster, characterised by sweet (sw), floral (fl) and hay (hy) odours. The second cluster - stored of oils - was formed by samples with off-flavour, caused by progressive oxidation, located on the PCA plot in the region of oxidized (ox) and acidic (ac) vectors, with the oxidized-like being the main. The

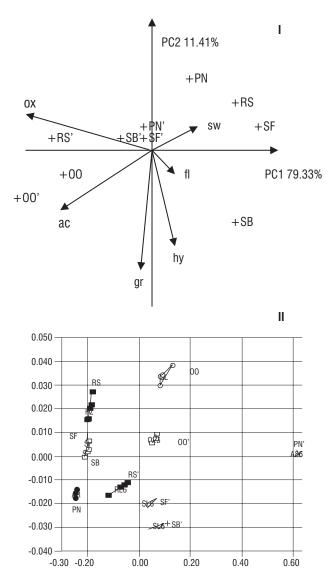


FIGURE 1. The PCA plot of plant oils fresh and stored for 5 days at  $60^{\circ}$ C.

Graph I – The PCA interpretation of sensory data, Graph II – The PCA interpretation of electronic nose data.

Sample codes: fresh oils – (RS) rapeseed oil; (SB) soybean oil; (PN) peanut oil; (SF) sunflower oil; (OO) olive oil; stored oils – (RS') rapeseed oil; (SB') soybean oil; (PN') peanut oil; (SF') sunflower oil; (OO') olive oil. Descriptors: acidic (ac); sweet (sw); green (gr); floral (fl); oxidized (ox); hay (hy)

last group consisting of olive oil samples (OO and OO') was also characterised by acidic (ac), oxidized (ox) and green (gr) attributes with acidic (ac) odour as predominant.

Graph II in Figure 1 shows the PCA projection of electronic nose data analysis in the samples of oils. For electronic nose technique optimization of sensors was done. After sensors optimization, only 10 sensors out of 18 were used to discriminate between samples (LY/LG, LY/G, P30/1, P30/2, P40/2, PA2, T30/1, T40/2, T70/2 and TA2). According to the manufacturer, LY/LG sensors are sensitive to fluorine, chlorine, nitrogen oxide and ozone and are used to detect oxidizing gases. Sensors LY/G are used for gas monitoring and are sensitive to ammonia, amines, and carbon monoxide. Sensors P30/1 and T30/1 have been used for organic compounds detect and are sensitive to solvents. Sensors P30/2, PA2, and TA2 are sensitive to alcohol and are also used for organic compounds detection. Sensors P40/2 and T40/2 are used to detect oxidizing gases and are sensitive to chlorine. Sensors T70/2 have been used for organic compounds detection and are sensitive to aromatic compounds like toluene and xylene [Alpha M.O.S., 2002b]. The PCA provided good separation of samples with 98.97% of the variation accounted for PC1 and 0.59% accounted for PC2. A discrimination index of 96% was achieved for the examined samples.

Electronic and the human nose gave similar, however not the same samples plot. Separation of samples with oxidized off-flavour from fresh samples and grouping samples of olive oil – fresh and stored – into one cluster was observed. Considering the map of the PCA performed on the data sets obtained from electronic nose, fresh samples of oils mostly presented negative score values according to PC1 whereas samples stored for 5 days at 60°C had positive scores according to PC1. Euclidian distance between a group of fresh and stored olive oil was 0.035 and was less than for other samples. It was in agreement with small differences between the total oxidation value of fresh and stored olive oil samples (Table 1).

Partial least squares analysis (PLS) was used to correlate sensory attributes with the electronic nose responses. Response data from the electronic nose sensors were defined as the X-matrix and the means of descriptor scores after panel evaluation were defined as the Y-matrix. A partial least squares analysis was calculated. The result gave correlation between the electronic and human nose data from 0.66 to 0.82 (p<0.05) (Table 2). The best linear correlation – 0.82 – was found for the acidic (ac), sweet (sw) and oxidised (ox) flavour attributes, from which oxidized and acidic ones were the dominating descriptors. Our result showed that the

TABLE 2. Correlation between sensory attributes and electronic nose responses of plant oils, flakes and meatballs before and after storage.

| Sensory attributes                               | PLS correlation |  |  |
|--|-----------------|--|--|
| Fresh and stored oils for 5 days at 60°C         |                 |  |  |
| Acidic   | 0.82            |  |  |
| Sweet  | 0.82            |  |  |
| Green  | 0.66            |  |  |
| Floral   | 0.78            |  |  |
| Oxidized   | 0.82            |  |  |
| Hay  | 0.66            |  |  |
| Fresh and stored corn flakes and oats            |                 |  |  |
| for 20 days at 60°C                              |                 |  |  |
| Acidic   | 0.85            |  |  |
| Sweet  | 0.88            |  |  |
| Green  | 0.84            |  |  |
| Floral   | 0.94            |  |  |
| Oxidized   | 0.82            |  |  |
| Hay  | 0.96            |  |  |
| Fresh and frozen meatballs for 6 months at -20°C |                 |  |  |
| Meaty  | 0.98            |  |  |
| Fatty/oily                                       | 0.99            |  |  |
| Herbal   | 0.96            |  |  |
| Chemical   | 0.98            |  |  |
| Oxidized   | 0.98            |  |  |

electronic nose was capable of measuring changes in volatile compounds associated with oil oxidation. Shen *et al.* [2001] also suggested that electronic nose was able to detect the progress of lipid oxidation and could be used to supplement data obtained from sensory evaluation. Authors obtained correlation value ranging from 0.79 to 0.99 (p<0.05) between electronic nose responses and sensory evaluation of canola, corn and soybean oils stored for 12 days at 60°C. In our previous work [Mildner-Szkudlarz *et al.*, 2003], we also found similarities between PCA of sensory analysis and PCA of chromatographic data of rapeseed oil stored for 10 days at 60°C. Biswas *et al.* [2004] observed a correlation between electronic nose response and analysis of volatile compounds by SPME-GC/MS of olive and sunflower oils.

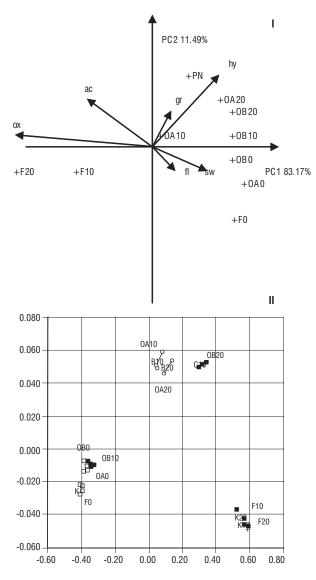


FIGURE 2. The PCA plot of oats and corn flakes fresh and stored for 20 days at  $60^{\circ}$ C.

Graph I – The PCA interpretation of sensory data, Graph II – The PCA interpretation of electronic nose data.

Sample codes: fresh samples – (OA0) oats; (OB0) oats; (F0) corn flakes; samples stored for 10 days – (OA10) oats; (OB10) oats; (F10) corn flakes; samples stored for 20 days – (OA20) oats; (OB20) oats; (F20) corn flakes. Descriptors: acidic (ac); sweet (sw); green (gr); floral (fl); oxidized (ox); hay (hy)

### Fresh and stored corn flakes and rolled oats

Figure 2 shows the comparison of PCA of sensory data with PCA interpretation of the electronic nose data of fresh and stored corn flakes and rolled oats.

Samples of fresh and stored two different rolled oats – OA, OB and corn flakes – F were subjected to the PCA projection to find discrimination according to their sensory quality (Graph I in Figure 2). Oxidized (ox), hay (hy), acidic (ac) were the major odour attributes responsible for the discrimination. Samples of F0, OA0, and OB0 were similar and almost odourless characterised by sweet (sw) and floral (fl) odour. The second cluster – OA10, OA20, OB10 and OB20 – was located on the PCA plot in the region of hay (hy) and green (gr) vectors. The last group formed samples of F10 and F20. These samples were characterised by an undesirable sensory quality with oxidized (ox) and acidic (ac) attributes.

The electronic nose was also able to differentiate all samples when the data were subjected to PCA. Graph II in Figure 2 presents the PCA projection of electronic nose data analysis in the samples of oats and corn flakes. After sensors optimization, only 8 sensors out of 18 were used to discriminate between samples (LY/AA, LY/Gh, P30/1, P40/2, T30/1, T40/2, T70/2 and TA2). According to the manufacturer, sensors LY/Gh are sensitive to ammonia and amines and are used for toxic gases detection. Sensors LY/AA are sensitive to alcohol and are also used for organic compounds detect [Alpha M.O.S., 2002b]. The first PC described 99.0% of the variation; the second one (PC2) described 0.93%. A discrimination index of 93% was achieved for the examined samples. Location of samples in PCA plot was generally similar for both methods. The main differences compared to PCA of sensory profile data was concerned with samples of OB10. In PCA of the electronic nose data this sample was situated in region of fresh samples (OA0, OB0 and F0). Euclidian distance between OB0 and OB10 was 0.039 and was much less then for a group of OA0 - OA10 (0.43). Comparing samples stored for 20 days, the shortest Euclidian distance was for samples OA (0.49), suggesting that these rolled oats oxidized slower then samples OB (0.70). However, there were no significant differences between the total oxidation values of those samples. The longest Euclidian distances were between group of F0, F10, and F0, F20 (0.98, 0.97, respectively). That observation supported the highest total oxidation values of corn flakes. Molteberg et al. [1996] reported that the whole unblemished grains under normal storage conditions are stable, but the processes of flaking damage the grain and activate an endogenous lipolytic enzyme system that can cause rancidity. Ideally, heating provided optimum stability of the product if the treatment is sufficient to inactivate lipolytic enzymes, but mild enough to protect the natural antioxidants [Sides et al., 2001]. However, heat treatment generates reactions of metal ions with lipids and increases oxidation regardless of inactivation of the oxidative enzymes [Sjoval et al. 1997].

The result of PLS analysis gave correlation between the electronic nose and panellists data from 0.82 to 0.96 (p<0.05). The best linear correlation was found for the hay (hy) flavour attribute. Our result showed that the electronic nose was able to detect changes in the volatile profile of oats and corn flakes with tendency to rancidity and differentiate samples according to the heat processing. Sides *et al.* [2001], using the same type of the electronic nose – FOX 4000, were also able to discriminate samples of oats at different stage of the processing (raw oats, groats, kiln dried de-hulled oats and flaked).

#### Fresh and frozen meatballs

The last group of food products, which we used to compare electronic nose and human nose response, were fresh and frozen meatballs produced with and without the addition of antioxidants. Samples with the addition of BHT, rosemary ethanolic extract and green tea ethanolic extract have been marked as MB, MR and MT, respectively. Samples without the addition of antioxidants have been marked as MC. Figure 3 shows similarity of PCA plot of sensory and electronic nose data of fresh (at the beginning of the storage) and after 6 months of storage of meatballs. Based on sensory analvsis it was possible to differentiate between fresh samples according to addition of antioxidants (Graph I in Figure 3). Herbal (he), fatty (fa) and meaty (me) were the major odour attributes responsible for the differentiation. Sample MR to which rosemary extract was added differed in the profile of volatiles at the beginning of storage from the other samples and was located on the PCA plot in the region of herbal (he) attribute. After 6 months of storage oxidized (ox) and herbal (he) were the dominating descriptors responsible for discrimination. Samples MT' with green tea extract were similar to the control samples with oxidized off-flavor. The highest intensity of oxidized flavor was observed in the control sample, slightly lower in that with green tea extract and the lowest in the samples with the addition of the rosemary extract and BHT.

The PCA plot of the electronic nose data also indicated considerable separation of the samples (Graph II in Figure 3). After sensors optimization, only 2 (at the beginning of the storage) and 5 (at the end of the storage) sensors were used to discriminate between samples (LY/LG, P30/2 and LY/LG, LY/AA, P30/1, P30/2, T40/2). At the beginning of the storage the first PC described 86.28% of the variation, the second one (PC2) - 13.72%. After 6 months of storage the first PC described 71.80% of the variation, the second one (PC2) - 26.73%. A discrimination index of 91% and 87% was achieved for the examined samples. At the beginning of storage the samples were also differentiated according to addition of antioxidants. At the end of storage the samples to which rosemary extract was added were located near BHT added samples, despite the detectable odour of rosemary, which suggested their good quality. Moreover, Euclidian distance between rosemary and BHT added samples was 0.007 and was a lot less than for the other samples. Out of the antioxidants analysed, the rosemary extract had similar antioxidant activity as BHT whereas green tea extract showed the weakest antioxidant properties under the examined conditions. Results of sensory and electronic nose evaluations were in agreement with chemical analyses (Totox value).

The result of PLS analysis gave a significant correlation between the electronic and sensory analysis from 0.96 to 0.99 (p<0.05) for samples stored for 6 months. The best linear correlation was found for the oxidized (ox) flavour attribute (Figure 4). Using the same electronic nose Braggins & Frost [1997] studied volatile compounds of raw and cooked minced lamb meat stored in  $CO_2$  atmosphere, fro-

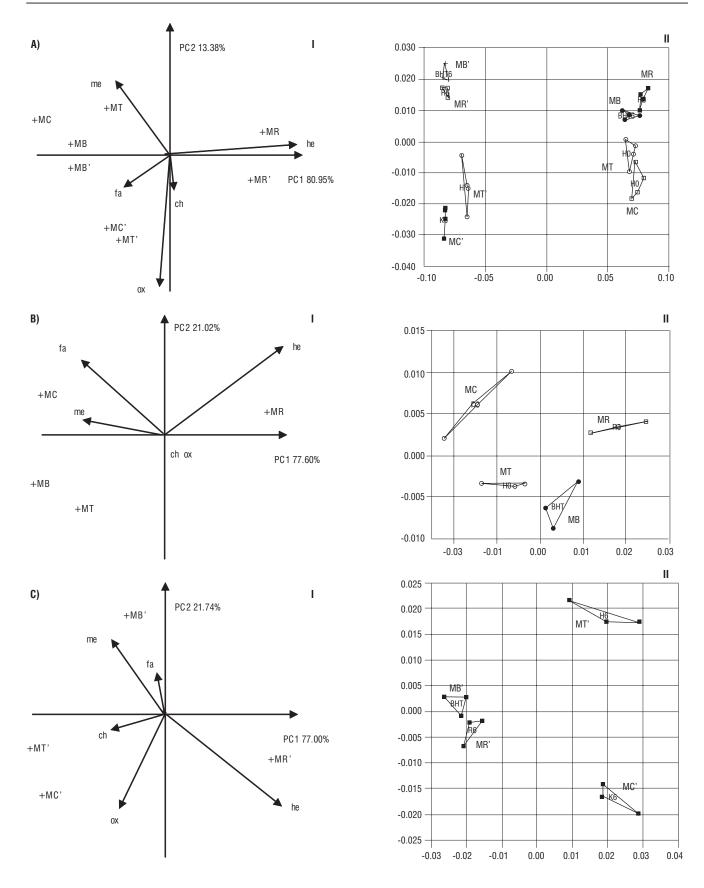


FIGURE 3. The PCA plot of fresh and frozen meat product stored for 6 months at -20°C.

A) – all fresh and stored samples, B) – fresh samples, C) – samples after 6 months of storage; Graph I – PCA interpretation of sensory data, Graph II – PCA interpretation of electronic nose data.

Sample codes: (MC) control samples, without addition of antioxidants (MB) samples with addition of BHT; (MR) samples with addition of rosemary ethanolic extract; (MT) samples with addition of green tea ethanolic extract. Samples at the end of the storage marked as: MC', MB', MR', MT'. Descriptors: meaty (me), fatty/oily (fa), herbal (he), chemical (ch), oxidized (ox).

zen, and vacuum packed. Canonical discriminant analysis (CDA) was able to discriminate between samples stored over a time period from four to fourteen weeks. Using FOX 2000 consisting of six MOS sensors Vernat-Rossi *et al.* [1996] distinguished dry sausages and cured ham samples of different quality. Using FDA (functional discrimination analysis) they found that it was possible to distinguish between samples of dry sausages and cured ham with an aroma defect with satisfactory correlation coefficient (0.94 and 0.87, respectively). Eklöv *et al.* [1997] made a comparison between the electronic nose consisting of four MOS sensors and ten MOSFET sensors and sensory panel evaluation of fermented sausages. Both techniques were able to differentiate samples and were sensitive enough to detect small quality differences between the samples.

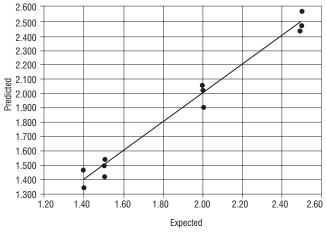


FIGURE 4. Results from prediction of oxidized flavour attribute of fresh and frozen meatballs stored for 6 months at  $-20^{\circ}$ C (PLS correlation -0.98).

### CONCLUSIONS

In all presented applications the electronic nose provided samples discrimination based on their degree of lipid oxidation. It has been shown that samples grouping resulting from electronic nose data acquisition is as distinct as in PCA performed on sensory data. Examples shown indicate that electronic nose can be used for discrimination of fresh samples from the oxidized ones. Although the electronic nose does not describe the character of odour notes perceived by a human nose, its potential to aid or sometimes replace sensory analysis can be utilized for routine product control in case when rapid discrimination from well-defined quality standards is required.

#### ACKNOWLEDGEMENTS

This research project was financed by the State Committee for Scientific Research (Poland) – project No 2P06T 020 26.

## REFERENCES

- 1. Alpha M.O.S., Statistical Analysis. Technical Note N-DT-01, 2002a.
- 2. Alpha M.O.S., Sensors Range. Technical Note N-SAS-03, 2002b.

- Baryłko-Piekielna N., Zawirska-Wojtasiak R., Kornelson C., Rothe M., Interlaboratory reproducibility of sensory profiling of margarines. 1992, *in*: Aroma Production and Application (eds. M. Rothe, H.P. Kruse). Deutches Institut für Ehrnärungsforschung, Potsdam-Rehbrücke, pp. 301–311.
- Biswas S., Heindselmen K., Wohltjen H., Staff Ch., Differentiation of vegetable oils and determination of sunflower oil oxidation using a surface acoustic wave sensing device. Food Contr., 2004, 15, 19–26.
- 5. Braggins T.J., Frost D.A., The effect of extended chilled storage in  $CO_2$  atmosphere on the odour and flavour of sheepmeat as assessed by sensory panel and an electronic nose. 1997, *in*: Proceedings of the 43<sup>rd</sup> ICoMST, New Zealand, pp. 198–199.
- Broadbent C.J., Pike O.A., Oil stability index correlated with sensory determination of oxidative stability in canola oil. J. Am. Oil Chem. Soc., 2003, 80, 59–63.
- Eklöv T., Johansson G., Winquist F., Lundström I., Monitoring sausage fermentation using an electronic nose. 1997, *in*: Methods to Improve the Selectivity of Gas Sensors (ed. T. Eklöv). Licentiate thesis no 565, Department of Physics and Measurement Technology, University of Linköping, Sweden, pp. 40–50.
- Gardner J.W., Bartlett P.N., Intelligent Chem-SADs for artificial odor-sensing of coffees and lager beers. 1994, *in*: Olfaction and Taste (eds. K. Kurihara, N. Suzuki, H. Ogawa). Proceeding of the 11<sup>th</sup> Symposium on Olfaction and Taste, Tokyo, Springer--Verlag, pp. 660–693.
- 9. ISO 3960-1977(E), International Norm ISO 3960-1977(E): Animal and vegetable oils and fats – Determination of peroxide value.
- ISO 6885:1988, International Norm ISO 6885:1988 Edible vegetable fats. Determination of anisidine value and calculation of total oxidation value Totox.
- Lawless H., The sense of smell in food quality and sensory evaluation. J. Food Qual., 1991, 14, 33–60.
- Mildner-Szkudlarz S., Jeleń H.H., Zawirska-Wojtasiak R., Wąsowicz E., Application of headspace-solid phase microextraction and multivariate analysis for plant oil differentiation. Food Chem., 2003, 83, 515–522.
- Molteberg E.L., Magnus E.M., Bjore J.M., Nilsson A., Sensory and chemical studies of lipid oxidation in raw and heat-treated oat flour. Cereal Chem., 1996, 73, 579–587.
- Schaller, E., Bosset, J.O., "Electronic noses" and their application in the food industry: A review. Seminars in Food Analysis, 1998, 3, 119–124.
- Shen, N., Moizuddin, S., Wilson, L., Duvick, S., White, P., Pollak, L., Relationship of electronic nose analyses and sensory evaluation of vegetable oils during storage. J. Am. Oil Chem. Soc., 2001, 78, 937–940.
- Sides A., Robards K., Helliwell S., An M., Changes in the volatile profile of oats induced by processing. J. Agric. Food Chem., 2001, 49, 2125–2130.
- Sjoval O., Lapvetelainen A., Johansson A., Kallio H., Analysis of volatiles formed during extruded oats. J. Agric. Food Chem., 1997, 45, 4452–4455.
- Stampanoni K.Ch.R., Basic flavour descriptive language. Przem. Spoż., 1998, 4, 36–39.
- Vernat-Rossi V., Garcia C., Talon R., Denoyer C., Berdaguè J.L., Rapid discrimination of meat products and bacterial strains using semiconductor gas sensors. Sens. Actuators B., 1996, 37, 43–48.
- Wąsowicz E., Gramza A., Hęś M., Jeleń H.H., Korczak J., Małecka M., Mildner-Szkudlarz S., Rudzińska M., Samotyja U., Zawirska-Wojtasiak R., Oxidation of lipids in food. Pol. J. Food Nutr. Sci., 2004, 13/54, 87–100.

Received February 2006. Revision received June and accepted August 2006.

# PORÓWNANIE ANALIZY SENSORYCZNEJ I ELEKTRONICZNEGO NOSA DO OCENY ZAPACHU PRODUKTÓW O RÓŻNYM STOPNIU UTLENIENIA LIPIDÓW

### Sylwia Mildner-Szkudlarz, Renata Zawirska-Wojtasiak, Józef Korczak, Henryk H. Jeleń

#### Wydział Nauk o Żywności i Żywieniu, Akademia Rolnicza im Augusta Cieszkowskiego w Poznaniu, Poznań

W pracy podjęto próbę zweryfikowania przydatności elektronicznego nosa i obróbki danych za pomocą analizy składowych głównych (PCA) do dyskryminacji żywności różnej jakości. W badanych próbach oceniono zapach za pomocą elektronicznego nosa typu MOS i analizy sensorycznej oraz wykonano oznaczenia wartości całkowitego stopnia utlenienia (Totox). Lotne związki prób świeżych oraz poddanych testom przyspieszonego starzenia w 60°C izolowano techniką statycznego headspace. Uzyskane wyniki badań dowodzą, że elektroniczny nos jest narzędziem, który może w zadawalający sposób uzupełniać oceny zespołu sensorycznego. Uzyskano wysokie korelacje od 0,66 do 0,99 pomiędzy odpowiedzią sensorów elektronicznego nosa a natężeniem charakterystycznych deskryptorów zapachu w profilowej ocenie sensorycznej (tab. 2, rys. 4). W oparciu o opracowane metody i obróbkę danych za pomocą analizy składowych głównych (PCA) możliwe było różnicowanie prób według ich jakości oraz monitorowanie obcego zapachu związanego z utlenieniem kwasów tłuszczowych.