Increasing Electronic Nose Recognition Ability by Laser Irradiation

Massacane Alejandra[1], Vorobioff Juan[1], Pierpauli Karina[1], Boggio Norberto[1, 2], Reich Silvia[3], Rinaldi Carlos[1, 2], Boselli Alfredo[1], Lamagna Alberto[1], Azcárate M. Laura [2, 4], Codnia Jorge [4], Manzano Francisco[4]

1- Comisión Nacional de Energía Atómica (CNEA)- Gerencia de Desarrollo Tecnológico y Proyectos Especiales (Grupo MEMS) Av. General Paz 1499 – San Martín – Buenos Aires
2- Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina
3- Escuela de Ciencia y Tecnología, Universidad de San Martín, Argentina
4- Centro de Investigaciones en Láseres y Aplicaciones CEILAP (CITEFA-CONICET), Argentina

Abstract: We present a method to increase the capability of an electronic nose to discriminate between a priori similar odours. We analyze the case of olive oil because it is well known that the characteristics of its aroma impair in many cases the discrimination between different kinds of olive oils especially when they are from similar geographic regions. In the present work we study how to improve the electronic nose performance for the above mentioned discrimination by the use of two IR laser wavelengths for vaporization.

Keywords: laser, e nose, olive oil,
PACS: 85.85+j

INTRODUCTION

Argentina has an increasing interest in assessing olive oil quality since it has become an important exportation product. Most indicators of this activity have improved in recent years, both for table olives and for olive oils, thus allowing Argentina to increase its market share and its positioning as a global producer. In 2006 Argentina was the 10th major producer of olive oil.

Odour is an important parameter determining the sensory quality of olive oils and it is therefore of interest to investigate if volatile compounds contributing to the characteristic odour can be measured as a quality indicator. In the last decades many efforts have been made to study the aromatic fraction of olive oils based mainly on chromatographic determinations [1]. However, these analytical techniques are time-consuming and require sophisticated equipment as well as skilled personnel.

The use of an electronic nose for quality evaluation as a means of olfactory sensing is becoming widespread due to its advantages of low cost, good reliability and high portability. Electronic noses based on different sensor technologies and using different recognition schemes have been employed for this task [2, 3].

On the other hand the high concentration of volatile compounds are not necessarily the principal contributors of odour. For example, Reiners and Grosch [4]reported a concentration of 6770 lg/g for trans-2-hexenal with an odour activity value of 16 whereas 1-penten-3-one with a much lower concentration of 26 lg/g had a higher odour activity value of 36. [5]

The aroma of virgin olive oil is characterized by various volatile compounds that include carbonyl compounds, alcohols, esters and hydrocarbons [6]. The C6 and C5 substances, especially C6 linear unsaturated and saturated aldehydes and alcohols, represent the most important fraction of the volatile compounds [5, 7]. Also, from a quantitative point of view, large amounts of these substances are generally found in high quality oils. These are the compounds which are responsible for the ‘‘green flavor” of the virgin olive oil, while the esters are mainly related to the ‘‘floral” sensory notes.

When samples of olive oil are analyzed with an electronic nose, the standard procedure is to put a fixed quantity in a vial and sense the headspace. The important drawback of this

CP1137, *Olfaction and Electronic Nose: Proceedings of the 13th International Symposium*, edited by M. Pardo and G. Sberveglieri

method is that the concentration of some compounds in the headspace may be quite different than their concentration in the liquid phase. It is for example the case for methanol and ethanol [1], whose concentrations in the vapor phase are significantly higher than their presence in the liquid and, furthermore, of no importance in order to define the olive oil characteristics. On the other hand, those substances responsibles of the organoleptic properties (such as hexanal, and trans-2-hexanal) which are abundant compounds [8, 9] in the oil due to their low volatility, are scarcely present in the headspace.

In the present work we study the relevance of improving the electronic nose performance for discriminating between different olive oils by the use of two IR laser wavelengths. Heating of the liquid sample by the use of an IR laser is a promising technique to modify the headspace either by volatilizing other organic compounds or by cracking them and thus improve the selectivity of the electronic nose overall response.

The role of the laser wavelength is particularly analyzed since the quality and the quantity of the chemical compounds incorporated to the headspace by laser heating depend on the irradiation techniques. We show that the increase in the electronic nose selectivity is dramatically changed by the use of laser irradiation and it is rather insensitive to the recognition pattern employed.

EXPERIMENTAL

We prepared 5 samples of two different olive oils bought at the local market. Henceforth denominated oil A and oil B. About 15 ml of oil was placed inside a 100 ml vial and the headspace was analyzed using a Cyrano 320^{TM} nose. The nose response is composed of the 32 sensors signals.

The three following analytical methods were implemented to measure the headspace of the olive oil samples.

Method I: The samples were analyzed without laser irradiation.

Method II: The oil samples, A and B, were irradiated with Nd:YAG laser (Continuum, Surelite I) pulses of 1064 nm at a repetition rate of 10 Hz. The pulse length was 5 ns, and the output energy was 80 mJ. The laser radiation was collimated, the area of the spot on the sample surface was 0.15 cm^2 and the laser fluence 2.14 J/cm^2.

Method III: The oil samples, A and B, were irradiated with a homemade pulsed TEA CO_2 laser [10] emitting in the P(20) line, (10.59 μm), of the 10.6 μm emission band. The pulse length was 100 ns and the output energy was 1.45 ± 0.04 J/pulse. The laser radiation was focused on the sample using a 50 cm focal length mirror. The area of the spot on the sample surface was 0.68 cm^2 and the laser fluence 2.14 J/cm^2.

It has to be stressed that the same protocols were applied to each method The protocols concerned not only the electronic nose parameters but also the ambient temperature and humidity since all measurements were performed in the same air conditioned laboratory.

The software provided by the Cyrano 320^{TM} e-nose allowed the processing of the raw data given by the sensors. Figure 1 shows typical data acquired by one of the 32 sensors. In order to compare the effects of the laser irradiation, the same olive oil sample, A, was measured under the three methods described above. As it can be seen in Figure 1, the signal-to-noise ratio (S/R) is considerably increased by the laser vaporization (blue and red lines) and the blue line corresponding to Method III shows the highest S/R ratio.

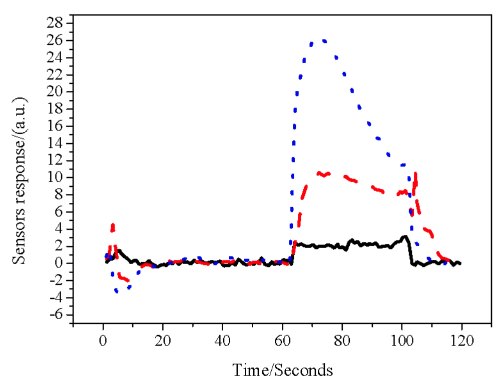

FIGURE 1: Time dependence sensor response. (—) Method I, (----) Method II, and (····) Method III.

RESULTS AND DISCUSSION

The software provided by the Cyrano 320 e-nose takes the ratio of the maximum value of each signal to the base-line value and provides a Principal Components Analysis (PCA). This type of analysis is not quite adequate when the different sensors may have distinct desorption times, as it was in our case and so, in order to take a better advantage of the information contained in each signal, we have taken the integral of each signal divided by the base line integral. This procedure takes into account the absorption and desorption rates.

Figures 2, 3 and 4 show the PCA results for Methods I, II and III, respectively. The reliability of the PCA is verified since, for all methods, the largest contribution to the total variance is given by the first two principal components. It can be straightforward deduced from Figures 2, that both olive oils are indistinguishable when using Method I. On the other hand, they are well discriminated when the sample is irradiated by any of the two IR láser and the headspace is subsequently measured (Method II and III). Figure 3 and 4 illustrate this fact.

In order to quantify the PCA discrimination we have used the silhouette value (from MatLab 7.0 Software). This parameter measures the existence of distinct clusters and it is defined for the score plane as:

$$S(i) = \frac{(\min(b(i,k)) - a(i))}{\max(a(i), \min(b(i,k))}$$

where *a(i)* is the average distance from the ith point to the other points in this cluster, and *b(i,k)* is the average distance from the ith point of cluster *i* to cluster *k*. The silhouette parameter ranges from -1 to +1 and the best discrimination corresponds to value 1.

Table I: silhouette values for PCA discrimination for the different methods.

Method I	**Method II**	**Method III**
0.486	0.869	0.954

According to these results the best discrimation of these olive oils is performed by Method III.

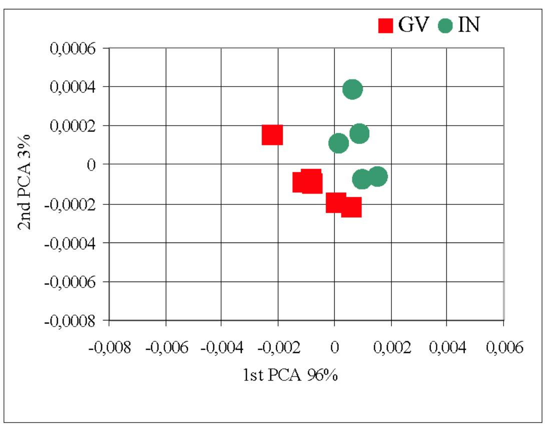

FIGURE 2: PCA for olive oils analyzed with Method I

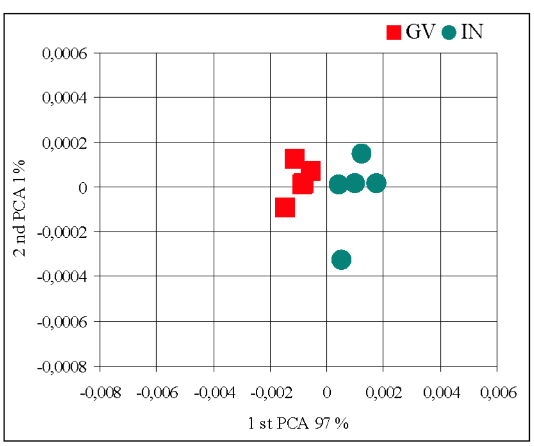

FIGURE 3: PCA for olive oils analyzed with Method II

CONCLUSIONS

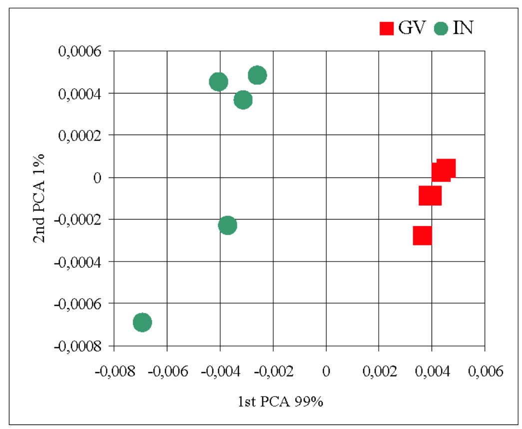

FIGURE 4: PCA for olive oils analyzed with Method III.

This work reports a method to improve the ability of an electronic e-nose to discriminate between *a priori* similar odours by laser irradiation of the sample. We have applied this technique to the case of virgin olive oils. We have also explored how different laser characteristics may improve this task.

We have concluded that the use of IR laser increases the sensitivity of the e-nose performance. Furthermore, the use of a CO_2 laser allows a better discrimination than the use of the Nd:YAG laser. The IR láser wavelength influence the discriminatoy capabilities of the method. It has also to be mentioned that, the signal to noise ratio (S/N) using the CO_2 laser is increased by an order of magnitude with respect to the S/N without laser vaporization effect.

A coming work is in progress where we anlalise the influence of the IR laser energy in the sensitivity of the method.

REFERENCES

[1]- Characterization of olive oil volatiles by multi-step direct thermal desorption–comprehensive gas chromatography–time-of-flight mass spectrometry using a programmed temperature vaporizing injector Journal of Chromatography A, Volume 1186, Issues 1-2, 2008, Pages 228-235 Sjaak de Koning, Erwin Kaal, Hans-Gerd Janssen, Chris van Platerink, Udo A.Th. Brinkman

[2]- The potential of different techniques for volatile compounds analysis coupled with PCA for the detection of the adulteration of olive oil with hazelnut oil Food Chemistry, Volume 110, Issue 3, 1, 2008, Pages 751-761 Sylwia Mildner-Szkudlarz, Henryk H. Jeleń

[3]- Evaluation of different storage conditions of extra virgin olive oils with an innovative recognition tool built by means of electronic nose and electronic tongue Food Chemistry, Volume 101, Issue 2, 2007, Pages 485-491 M.S. Cosio, D. Ballabio, S. Benedetti, C. Gigliotti

[4]- Odorants of virgin olive oils with different flavor profiles. Journal of Agricultural and Food Chemistry, 1998, Volume 46, Issue 7, Pages 2754 -2763

[5]-Olive oil volatile compounds, flavour development and quality: A critical review.
Food Chemistry Volume 100, Issue 1, 2007, Pages 273-286
C.M. Kalua , a, , M.S. Allena, D.R. Bedgood, Jra, A.G. Bishopa, P.D. Prenzlera and K. Robardsa.

[6]- F. Lacoste, in: Proceedings of the User Forum of the NOSE network, Ispra, VA, 1999.

[7]-Monitoring of virgin olive oil volatile compauns evolution during olive malaxation by an array of metal oxide sensors
Food Chemistry, Volume 113, 2009, Pages 345 - 350
Esposto E., Montedoro J., Selvaggini R., Rico I., Taticchi A., Urbani S., Servili M.

[8]- Geographical origin and authentication of extra virgin olive oils by an electronic nose in combination with artificial neural networks Analytica Chimica Acta, Volume 567, Issue 2, 2006, Pages 202-210 Maria S. Cosio, Davide Ballabio, Simona Benedetti, Carmelina Gigliotti

[9]- Comparison and integration of arrays of quartz resonators and metal-oxide semiconductor chemoresistors in the quality evaluation of olive oils Sensors and Actuators B: Chemical, Volume 78, Issues 1-3, 2001, Pages 303-309 Corrado Di Natale, Antonella Macagnano, Sara Nardis, Roberto Paolesse, Christian Falconi, Emanuela Proietti, Pietro Siciliano, Roberto Rella, Antonella Taurino, Arnaldo D'Amico

[10]-Construcción de un láser de CO_2 TEA.
Anales AFA Volume 8, 1996, Pages 34-36
D. Petillo, J. Codnia, M. L. Azcárate.