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Electronic Nose Study of Powdered Garlic

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Abstract: An electronic nose was used to study the odour profile of garlic, separating the powered samples of eight cultivars and proving to be useful to discriminate garlic specimen dried by lyophilization and oven-dried and humidified specimen (before dried by both techniques) for each cultivar. Pattern recognition and multivariate analysis of the electronic nose data has enabled to easily separate the garlic cultivars, to clearly discriminate the lyophilized or oven-dried specimen and the non humidified samples from the humidified powders maintaining, in every case, the cultivars identification. The humidification of lyophilized powders has shown a sharp separation of cultivars, otherwise, in the humidified oven-dried powders, their identification resulted less precise. This fact enabled to infer that lyophilized powders (either dry or humidified) better retained their odour profile than oven-dried powders, maintaining the properties of each cultivar. *Copyright © 2009 IFSA.*

Keywords: Electronic nose, Garlic, Odour, Lyophilization, Oven-drying

1. Introduction

Garlic has been playing one of the most important dietary and medicinal roles in human being for centuries. It has been cultivated since ancient times, used as a spice and flavouring and, due to its potential benefits in preventive and curative medicine, has been used in many cultures [1, 2, 3]. Garlic bulbs are stored for several months after harvest to ensure year-round supplies for customers, the storage conditions are important to prevent loss of shelf life and quality [4, 5]. Characteristic flavour compounds of freshly cut garlic are enzymatically produced from flavour precursors of *S*-alk(en)yl-L-cysteine sulfoxides. Another group of nonvolatile flavour precursors is glutamyl-*S*-alk(en)-cysteines [6]. During storage of garlic cloves glutamyl-*S*-alk(en)ylcysteines could be converted to alk(en)ylcysteine sulfoxides [7, 8].When the garlic tissues are damaged, alk(en)yl thiosulfinates, the primary flavour compounds of fresh garlic, could be released enzymatically from related alk(en)ylcysteine sulfoxides. Thiosulfinates are thermally unstable and converted to successive compounds of alk(en)yl polysulfides, dithiins, or ajoenes, thus contributing to the flavour of garlic products [9].

Alternative methods (lyophilization and oven-drying) have been studied to preserve in time the original odour of garlic. To export garlic's with fine particular flavour to be used for demanding "gourmet" kitchen, it is required the knowledge of garlic's odour profile and the consideration of parameters affecting it. The electronic nose has proved to be a suitable tool to satisfy these expectations since an important criterion for customers choice is smelling.

These methods not only enable to prolong garlic's useful life, it also conserves the organoleptic and bioactive compounds present in this vegetable. In the garlic powder (obtained by dehydrations methods), the aromatic precursors and the enzyme responsible of its hydrolysis, the alliinase, are preserved and in the presence of humidity the hydrolysis reaction is produced with the consequently formation of tiosulphinates generating the characteristic garlic odour as it has been stated [10, 11, 12].

Odours are produced by the specific combination of many different volatile molecules, each one in different concentration. The real odour perception depends on the mutual interaction of all compounds. Consequently, to analyze small quantities of compounds by conventional techniques sometimes it, results impossible due to their cost and required time. Modern analysis and tools like the electronic nose (EN) can perceive odour in a similar way to that of the human nose. This equipment has shown to be useful for other applications such as medicinal plants [13, 14], thermophilic periods of compostage maturity [15], monitoring of degradation products in olive oil [16], environmental contamination [17], among others. In a previous work, the authors have successfully separate fresh garlic cultivars with an electronic nose [18].

The aim of this work was to differentiate odour in different cultivars of garlic obtained by two dehydratated methods (lyophilized or dried (with and without humidification)) to evaluate which method enabled us to retain better the odour of garlic powders.

2. Experimental Method

The experiment was divided in two steps: I) garlic powders obtained by two different dehydration methods were evaluated by an electronic nose ; II) specimen were humidified pouring two water drops in each vial of the first experience and electronic nose measurements were performed under the same conditions.

2.1. Samples

Garlic cloves of eight different cultivars (Fuego, Sureño, Perla, Castaño, Gostoso, Nieve, Norteño and Unión, (being the original Spanish names given at INTA preserved) cultivated at INTA-La Consulta, Mendoza (Argentina) were peeled, weighted, cut into slices and dehydrated by two different methods:

I) Oven-drying and II) lyophilization. In the first case, samples were dried in oven at 50 ^{o}C for 24 h. The second process consisted in lyophilization in a Virtis-Freeze mobile (12 L). Freezing in liquid nitrogen was performed in order to produce an immediate cooling and to avoid the enzymatic hydrolysis of precursor compounds to preserve the flavour. Samples remained in the lyophilizing equipment for 24 h and then, they were placed in sealed vials to preserve them from humidity until EN measurements were performed.

2.2. Electronic Nose

An electronic nose MOSES II (Modular Sensor System) was used to discriminate odours of garlic powders. MOSES II contains two modules of gas sensors, one of them composed of eight quartz microbalance sensors (QMS). This type of sensors consists of vibrating quartz crystals covered with polymeric selective coatings, on which gases are adsorbed. The initial vibration frequency (ν_0) of crystals decreases according to the mass increase due to the gases adsorption and the difference between ν_0 and the final frequency (ν_f) results proportional to the adsorbed gas concentration [19]. The other module of sensors (SnO_2) is composed by eight pure and doped semiconductive SnO_2 sensors. Doping with different elements increases SnO_2 selectivity for different gases. The SnO_2 surface conductivity changes as the semiconductor adsorbs oxidizing or reductive gases [20, 21, 22]. The adopted configuration results very flexible for general purposes and convenient for a wide range of applications.

2.2.1. Samples Measured with Electronic Nose

Samples of the eight garlic powdered cultivars (0.150 g) were placed in four vials each one. Vials were hermetically sealed with teflon caps and aluminium seals. Samples were stabilized at 50 °C for 15 min (incubation time) with an interval of 20 min between vials in an 86.50 Dani headspace sampler and introduced into the MOSES II. Synthetic air was employed as carrier gas with a flow of 30 mL/min and a voltage of 275 mV was applied to the SnO_2 sensors.

2.3. Statistical Analysis

The 16 signals of sensors were processed statistically by Stepwise Linear Discriminant Analysis (Step-LDA) using Mahalanobis distance or unexplained variance for entering or removing new variables was applied on the following four sets of data values corresponding to sensor response curve relevant properties: original values reported by the electronic nose; normalized values; main Principal Components and main normalized Principal Components.

All built predictive models of group membership were evaluated by cross validation, selecting the best classifier for each data subset. First two discriminant functions of each selected model were plotted in 2-dimensional graphs to visualize between-group separations.

In the plots representing the selected models, the "TXY" notation was used, where: X = 0 for the dried powders and X = 1 for the lyophilized specimen and Y = 0 for non humidified and Y = 1 for the humidified specimen. In such cases, "T00" means "dried and non humidified", "T01": "dried and humidified", "T10": "lyophilized non humidified" and "T11": "lyophilized and humidified".

3. Results and Discussion

3.1. Oven-dried and Lyophilized Garlic's (Step I)

Applying the stepwise linear discriminant analysis to the principal components of the 16 signals properties, a 95 % successful classification was reached with cross validation. Fig. 1 shows values of the two first discriminant functions of each specimen, accounting 95.7 % of the system variability (77.3 % for the first and 18.4 % for the second one). It is easy to observe that data of the dried garlic powders appear on the upper right zone of the plot, while the data of lyophilized powders are on the lower left zone, being possible to draw a line separating both data sets. On the same way, this model enabled to completely identify the dehydration method of powders. Inside each zone, the correct discrimination of cultivars could be easily separated.

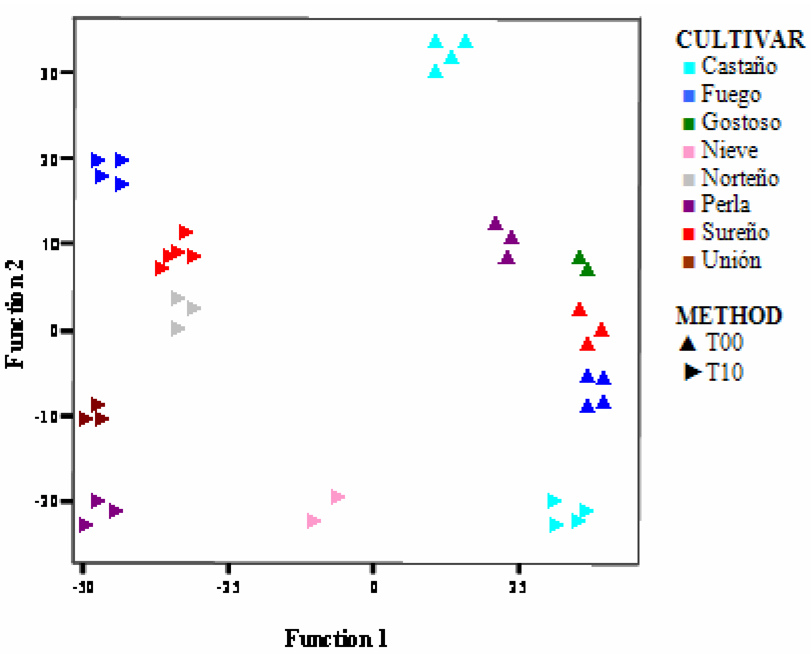

Fig. 1. Stepwise linear discriminant analysis applied to the principal components of the 16 signals properties of the electronic nose for oven-dried (T00: ▲) and lyophilized (T10: ►) cultivars, non humidified with distilled water.

Appling the stepwise LDA on the normalized properties of sensors signals data of EN, it was possible to generate a model using cross validation, results accounted 100 % successful for all the cases to separate the cultivars of dried specimen. On the other hand, applying the same stepwise LDA stated for dried samples, using data of principal components of properties not normalized signals of EN, results showed a 100 % of success for all cases to separate the cultivars of lyophilized samples.

3.2. Oven-dried and Lyophilized Garlic (Humidified with Distilled Water) (Step II)

Applying the stepwise LDA to the set of properties of the sensors signals of EN a model was applied obtaining a 92.3 % successful classification by cross validation for dried and lyophilized garlic.

In Fig. 2, the two most important discriminant function of the model explained the 98.8 % and 0.6 % of the variance, respectively. A considerable separation between cases corresponding to dried and lyophilized garlic powders was obtained. Using the model with the original properties of signals without normalization, it could be concluded that, by the humidification of specimen, the lyophilized powders exhibited higher signal intensity in comparison to dried powders, even belonging both to the same cultivar. It was also observed that lyophilized powders exhibited a better separation among cultivars in comparison with that of dried powders. Applying again the stepwise LDA on the normalized properties of sensors signals, it was possible to generate a model, which classification by cross validation resulted 88.2 % successful for all cases to separate the cultivars of humidified dried specimen.

For humidified lyophilized samples a model was generated, similar to that above described, using the properties of the non normalized signals, obtains a 100 % of success.

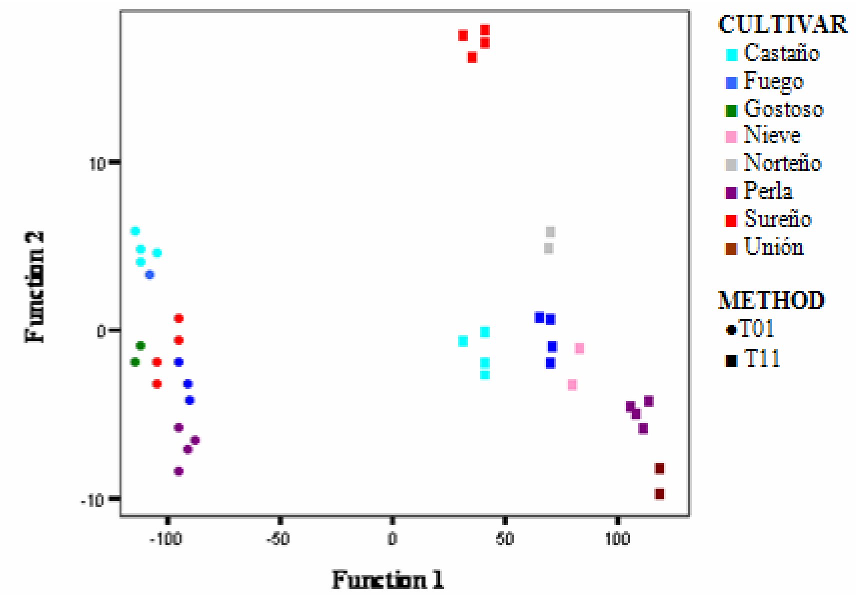

Fig. 2. Stepwise linear discriminant analysis of the 16 signals properties of the electronic nose for oven-dried (T01: ●) and lyophilized (T11: ■) cultivars, humidified with distilled water.

3.3. Comparison between Oven-dried Specimen (with and without Humidification)

Analyzing the set dried specimens (with and without humidification) the stepwise LDA method was applied on the principal components of sensor curves properties, enabling to build a model able to correctly classify by cross validation the 100 % of cases. In Fig. 3, the plot of the two principal discriminant functions, representing the 99.2 % and the 0.2 % of the variance, showed that, humidifying the dried powders, an important change in the sensors behaviour was produced. The third discriminant function not represented in Fig. 3 exhibits the same weight than the second one, since it explained an additional 0.2 % of the variability. This fact clarified why the Sureño and Gostoso cultivars (non humidified) had been correctly classified by the model, even than in the two-dimensional plot, both cultivars did not appear enough separated.

3.4. Comparison between Lyophilized Specimens (with and without Humidification)

Analyzing samples of lyophilized powders (with and without humidification) the stepwise LDA applied on the principal components of the sensor curves properties, enabled to build a model correctly classifying by cross validation the 97.7 % of cases.

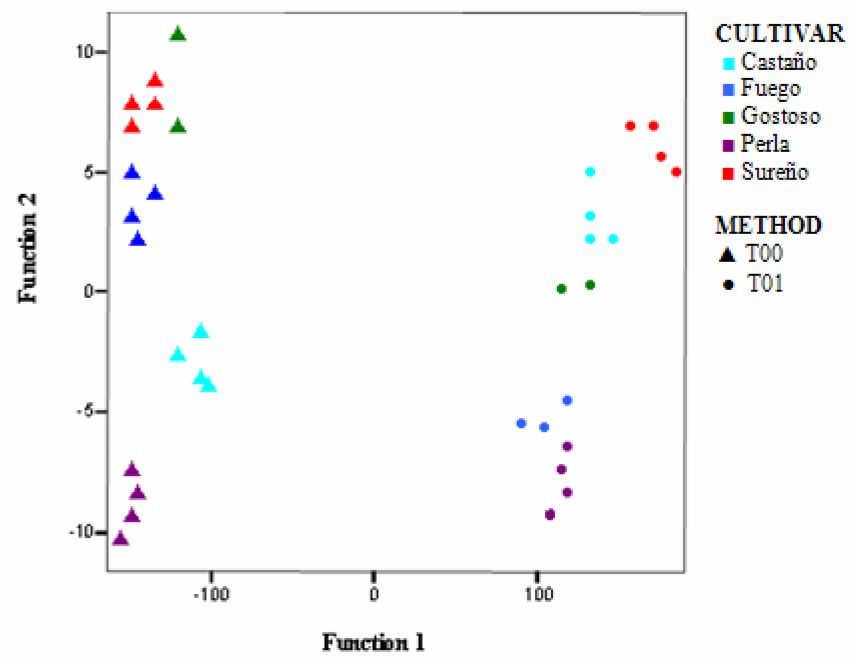

Fig. 3. Stepwise linear discriminant analysis applied on the principal components of the properties of the sensors curves of the electronic nose for oven-dried-non humidified with distilled water (T00: ▲) and oven-dried- humidified with distilled water (T01: ●) cultivars.

The plot of Fig. 4 shows the two discriminant principal functions, representing the 87.6 % and the 11.4 % of the variance (99 %) and enabling to observe a clear separation among cultivars; it is possible to observe the changes caused by the effect of humidification of the lyophilized garlic powders and the correct cultivars separation.

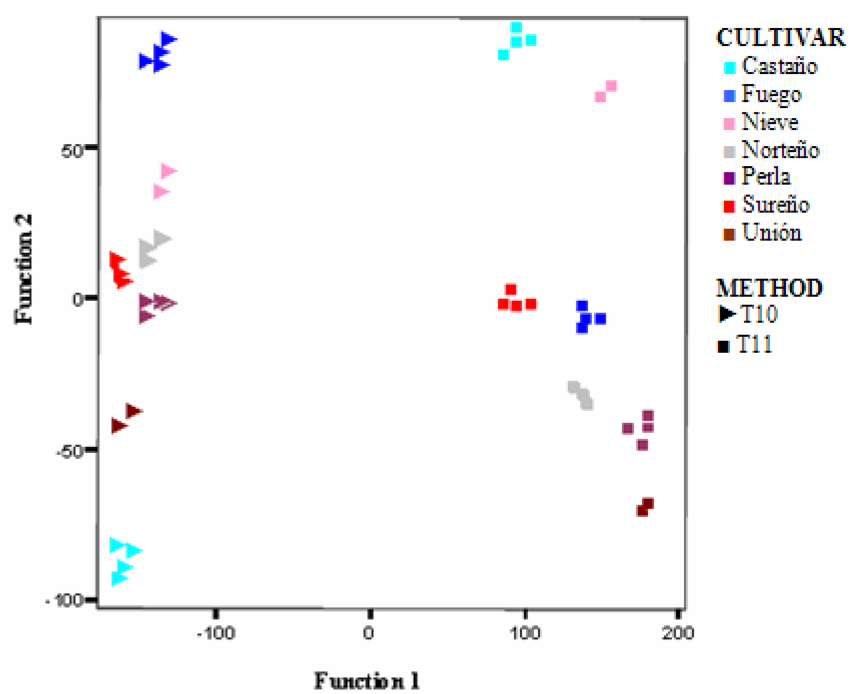

Fig. 4. Stepwise linear discriminant analysis applied on the principal components of the properties of the sensors curves of the electronic nose for lyophilized- non humidified with distilled water (T10: ►) and lyophilized- humidified with distilled water (T11: ■) cultivars.

3.5. Unified Model

Including all the samples (dried and lyophilized, with and without humidification) a model could be built reaching a correct 87.3 % classification, by cross validation (69 success and 10 errors) applying the stepwise LDA on the principal components of the sensor curves properties (data of EN). The three discriminant principal functions explained 95.6 %, 3.3 % and 0.5 % of the variance, respectively. Fig. 5 represents the bidimensional plot of the two first functions (summarizing 98.9 %). It enabled to observe that every non humidified specimen exhibited a similar behaviour, clustering in the inferior left zone of the plot. It is also observed that by humidification, the behaviour of oven-dried powders resulted different from that of lyophilized powders exhibiting a clearer separation among cultivars.

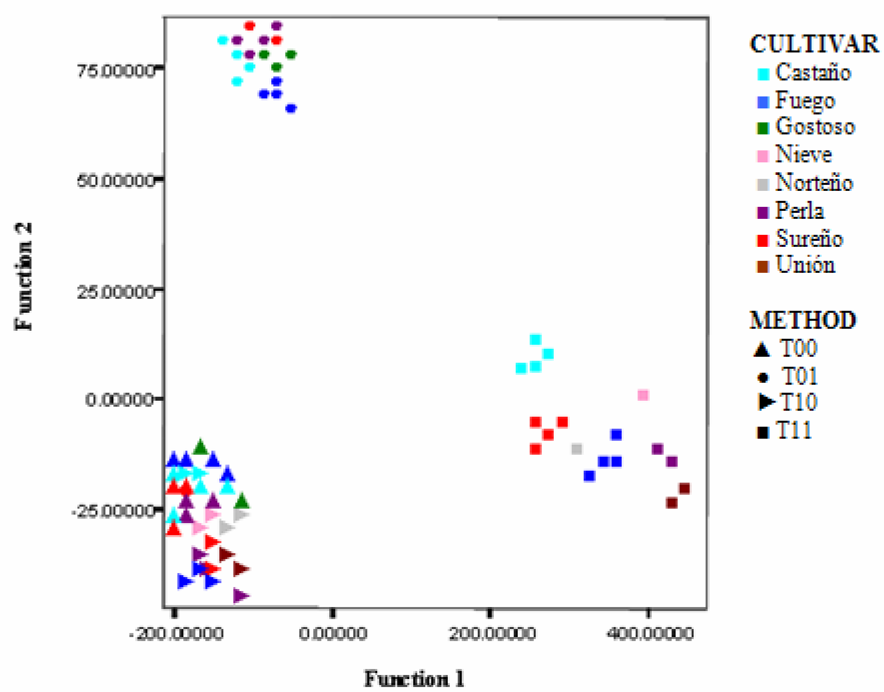

Fig. 5. Stepwise linear discriminant analysis applied on the principal components of the properties of the sensors curves of the electronic nose (using all the cases) for oven-dried-non humidified with distilled water (T00: ▲); oven-dried- humidified with distilled water (T01: ●); lyophilized-non humidified with distilled water (T10: ►) and lyophilized- humidified with distilled water (T11: ■) cultivars.

4. Conclusions

- The electronic nose enabled to separate the different garlic cultivars, either for lyophilized or oven-dried powders (with and without humidification) attaining in many cases, a classification with 100 % of success. Oven-dried powders were clearly differentiated by the electronic nose from lyophilized powders, and the cultivars identification in both cases was maintained;
- Non humidified powders were clearly differentiated from humidified powders. Differences among cultivars were maintained after humidification, either for dried or lyophilized powders.
- Cultivars could be successfully classified (100 %) for the following groups: a) oven-dried non humidified powders; b) lyophilized powders; c) lyophilized humidified powders. The classification was not so successful (88%) for garlic oven-dried humidified powders;
- As models were applied on the signals of non normalized specimen, major signals were obtained from humidified lyophilized powders in comparison with those of humidified dried powders. This

fact enabled to infer that lyophilized powders better retained the odour profile than oven-dried powders, maintaining the properties of each cultivar, since the cultivars separation for humidified lyophilized powders was considerably more significant.

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References

[1]. B. Bozina, N. Mimica-Dukicb, I. Samojlikc, A. Gorand and R. Igicd, Phenolics as antioxidants in garlic (Allium sativum L., Alliaceae), *Food Chemistry*, Vol. 111, 2008, pp. 925-929.
[2]. J. E. Lancaster, M. J. Boland, in: H. D. Rabinowitch, J. L. Brewster (Eds), Flavor Biochemistry, Onions and Allied Crops, Vol. III, *Boca Raton*, FL, 1990, p. 33-72.
[3]. Rahman, K. Garlic and aging: New insights into an old remedy, *Ageing Res. Re*V*.,* Vol. 2, 2003, pp. 39-56.
[4]. L. Méndez Lagunas and Castaigne. F., Effect of temperature cycling on allinase activity in garlic, *Food Chemistry*, Vol. 111, 2008, pp. 56-60.
[5]. Cantwell, M. I., Kang, J., Hong, G. Heat treatments control sprouting and rooting of garlic cloves, *Posthar*V*est Biol. Technol.,* Vol. 30, 2003, pp. 57-65.
[6]. Mutsch-Eckner, M., Sticher, O., Meier, B. Reversed-phase high-performance liquid chromatography of S-alk(en)yl-L-cysteinederivatives in Allium sativum including the determinationof (+)-S-allyl-L-cysteine sulphoxide, ç-L-glutamyl-Sallyl-L-cysteine and ç-L-glutamyl-S-(trans-1-propenyl)-Lcysteine, *J. Chromatogr.,* Vol. 625, 1992, pp. 183-190.
[7]. Lancaster, J. E., Shaw, M. L., ç-Glutamyl peptides in the biosynthesis of S-alk(en)yl-L-cysteine sulphoxides (flavour precursors) in Allium, *Phytochemistry*, Vol. 28, 1989, pp. 455-460.
[8]. Lawson, L. D., Wang, Z. J., Hughes, B. G., ç-Glytamyl-*S*alkylcysteines in garlic and other *Allium* spp.: precursors of age-dependent *trans*-1-propenyl thiosulfinates, *J. Nat. Prod*., Vol. 54, 1991a, pp. 436-444.
[9]. Block, E. The organosulfur chemistry of the genus *Allium*s Implications for the organic chemistry of sulfur, *Angew. Chem., Int. Ed. Engl.,* Vol. 31, 1992, pp. 1135-1178.
[10].M. E. Rybak, E. M. Calvey and J. M. Harnly, Quantitative determination of allicin in garlic: Supercritical fluid extraction and standard addition of allicin, *Journal of Agricultural and Food Chemistry*, Vol. 53, 2004, pp. 682–687.
[11].L. D. Lawson and Z. L. Wang, Low allicin release from garlic supplements: A major problem due to the sensitives of alliinase activity, *Journal of Agricultural and Food Chemistry*, Vol. 49, 2001, pp. 2592–2599.
[12].H. Jansen, B. Muller and K. Knobloch, Characterization of an allicin lyase preparation from garlic (Allium sativum), *Planta Medica*, Vol. 55, 1989, pp. 434–439.
[13].R. E. Baby, M. D. Cabezas, E. R. Castro, Filip, N. E. Walsöe de Reca, Quality Control of Medicinal Plants with an Electronic Nose, *Sensors and Actuators, B, Chem*, 106, 2005, pp. 24-28.
[14].R. E. Baby, M. D. Cabezas, A. Kutschker, V. M. Messina, N. E. Walsöe de Reca, Discrimination of different Valerian types with an Electronic Nose, *The Journal of the Argentine Chemical Society*, Vol. 93, 2005, pp. 43-50.
[15].R. E. Baby, M. D. Cabezas, V. Labud, F. Marqui, N. E. Walsöe de Reca, Evolution of thermophilic period in biosolids composting analyzed with an electronic nose, *Sensors and Actuators, B, Chem*., Vol. 106, 2005, pp. 44-51.
[16].V. M. Messina, R. E. Baby, A. Calvino, M. D. Cabezas, N. E. Walsöe de Reca, Degradation of Olive Oil by Light or Heating. Electronic Nose and Sensory Data Analysis, *The Journal of the Argentine Chemical Society*, Vol. 93, 2005, pp. 57-67.
[17].R. E. Baby, M. D. Cabezas, N. E. Walsöe de Reca, Electronic nose: an useful tool for monitoring the environmental contamination, *Sensors and Actuators, B, Chem*, Vol. 69, 2000, pp. 214-218.
[18].M. Bauzá, M. Sance, C. Formica, J. L. Burba, R. E. Baby, M. D. Cabezas, V. M. Messina, N. E. Walsöe de Reca, Correlación de la discriminación olfativa de cultivares de ajo con panel sensorial y con una nariz electrónica, *Industria y Química*, Vol. 350, 2005, pp. 10-12.

[19]. Mitrovics, J., Ulmer, H., Noetzel, G., Weimar, U, Göpel, W., *Proceedings Transducers*, 1997, Chicago, pp. 1-4.
[20]. Göpel, W., New materials and transducers for chemical sensors, *Sensors and Actuators B*., Vol. 18, 1994a, pp. 1-21.
[21]. Göpel, W., Schweizer-Berberich, P. M.,Vaihinger, S. Characterisation of food freshness with sensor arrays, *Sensors and Actuators B*, Vol. 18, 1994b, pp. 282-290.
[22]. R. E. Baby, M. D. Cabezas, N. E. Walsöe de Reca, ¿Qué informaciones nos puede brindar una nariz electrónica sobre los Alimentos?, *Industria y Química*, Vol. 341, 1999, pp. 34-38.

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- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
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