Optimization of Metal Oxide Gas Sensor in Electronic Nose to Monitor Odor Profiles of Garlic Scape

Valeria Messina, María Sance, Gabriela Grigioni, and Noemí Walsöe de Reca

***Abstract*— Response of metal-oxide sensors based on tin dioxide SnO_2 (P and T) and chromium titanium oxide, and on tungsten oxide (LY) were used to analyze different cultivars of garlic scapes. Temperature and time for sample incubation were set at two temperatures (40 °C and 50 °C) and at two incubation times (6 and 10 min). All the sensors presented saturation at 50 °C. A temperature set at 40 °C had optimal responses for all the sensors. Conditions established in the first place (40 °C during 6-min incubation) were used to evaluate five types of different cultivars of fresh garlic scape in order to evaluate sensors. Linear discrimant analysis with Wilks' lambda stepwise method was applied to investigate the grouping of garlic scapes as a function of the cultivar. Two discriminant functions (DF_1 and DF_2) were obtained that explained 93.7% and 5% of the total variance, respectively. On the other hand, the same cultivars were analyzed among storage (three days). Data showed that changes among storage could be detected by LY, T, and P sensors among each cultivar (LY and T for Sureño; L for Castaño; P for Gostoso; LY, P, and T for Fuego and P for Morado). Differences among odor are related to the amount of volatile compounds (allicins and sulfide compounds) present, which are presumed to be responsible for their distinct flavors and aromas in each cultivar.**

***Index Terms*— MOX sensors, n-type sensors, cultivars, odour.**

I. Introduction

THE allicins and sulfide compounds in Allium plants are presumed to be responsible for their distinct flavors and aromas. Among the most important volatile compounds present we can find organosulfur compounds such as diallyl disulfide, diallyl sulfide, diallyl trisulfide, methyl allyl disulfide, methyl allyl trisulfide, dimethyl trisulfide and DATS. Dimethyl Trisulphide, Allyl Mercaptan, Allyl mMethyl Disulphide, Allyl Methyl Sulphide, Allyl Methyl Sulfoxide and Allyl Methyl Sulfone [1].

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V. Messina and N. W. de Reca are with the Solid Research Center, Scientific and Technological Research Institute for Defense, UNIDEF (Strategic I & D for Defense)-CONICET-MINDEF (Ministry of Defense), Buenos Aires 1603, Argentina, and also with the National Council for Scientific and Technical Research, Buenos Aires 1603, Argentina (e-mail: vmessina@citedef.gob.ar; walsoe@citedef.gob.ar).

M. Sance is with the University of Agronomic Science, Bucharest 013701, Argentina (e-mail: msance@fca.uncu.edu.ar).

G. Grigioni is with the Food Technology Institute, Agro industrial Research Center, National Institute of Agricultural Technology, Buenos Aires 1417, Argentina, and also with the National Council for Scientific and Technical Research, Buenos Aires 1603, Argentina (e-mail: ggrigioni@cnia.inta.gov.ar).

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Several authors have stated the chemical distinctions between the species in the amount and types of compounds present in Allium plants using conventional analysis such as Gas Chromatography [1]–[4].

Through Principal Component Analysis (PCA) applied to GC-SPME differentiating has been applied on garlic, based on diversity in garlic genes, the country of origin [2], the type of food preparation technique [3], and morphological characteristics of garlic [4].

Electronic nose device was introduced in the market in the 90's. It can be defined as an instrument equipped with chemical sensors and a program with a chemometric pattern recognition that is able to recognize and compare individual or complex odours of substances [5].

The data obtained with this instrument is qualitative. It analyzes and recognizes complex odours olfactory traces, evaluating together the volatile components of the sample to analyze or classify, imitating the human system olfactory [6]–[8].

Different types of sensors have been studied among the years for different fields, to evaluate the application of these sensors [9]–[13].

Response of metal oxide sensors (MOX) in electronic nose has been published by one of the authors of this paper [14]. The author stated that MOX sensors were useful tools to different cultivars of garlic cloves obtained by different drying process (lyophilized and oven dried). Sensors were able to differentiate by cultivar and by method of drying.

In horticulture field, to our knowledge however, there is no published data on the study of garlic scapes using metal oxide (MOX) sensors.

The aim of this research was to develop an application and to optimize metal oxide sensors in different cultivars of garlic scapes to be applied in horticulture field as a useful tool for quality control process.

II. Design and Experimentation

A. Electronic Nose Device Description

An electronic nose system α-PROMETHEUS (Alpha MOS, Toulouse, France) was used. The device has two main units, i.e. a sensor array system (α-FOX 4000, France) and a fingerprint mass spectrometer (α-KRONOS, France) with an electron impact quadrupole analyzer. Both units are equipped with a headspace auto-sampler HS100 (Alpha MOS, Toulouse, France).

The α-FOX contains eighteen metal oxide sensors: six LY ((LY2/AA, LY2/G, LY2/gCT, LY2/gCTI, LY2/Gh, LY2/LG); seven P (P10/1, P10/2, P30/1, P30/2, P40/1, P40/2, PA2) and five T (T30/1, T40/2, T40/1, TA2, T70/2)).

P and T are metal oxide sensors. They are based on tin dioxide SnO_2 (n-type semiconductor), the difference between them resides in the geometry of the sensors.

The LY sensors are metal oxide ones based on chromium titanium oxide (p-type semiconductor) and on tungsten oxide (n-type semiconductor). In the presence of a reducing gas, there is absorption with an electronic exchange of gas towards the sensors: the conductance of the n-type increase while for the p-type the resistance will increase, due that n-type are based on tin dioxide SnO_2 and p-type are based on chromium titanium oxide.

B. Plant Samples

Samples of garlic scapes of different cultivars (Sureño, Castaño, Morado, Fuego and Gostoso (being the original Spanish names given at INTA preserved)) were harvested in La Consulta, Mendoza (Argentina) at the Institute of Agricultural Technology (INTA). Scapes were collected in 2012 and removed with their bulb just after the initiation of curling and immediately stored at 5 °C ± 1 °C until analysis.

Sureño cultivar was chosen as reference to optimize the electronic nose protocol due it has been selected over the years as the result of random mutations and to the response of them to agroclimatic conditions. On the other hand, Sureño is a commercial type of garlic coming from the Red family, eco-physiological group IV.

C. Electronic Nose Protocol Analysis

The experimental part was divided into two steps. The first step was carried out in order to define the protocol of analysis by setting up parameters for the samples (temperature, time of incubation and agitation intensity) and for the equipment (duration of the acquisition period, volume of headspace injected, time between samples measurements).

MOX sensors array were evaluated at two temperatures (40 °C and 50 °C) and at two incubation times (6 and 10 min) using a reference cultivar (Sureño).

The selection of temperature 40 °C and 50 °C was based on treatment of process described by reference [15] and [16] (following modification for reference [16]: Temperature: 35 °C was modified for 40 °C). The incubation times (6 and 10 min) were selected according to reference [14] (Time: 15 min was modified for 6 and 10 min).

Samples were cut in slices with a knife in order to increase the area/volume ratio to form a batch; no chopping procedure was used in order to minimize the damage. Then, an aliquot of 3.00 g ± 0.05 g was placed in five 10 ml glass vial equipped with a magnetic cap and silicon septum.

The criterion used to determine the best combination of all the parameters was that the coefficient of signal variation of each sensor (measured at the maximum amplitude) was less than 3% when similar samples were analyzed [17].

D. Analysis of Different Garlic Scape Cultivars

The methodology and experimental conditions established in the first step was applied to all cultivars. Analyses were carried out by triplicate.

E. Statistical Analysis

Electronic nose data was analyzed applying Linear Discriminant Analysis (LDA) with Wilks' lambda stepwise method for variable selection. The criterion used was the significance of F with a maximum of 0.05 to enter and a minimum of 0.10 to exit. LDA was applied as a classification procedure to obtain an equation by which garlic scape samples could be classified. SPSS-Advanced Statistics 12 software (SPSS Inc., Chicago, IL) was used.

III. Results and Discussion

A. Electronic Nose System Characteristics

An electronic nose system must satisfy reproducibility, long term stability, identification capability and model robustness. In order to monitor these requirements, standardized chemicals aqueous solutions were analyzed.

The solutions used were propanol (Aldrich®) 0.001 g/ml, acetone (Aldrich®) 0.001 g/ml and isopropanol (Aldrich®) 0.0005 g/ml; all solutions prepared with HPLC degree water. Measurements were performed over a period of one week, the lapse of time needed to evaluate all samples.

In each time of analysis, a total of 10 standards (i.e. three replicates with 1 ml of each standard plus one vial containing 1 ml of propanol, the first vial is not considered in the analysis) were analyzed following a pre-established procedure.

B. Selection of Electronic Nose Parameters

The applied experimental design, at temperature 50 °C and both incubation times (6 and 10 min), the eighteen sensors showed saturation (data non shown). This can be attributed to high concentration of volatile compounds release from the samples.

Applying 40 °C and two incubation times 6 and 10 min, the variation coefficient of each sensor for 6 min of incubation time, data showed values under 3%. Besides, data obtained at 10 min were above 3%.

Fig. 1 shows the response of the six LY and the seven P and five T sensors for Sureño cultivar during 6 and 10min of incubation time.

The protocol of selected analysis was defined as followed: during the acquisition process, samples were kept at 40 °C for 6 min and shaken at 500 rpm in order to obtain equilibrium in the headspace.

An aliquot of 1 ml per vial was taken using a syringe, which was pre-heated at 50 °C to avoid condensation. Then, 100 ul was injected into the α-FOX injection port. The device was continuously purged with dry air (synthetic air N35, Air Liquid) set at 150 $\min^{-1}$. The acquisition time was set at 120s

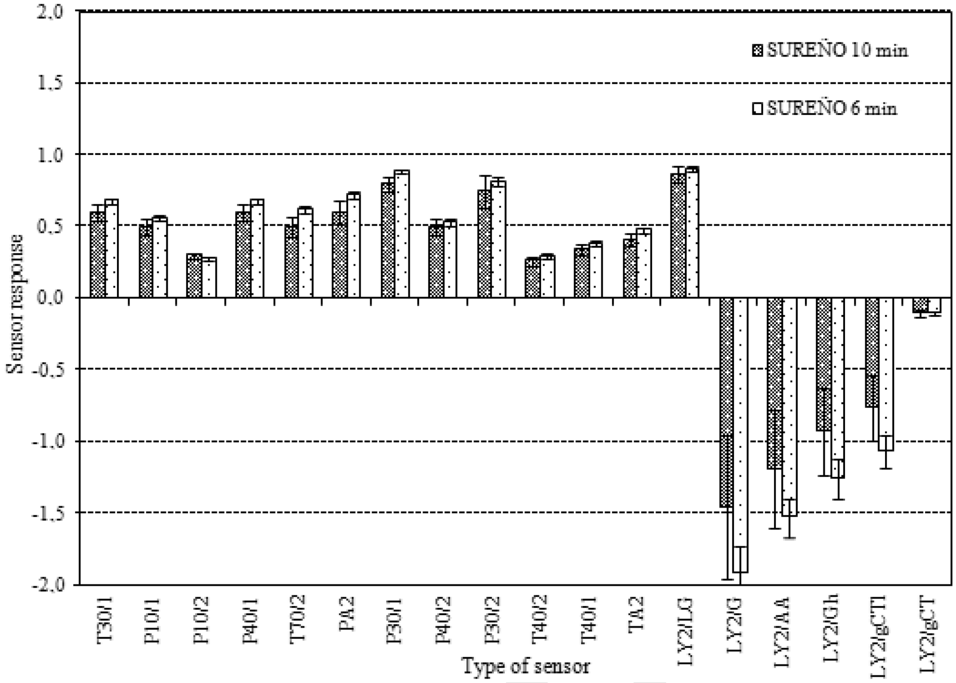

Fig. 1. Response of the six LP, five T and seven P-MOX sensors for Sureño Cultivar at 40 °C at 6 and 10 min of incubation time.

and the delay time (time elapsed between subsequent analyses) was 18 min.

These experimental conditions ensured that each step during data acquisition was enough to establish a correct baseline, to collect volatile compounds and to allow the recovery up of sensors between sample analyses. All samples were analyzed in triplicate.

The maximum amplitude in the sensor response curve was considered for analysis.

C. Analysis of Fresh Cultivars of Garlic Scapes

Five types of fresh garlic scapes coming from different cultivars were analyzed using Linear Discrimant Analysis with Wilks' lambda stepwise method to investigate the grouping of scapes odour profile as a function of the cultivar. Two discriminant functions (DF) were obtained explaining 93.7% and 5.0% of the total variance respectively (Fig. 2), with a success rate of correct classification of each sample in their respective group (i.e.: cultivar) of 86.7% and 53.3% of the original cases and after cross validation.

The canonical variables form the following equations of the corresponding linear discriminant function is (DFi with i = 1–2) where *Sj* represent sensor *type:*

$$DF_1 = 4.309{*}S_{(LY2/LG)} + 3.764{*}S_{(P40/1)} - 7.434{*}S_{(P30/2)} \quad (1)$$

$$DF_2 = -0.25{*}S_{(LY2/LG)} - 1.997{*}S_{(P40/1)} + 2.866{*}S_{(P30/2)} \quad (2)$$

Reference [18] reported 23 kinds of volatile components present in fresh Chinese garlic scapes applying Headspace Sampling GC-MS Analysis. Among the analyzed volatile

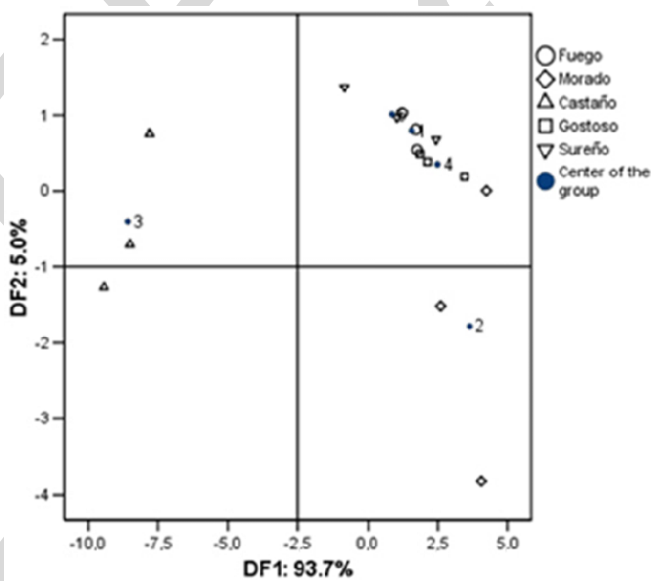

Fig. 2. Discriminant analysis of electronic nose data corresponding to different cultivars of garlic scapes (Fuego (○); Morado (◊); Castaño (△); Gostoso (□); and Sureño (▽)). AQ:1

compounds, 15 belonged to compounds containing sulfur. The amounts of volatile compounds containing sulfur were within 99.4% of the samples analyzed.

On the other hand, the six main components found in garlic scapes by reference [18] were: diallyl disulfide(66.52%);1,3dithiane(15.44%); diallylsulfide(7.15%), dimethyldisulfide (1.24%); diallyl sulfide 1.09%) and 2-allyl methyl sulfide (2.66%). The responses of the LY and P MOX sensors among cultivars are due to its volatile compound composition.

D. Analysis of Cultivars of Garlic Scapes Under Storage

When fresh garlic is cut an enzymatic reaction is produced and precursors of S-alk(en)yl-L-cysteine sulfoxides appears, but 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 [19], [20]. Thiosulfinates are thermally unstable and converted to successive compounds of alk(en)yl polysulfides, dithiins, or ajoenes, thus contributing to changes in the flavour of garlic [21], [22].

In order to evaluate LY, P and T sensors response among storage, the same cultivars stated in *Plant Samples*, were analyzed during 3 consecutive days. Samples were stored under refrigeration at 5 °C ± 1 °C.

Linear Discrimant Analysis with Wilks' lambda stepwise method was applied to investigate the grouping of storage (Day 1; Day 2 and Day 3) as a function of the cultivar. The canonical variables form the following equations of the corresponding linear discriminant function for the five cultivars is (DFi with i = 1–2), where *Sj* represent sensor *type:*

Sureño

DF_1 explained 79.4% and $DF_2$20.6 % of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 100% and 100% of the original cases and after cross validation.

$$DF_1 = 14.441{*}S_{(LY2/G)} + 6.524{*}S_{(LY2/AA)} + 5.490{*}S_{(LY2/gCT)} + 25.621{*}S_{(T30/1)} \quad (3)$$

$$DF_2 = 18.389{*}S_{(LY2/G)} - 5.183{*}S_{(LY2/AA)} + 1.235{*}S_{(LY2/gCT)} + 14.408{*}S_{(T30/1)} \quad (4)$$

Castaño

DF_1 explained 94.6% and DF_2 5.4% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 77.8% and 66.7% of the original cases and after cross validation.

$$DF_1 = 2.452{*}S_{(LY2/G)} + 2.791{*}S_{(LY2/gCT)} \quad (5)$$

$$DF_2 = 1.404{*}S_{(LY2/G)} + 0.446{*}S_{(LY2/gCT)} \quad (6)$$

Morado

DF_1 explained 94.6% and DF_2 5.4% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 77.8% and 66.7% of the original cases and after cross validation.

$$DF_1 = -2.487{*}S_{(PA2)} + 9.960{*}S_{(P30/1)} - 7.466{*}S_{(P30/2)} \quad (7)$$

$$DF_2 = 8.617{*}S_{(PA2)} - 11.593{*}S_{(P30/1)} + 3.519{*}S_{(P30/2)} \quad (8)$$

Gostoso

DF_1 explained 98.5% and $DF_2$1.5% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 100% and 100% of the original cases and after cross validation.

$$DF_1 = 7.055{*}S_{(P10/1)} - 19.962{*}S_{(P30/1)} + 13.036{*}S_{(P40/1)} \quad (9)$$

$$DF_2 = 4.576{*}S_{(P10/1)} + 2.889{*}S_{(P30/1)} - 7.106{*}S_{(P40/1)} \quad (10)$$

Fuego

DF_1 explained 85.6% and $DF_2$14.4% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 100 % and 77.8 % of the original cases and after cross validation.

$$DF_1 = 4.726{*}S_{(LY2/gCT)} - 0.464{*}S_{(PA2)} - 6.927{*}S_{(P40/2)} + 11.874{*}S_{(TA2)} \quad (11)$$

$$DF_2 = 14.678{*}S_{(LY2/gCT)} - 26.002{*}S_{(PA2)} + 16.045{*}S_{(P40/2)} + 22.323{*}S_{(TA2)} \quad (12)$$

Reference [23] reported that in Korean garlic the predominant odorants were mainly sulfur compounds (allyl methyl trisulfide, diallyl trisulfide, 2-vinyl-4H-1, 3-dithiin, dimethyl trisulfide and diallyl disulfide). Additional characterizing compounds included acetaldehyde, guaiacol, p-vinylguaiacol, eugenol, (Z)-and (E)-isoeugenol, 4-hydroxy-2,5-dimethyl-3(2H)-furanone and vanillin corresponding to thermally-derived nonsulfur-containing compound. Based on these findings sulfur-containing compounds and thermally-derived nonsulfur-containing compounds it was stated that they were important contributors to the characteristic aroma, especially if they were submitted to temperature. LY, P and T sensors could be attributed to the compounds present in the storage of garlic scapes.

Changes in odour can be attributed also to another group of nonvolatile flavour precursors that appears, glutamyl-S-alk(en)-cysteines. During storage of garlic cloves glutamyl-S-alk(en)ylcysteines could be converted to alk(en)ylcysteine sulfoxides [24].

Data of electronic nose showed that changes in odour profile during storage, could be detected by LY, T and P sensors (LY and T: Sureño; L: Castaño; P: Gostoso and Morado; LY, P and T: Fuego).

Response of LY, P and T sensors are due to the differences in volatile compound among cultivars. Castaño, Sureño, Gostoso and Fuego belong to the Red family, eco-physiological group IV and Morado (Violet family, eco-physiological group II).

Results showed that the methodology applied is valid for garlic scapes. However, it is necessary to include in the future effects on crop and to increase the number of samples.

IV. Conclusion

LY and P sensors were able to differentiate among fresh and LY,T and P from stored cultivars.

Differences between LY and P sensors in fresh garlic scapes and in stored (LY, P and T sensors) are due to the volatile compound composition of each cultivar.

It is shown that, nowadays, the development of electronic nose methodology with chemical sensory arrays, constitutes a useful tool to analyze the odour profile of different products. It will be useful to incorporate this methodology in horticulture field due that the quality control can be performed quickly with these approach.

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Valeria Messina received the Ph.D. degree in bromatology. She is currently a Researcher with the Solid Research Center, Scientific and Technological Research Institute for Defense, UNIDEF (Strategic I & D for Defense)-CONICET-MINDEF (Ministry of Defense), Buenos Aires, Argentina. She is a member of the National Council for Scientific and Technical Research. AQ:2 AQ:3

María Sance received the Ph.D. degree in agronomy. She is currently a Researcher and Professor with the National University of Cuyo, Mendoza, Argentina. She is a member of the National Council for Scientific and Technical Research.

Gabriela Grigioni received the Ph.D. degree in physics. She is currently a Researcher with the Food Technology Institute, Agro industrial Research Center, National Institute of Agricultural Technology. She is a member of the National Council for Scientific and Technical Research. She is a Professor with the University of Moron, Buenos Aires, Argentina.

Noemí Walsöe de Reca received the Ph.D. degree in physics. She is currently a Director and Researcher with the Solid Research Center, Scientific and Technological Research Institute for Defense, UNIDEF (Strategic I & D for Defense)-CONICET-MINDEF (Ministry of Defense), Buenos Aires, Argentina. She is a member of the National Council for Scientific and Technical Research.

AUTHOR QUERIES

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V. Messina and N. W. de Reca are with the Solid Research Center, Scientific and Technological Research Institute for Defense, UNIDEF (Strategic I & D for Defense)-CONICET-MINDEF (Ministry of Defense), Buenos Aires 1603, Argentina, and also with the National Council for Scientific and Technical Research, Buenos Aires 1603, Argentina (e-mail: vmessina@citedef.gob.ar; walsoe@citedef.gob.ar).

M. Sance is with the University of Agronomic Science, Bucharest 013701, Argentina (e-mail: msance@fca.uncu.edu.ar).

G. Grigioni is with the Food Technology Institute, Agro industrial Research Center, National Institute of Agricultural Technology, Buenos Aires 1417, Argentina, and also with the National Council for Scientific and Technical Research, Buenos Aires 1603, Argentina (e-mail: ggrigioni@cnia.inta.gov.ar).

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Several authors have stated the chemical distinctions between the species in the amount and types of compounds present in Allium plants using conventional analysis such as Gas Chromatography [1]–[4].

Through Principal Component Analysis (PCA) applied to GC-SPME differentiating has been applied on garlic, based on diversity in garlic genes, the country of origin [2], the type of food preparation technique [3], and morphological characteristics of garlic [4].

Electronic nose device was introduced in the market in the 90's. It can be defined as an instrument equipped with chemical sensors and a program with a chemometric pattern recognition that is able to recognize and compare individual or complex odours of substances [5].

The data obtained with this instrument is qualitative. It analyzes and recognizes complex odours olfactory traces, evaluating together the volatile components of the sample to analyze or classify, imitating the human system olfactory [6]–[8].

Different types of sensors have been studied among the years for different fields, to evaluate the application of these sensors [9]–[13].

Response of metal oxide sensors (MOX) in electronic nose has been published by one of the authors of this paper [14]. The author stated that MOX sensors were useful tools to different cultivars of garlic cloves obtained by different drying process (lyophilized and oven dried). Sensors were able to differentiate by cultivar and by method of drying.

In horticulture field, to our knowledge however, there is no published data on the study of garlic scapes using metal oxide (MOX) sensors.

The aim of this research was to develop an application and to optimize metal oxide sensors in different cultivars of garlic scapes to be applied in horticulture field as a useful tool for quality control process.

II. Design and Experimentation

A. Electronic Nose Device Description

An electronic nose system α-PROMETHEUS (Alpha MOS, Toulouse, France) was used. The device has two main units, i.e. a sensor array system (α-FOX 4000, France) and a fingerprint mass spectrometer (α-KRONOS, France) with an electron impact quadrupole analyzer. Both units are equipped with a headspace auto-sampler HS100 (Alpha MOS, Toulouse, France).

The α-FOX contains eighteen metal oxide sensors: six LY ((LY2/AA, LY2/G, LY2/gCT, LY2/gCTI, LY2/Gh, LY2/LG); seven P (P10/1, P10/2, P30/1, P30/2, P40/1, P40/2, PA2) and five T (T30/1, T40/2, T40/1, TA2, T70/2)).

P and T are metal oxide sensors. They are based on tin dioxide SnO_2 (n-type semiconductor), the difference between them resides in the geometry of the sensors.

The LY sensors are metal oxide ones based on chromium titanium oxide (p-type semiconductor) and on tungsten oxide (n-type semiconductor). In the presence of a reducing gas, there is absorption with an electronic exchange of gas towards the sensors: the conductance of the n-type increase while for the p-type the resistance will increase, due that n-type are based on tin dioxide SnO_2 and p-type are based on chromium titanium oxide.

B. Plant Samples

Samples of garlic scapes of different cultivars (Sureño, Castaño, Morado, Fuego and Gostoso (being the original Spanish names given at INTA preserved)) were harvested in La Consulta, Mendoza (Argentina) at the Institute of Agricultural Technology (INTA). Scapes were collected in 2012 and removed with their bulb just after the initiation of curling and immediately stored at 5 °C $\pm$ 1 °C until analysis.

Sureño cultivar was chosen as reference to optimize the electronic nose protocol due it has been selected over the years as the result of random mutations and to the response of them to agroclimatic conditions. On the other hand, Sureño is a commercial type of garlic coming from the Red family, eco-physiological group IV.

C. Electronic Nose Protocol Analysis

The experimental part was divided into two steps. The first step was carried out in order to define the protocol of analysis by setting up parameters for the samples (temperature, time of incubation and agitation intensity) and for the equipment (duration of the acquisition period, volume of headspace injected, time between samples measurements).

MOX sensors array were evaluated at two temperatures (40 °C and 50 °C) and at two incubation times (6 and 10 min) using a reference cultivar (Sureño).

The selection of temperature 40 °C and 50 °C was based on treatment of process described by reference [15] and [16] (following modification for reference [16]: Temperature: 35 °C was modified for 40 °C). The incubation times (6 and 10 min) were selected according to reference [14] (Time: 15 min was modified for 6 and 10 min).

Samples were cut in slices with a knife in order to increase the area/volume ratio to form a batch; no chopping procedure was used in order to minimize the damage. Then, an aliquot of 3.00 g $\pm$ 0.05 g was placed in five 10 ml glass vial equipped with a magnetic cap and silicon septum.

The criterion used to determine the best combination of all the parameters was that the coefficient of signal variation of each sensor (measured at the maximum amplitude) was less than 3% when similar samples were analyzed [17].

D. Analysis of Different Garlic Scape Cultivars

The methodology and experimental conditions established in the first step was applied to all cultivars. Analyses were carried out by triplicate.

E. Statistical Analysis

Electronic nose data was analyzed applying Linear Discriminant Analysis (LDA) with Wilks' lambda stepwise method for variable selection. The criterion used was the significance of F with a maximum of 0.05 to enter and a minimum of 0.10 to exit. LDA was applied as a classification procedure to obtain an equation by which garlic scape samples could be classified. SPSS-Advanced Statistics 12 software (SPSS Inc., Chicago, IL) was used.

III. Results and Discussion

A. Electronic Nose System Characteristics

An electronic nose system must satisfy reproducibility, long term stability, identification capability and model robustness. In order to monitor these requirements, standardized chemicals aqueous solutions were analyzed.

The solutions used were propanol (Aldrich®) 0.001 g/ml, acetone (Aldrich®) 0.001 g/ml and isopropanol (Aldrich®) 0.0005 g/ml; all solutions prepared with HPLC degree water. Measurements were performed over a period of one week, the lapse of time needed to evaluate all samples.

In each time of analysis, a total of 10 standards (i.e. three replicates with 1 ml of each standard plus one vial containing 1 ml of propanol, the first vial is not considered in the analysis) were analyzed following a pre-established procedure.

B. Selection of Electronic Nose Parameters

The applied experimental design, at temperature 50 °C and both incubation times (6 and 10 min), the eighteen sensors showed saturation (data non shown). This can be attributed to high concentration of volatile compounds release from the samples.

Applying 40 °C and two incubation times 6 and 10 min, the variation coefficient of each sensor for 6 min of incubation time, data showed values under 3%. Besides, data obtained at 10 min were above 3%.

Fig. 1 shows the response of the six LY and the seven P and five T sensors for Sureño cultivar during 6 and 10min of incubation time.

The protocol of selected analysis was defined as followed: during the acquisition process, samples were kept at 40 °C for 6 min and shaken at 500 rpm in order to obtain equilibrium in the headspace.

An aliquot of 1 ml per vial was taken using a syringe, which was pre-heated at 50 °C to avoid condensation. Then, 100 ul was injected into the α-FOX injection port. The device was continuously purged with dry air (synthetic air N35, Air Liquid) set at 150 min^{-1}. The acquisition time was set at 120s

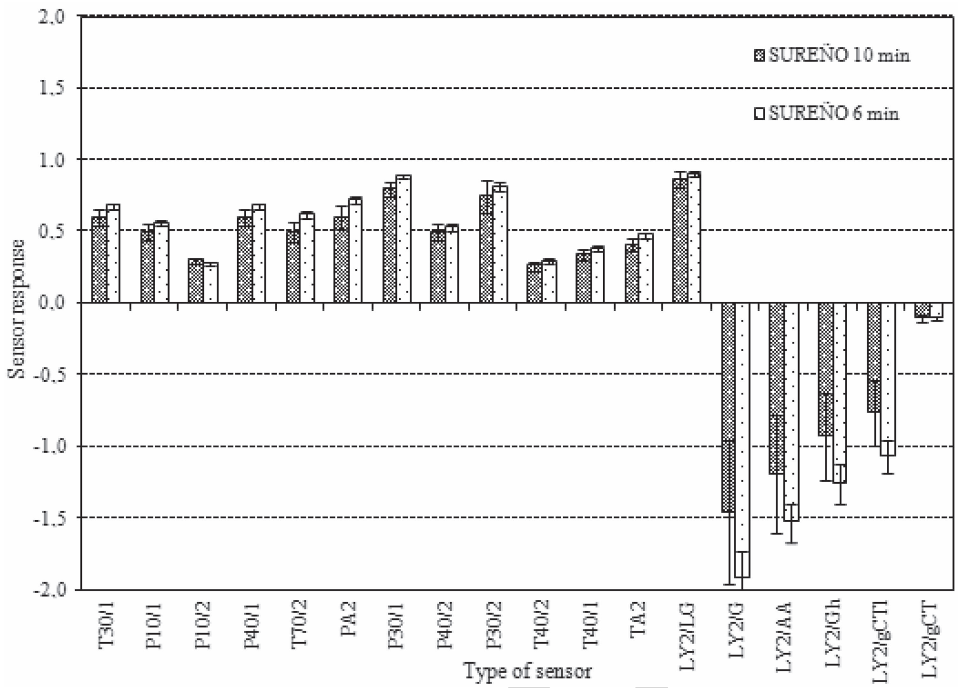

Fig. 1. Response of the six LP, five T and seven P-MOX sensors for Sureño Cultivar at 40 °C at 6 and 10 min of incubation time.

and the delay time (time elapsed between subsequent analyses) was 18 min.

These experimental conditions ensured that each step during data acquisition was enough to establish a correct baseline, to collect volatile compounds and to allow the recovery up of sensors between sample analyses. All samples were analyzed in triplicate.

The maximum amplitude in the sensor response curve was considered for analysis.

C. Analysis of Fresh Cultivars of Garlic Scapes

Five types of fresh garlic scapes coming from different cultivars were analyzed using Linear Discrimant Analysis with Wilks' lambda stepwise method to investigate the grouping of scapes odour profile as a function of the cultivar. Two discriminant functions (DF) were obtained explaining 93.7% and 5.0% of the total variance respectively (Fig. 2), with a success rate of correct classification of each sample in their respective group (i.e.: cultivar) of 86.7% and 53.3% of the original cases and after cross validation.

The canonical variables form the following equations of the corresponding linear discriminant function is (DFi with i = 1–2) where *Sj* represent sensor *type:*

$$DF_1 = 4.309 * S_{(LY2/LG)} + 3.764 * S_{(P40/1)} - 7.434 * S_{(P30/2)} \quad (1)$$

$$DF_2 = -0.25 * S_{(LY2/LG)} - 1.997 * S_{(P40/1)} + 2.866 * S_{(P30/2)} \quad (2)$$

Reference [18] reported 23 kinds of volatile components present in fresh Chinese garlic scapes applying Headspace Sampling GC-MS Analysis. Among the analyzed volatile compounds, 15 belonged to compounds containing sulfur. The amounts of volatile compounds containing sulfur were within 99.4% of the samples analyzed.

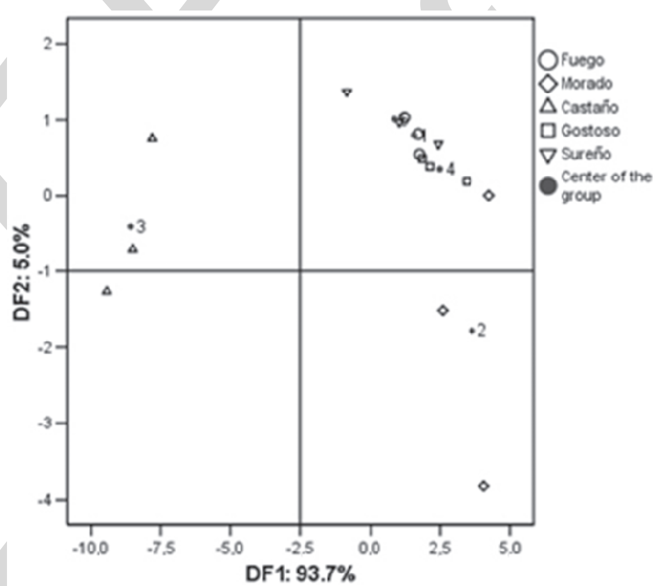

Fig. 2. Discriminant analysis of electronic nose data corresponding to different cultivars of garlic scapes (Fuego (○); Morado (◇); Castaño (△); Gostoso (□); and Sureño (▽)). AQ:1

On the other hand, the six main components found in garlic scapes by reference [18] were: diallyl disulfide(66.52%);1,3dithiane(15.44%); diallylsulfide(7.15%), dimethyldisulfide (1.24%); diallyl sulfide 1.09%) and 2-allyl methyl sulfide (2.66%). The responses of the LY and P MOX sensors among cultivars are due to its volatile compound composition.

D. Analysis of Cultivars of Garlic Scapes Under Storage

When fresh garlic is cut an enzymatic reaction is produced and precursors of S-alk(en)yl-L-cysteine sulfoxides appears, but 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 [19], [20]. Thiosulfinates are thermally unstable and converted to successive compounds of alk(en)yl polysulfides, dithiins, or ajoenes, thus contributing to changes in the flavour of garlic [21], [22].

In order to evaluate LY, P and T sensors response among storage, the same cultivars stated in *Plant Samples*, were analyzed during 3 consecutive days. Samples were stored under refrigeration at 5 °C ± 1 °C.

Linear Discrimant Analysis with Wilks' lambda stepwise method was applied to investigate the grouping of storage (Day 1; Day 2 and Day 3) as a function of the cultivar. The canonical variables form the following equations of the corresponding linear discriminant function for the five cultivars is (DFi with i = 1–2), where *Sj* represent sensor *type:*

Sureño

DF_1 explained 79.4% and $DF_2$20.6 % of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 100% and 100% of the original cases and after cross validation.

$$DF_1 = 14.441*S_{(LY2/G)} + 6.524*S_{(LY2/AA)} + 5.490*S_{(LY2/gCT)} + 25.621*S_{(T30/1)} \quad (3)$$

$$DF_2 = 18.389*S_{(LY2/G)} - 5.183*S_{(LY2/AA)} + 1.235*S_{(LY2/gCT)} + 14.408*S_{(T30/1)} \quad (4)$$

Castaño

DF_1 explained 94.6% and DF_2 5.4% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 77.8% and 66.7% of the original cases and after cross validation.

$$DF_1 = 2.452*S_{(LY2/G)} + 2.791*S_{(LY2/gCT)} \quad (5)$$

$$DF_2 = 1.404*S_{(LY2/G)} + 0.446*S_{(LY2/gCT)} \quad (6)$$

Morado

DF_1 explained 94.6% and DF_2 5.4% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 77.8% and 66.7% of the original cases and after cross validation.

$$DF_1 = -2.487*S_{(PA2)} + 9.960*S_{(P30/1)} - 7.466*S_{(P30/2)} \quad (7)$$

$$DF_2 = 8.617*S_{(PA2)} - 11.593*S_{(P30/1)} + 3.519*S_{(P30/2)} \quad (8)$$

Gostoso

DF_1 explained 98.5% and $DF_2$1.5% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 100% and 100% of the original cases and after cross validation.

$$DF_1 = 7.055*S_{(P10/1)} - 19.962*S_{(P30/1)} + 13.036*S_{(P40/1)} \quad (9)$$

$$DF_2 = 4.576*S_{(P10/1)} + 2.889*S_{(P30/1)} - 7.106*S_{(P40/1)} \quad (10)$$

Fuego

DF_1 explained 85.6% and $DF_2$14.4% of the total variance respectively, with a success rate of correct classification of each sample in their respective group of 100 % and 77.8 % of the original cases and after cross validation.

$$DF_1 = 4.726*S_{(LY2/gCT)} - 0.464*S_{(PA2)} - 6.927*S_{(P40/2)} + 11.874*S_{(TA2)} \quad (11)$$

$$DF_2 = 14.678*S_{(LY2/gCT)} - 26.002*S_{(PA2)} + 16.045*S_{(P40/2)} + 22.323*S_{(TA2)} \quad (12)$$

Reference [23] reported that in Korean garlic the predominant odorants were mainly sulfur compounds (allyl methyl trisulfide, diallyl trisulfide, 2-vinyl-4H-1, 3-dithiin, dimethyl trisulfide and diallyl disulfide). Additional characterizing compounds included acetaldehyde, guaiacol, p-vinylguaiacol, eugenol, (Z)-and (E)-isoeugenol, 4-hydroxy-2,5-dimethyl-3(2H)-furanone and vanillin corresponding to thermally-derived nonsulfur-containing compound. Based on these findings sulfur-containing compounds and thermally-derived nonsulfur-containing compounds it was stated that they were important contributors to the characteristic aroma, especially if they were submitted to temperature. LY, P and T sensors could be attributed to the compounds present in the storage of garlic scapes.

Changes in odour can be attributed also to another group of nonvolatile flavour precursors that appears, glutamyl-S-alk(en)-cysteines. During storage of garlic cloves glutamyl-S-alk(en)ylcysteines could be converted to alk(en)ylcysteine sulfoxides [24].

Data of electronic nose showed that changes in odour profile during storage, could be detected by LY, T and P sensors (LY and T: Sureño; L: Castaño; P: Gostoso and Morado; LY, P and T: Fuego).

Response of LY, P and T sensors are due to the differences in volatile compound among cultivars. Castaño, Sureño, Gostoso and Fuego belong to the Red family, eco-physiological group IV and Morado (Violet family, eco-physiological group II).

Results showed that the methodology applied is valid for garlic scapes. However, it is necessary to include in the future effects on crop and to increase the number of samples.

IV. Conclusion

LY and P sensors were able to differentiate among fresh and LY,T and P from stored cultivars.

Differences between LY and P sensors in fresh garlic scapes and in stored (LY, P and T sensors) are due to the volatile compound composition of each cultivar.

It is shown that, nowadays, the development of electronic nose methodology with chemical sensory arrays, constitutes a useful tool to analyze the odour profile of different products. It will be useful to incorporate this methodology in horticulture field due that the quality control can be performed quickly with these approach.

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Valeria Messina received the Ph.D. degree in bromatology. She is currently a Researcher with the Solid Research Center, Scientific and Technological Research Institute for Defense, UNIDEF (Strategic I & D for Defense)-CONICET-MINDEF (Ministry of Defense), Buenos Aires, Argentina. She is a member of the National Council for Scientific and Technical Research. AQ:2 AQ:3

María Sance received the Ph.D. degree in agronomy. She is currently a Researcher and Professor with the National University of Cuyo, Mendoza, Argentina. She is a member of the National Council for Scientific and Technical Research.

Gabriela Grigioni received the Ph.D. degree in physics. She is currently a Researcher with the Food Technology Institute, Agro industrial Research Center, National Institute of Agricultural Technology. She is a member of the National Council for Scientific and Technical Research. She is a Professor with the University of Moron, Buenos Aires, Argentina.

Noemí Walsöe de Reca received the Ph.D. degree in physics. She is currently a Director and Researcher with the Solid Research Center, Scientific and Technological Research Institute for Defense, UNIDEF (Strategic I & D for Defense)-CONICET-MINDEF (Ministry of Defense), Buenos Aires, Argentina. She is a member of the National Council for Scientific and Technical Research.

AUTHOR QUERIES

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