Determination of Soursop (*Annona muricata* L. cv. Elita) Fruit Volatiles during Ripening by Electronic Nose and Gas Chromatography Coupled to Mass Spectroscopy

Determinación de Compuestos Volátiles en Frutos de Guanábana (*Annona muricata* L. cv. Elita), durante la Maduración, por Nariz Electrónica y Cromatografía de Gases Acoplada a Espectroscopía de Masas

Carlos Julio Márquez Cardozo[1]; José Régulo Cartagena Valenzuela[2] and
Guillermo Antonio Correa Londoño[3]

Resumen. *La guanábana (**Annona muricata** L.) es una fruta tropical exótica que se cultiva comercialmente en Colombia. Su condición altamente perecedera justifica los estudios de manejo en poscosecha. Por esta razón, la evaluación de la maduración se hizo en primer lugar, por un sistema de medición de compuestos volátiles conocido como nariz electrónica (NE) y por otro lado mediante cromatografía de gases acoplada a espectrometría de masas mediante microextracción en fase sólida del espacio de cabeza (CG-EM/MEFS). El estudio del perfil de sustancias volátiles en las frutas es uno de los principales indicadores de los atributos sensoriales que tipifica la calidad organoléptica de los vegetales. La NE se constituye en una alternativa rápida, novedosa, económica y relativamente simple para determinar grupos de sustancias volátiles en frutos de interés comercial, bien sea enteros o en fracciones. En contraste, el uso de la CG-EM/MEFS puede verse limitado por su alto costo, no obstante ser una técnica altamente selectiva. Con base en la evaluación de la pulpa realizada con NE fue posible clasificar el estado de madurez de las frutas así: inmaduro, madurez intermedia, maduro y sobremaduro, siendo los sensores de mayor impacto el 2 (reactivo con óxidos de nitrógeno), el 6 (sensible al metano) y el 8 (sensible a alcoholes y compuestos parcialmente aromáticos). Por CG-EM/MEFS, se logró establecer que durante la etapa de poscosecha, la mayor proporción de compuestos volátiles pertenece al grupo de los ésteres, predominando el Hexanoato de metilo. De manera particular en frutas sobremaduras, la presencia de compuestos alcohólicos, coincide con la evaluación hecha con la NE, la cual mostró sensibilidad a alcoholes y compuestos aromáticos de amplio rango para las frutas evaluadas. El estudio realizado aporta a la caracterización en poscosecha de los volátiles, uno de los principales atributos sensoriales en las frutas tropicales.*

Palabras clave: Aroma, contribución sensorial, poscosecha, calidad de la fruta.

Abstract. *As an exotic highly perishable tropical fruit commercially grown in Colombia, soursop (**Annona muricata** L.) is currently in need of postharvest handling studies. Thus, the present research was conducted to characterize the volatile compounds of soursop cv. Elita during postharvest. For this purpose, fruit ripeness was evaluated, for one thing, by a volatile compound measuring system known as electronic nose (EN), and for another thing, by headspace solid phase microextraction and gas chromatography mass spectrometry (HS-SPME/GC-MS). The profile of volatile substances in fruits is one of the main indicators of the sensory attributes that typify the organoleptic quality of these products. The EN constitutes an economical, relatively simple, fast and innovative alternative to determine groups of volatile compounds in whole or fractionated samples from fruits of commercial interest. In contrast, and despite its being a highly selective technique, the use of SPME/CG-MS might be limited by its elevated cost. Based on EN assessment, fruit ripening stages were classified as unripe, half ripe, ripe and overripe. The most active EN sensors were numbers 2 sensitive to nitrogen oxides), 6 (sensitive to methane) and 8 (sensitive to alcohols and partially aromatic compounds). HS-SPME/GC-MS analysis allowed establishing that during postharvest, the major proportion of volatile compounds corresponded to esters, predominantly Methyl hexanoate. Particularly in overripe fruits, the presence of alcoholic compounds coincides with the EN assessment, which, for its part, detected mainly alcohols and a wide range of aromatic substances. The study contributes to the characterization of postharvest volatiles, which are one of the major sensory attributes of tropical fruits.*

Key words: Aroma, sensorial contribution, postharvest, fruit quality.

Fruits and vegetables are important components of a healthy diet. Their sufficient daily consumption can help prevent major disorders such as cardiovascular diseases and certain cancers. While the World Health Organization recommends a minimum intake of 120 kg / person / year (OMS, 2008), some European countries like France, Germany and Belgium meet this recommendation adequately, whereas the U.S. consumption is about 90 kg / person / year and in Colombia this figure is only about 40 kg / person /

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[1] Associate Professor. Universidad Nacional de Colombia – Sede Medellín – Facultad de Ciencias Agrarias - Departamento de Ingeniería Agrícola y Alimentos. A.A. 1779, Medellín, Colombia. <cjmarque@unal.edu.co>

[2] Associate Professor. Universidad Nacional de Colombia - Sede-Medellín – Facultad de Ciencias Agrarias - Departamento de Ingeniería Agronómica. A.A. 1779, Medellín, Colombia. <jrcartag@unal.edu.co>

[3] Associate Professor. Universidad Nacional de Colombia - Sede Medellín – Facultad de Ciencias Agrarias - Departamento de Ingeniería Agronómica. A.A. 1779, Medellín, Colombia. <gcorrea@unal.edu.co>

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year (Langreo, 2002; Espinal *et al*., 2005; Jacaboy and Keller, 2006). Annonaceae fruits are among the most desirable ones in the world due to their sweetness, creamy flesh and excellent flavor when ripe. Of the nearly 100 species, five are the most commercially important ones, including soursop (*Annona muricata* L.) (Pareek *et al*., 2011). This species is grown in the Caribbean, mainly in Bermuda, Bahamas, Cuba, the Dominican Republic, St. Vincent and the Grenadines, and Puerto Rico; in Central America (southern Mexico and Costa Rica); in South America (Colombia, Brazil, Ecuador and Venezuela); and elsewhere in southeastern China, Vietnam, Australia, New Zealand, West Africa, the Pacific Islands and, in general, in the equatorial belt (Rami *et al*., 1995; Orellana and Martínez, 2002; Cuadros, 2008).

Fruit ripening is a complex, genetically controlled process of synthesis and degradation of plant compounds (Giovannoni, 2004; Vrebalov *et al*., 2009, Klee and Giovannoni, 2011). Many of the changes that occur during ripening and postharvest directly affect the savor, shelf life, nutritional quality and sensorial attributes of fruits (Wu *et al*., 2005; Yashoda *et al*., 2005; Ornelas *et al*., 2008). Among the latter, aroma is a determining feature of fruit taste, resulting from the synthesis of a series of low molecular weight compounds of varying concentration and quantitative importance that are volatile at room temperature (Kader, 2008; Dávila-Aviña *et al*., 2011). Recent evidence on different types of fruits indicates that more than 600 compounds make up an aroma (Pereira *et al*., 2005), but only a very limited number of them (commonly known as impact compounds) is responsible for the characteristic odor of fruits and other foods (Gutiérrez *et al*., 2010).

A fruit's aroma is the result of a particularly varied and complex mixture of volatile compounds. The composition of this mixture is species specific, sometimes indicating the variety, cultivar and site of origin or ripening stage of the fruit (Cantillo *et al*., 2011; El Hadi *et al*., 2013). Different proportions of volatiles, as well as the presence or absence of other biomolecules, determine the aromatic properties of a fruit (Ayala-Zavalla *et al*., 2004). For its part, flavor arises from the interaction between organic acids, sugars and volatiles (Baldwin *et al*., 2008). Playing an important role in consumer satisfaction, this attribute certainly exerts further influence on fruit consumption (Pelayo *et al*., 2003).

The climacteric ripening of the Annonaceae was discovered by Biale and Barcus (1970). It is characterized by an increase in respiratory activity promoted by high ethylene production (Taiz and Zeiger, 2006), a process that is, in turn, highly dependent on ATP availability and, therefore, associated to fruit respiration (El Hadi *et al*., 2013). Many of the parameters of interest in fruit ripening such as pulp softening, color changes and volatile production (some of them responsible for aroma), and in general, the cascade of events featuring the postharvest period, are subject to the production and action of ethylene (Génard and Gouble, 2005; Song *et al*., 2008; Mattheis, 2013).

The determination of volatile plant compounds can be done by chromatographic techniques or by the "electronic nose" (EN) technique, an instrument that enables the qualitative and / or quantitative assessment of volatile substances. This is a quick measurement equipment which can be used in a non-destructive way with the whole fruit. However, to facilitate and speed up the process, this device can be used with fractions of fruit pulp, seeds or skin tissues, among others. The EN allows differentiating and recognizing volatile compounds with the aid of sensors, thus operating as an artificial smelling instrument (Rodríguez *et al*., 2009).

The EN technique has been used in combination with gas chromatography coupled to mass spectrometry to determine the evolution of volatile compounds in several fruits like "Jonagold" apple (*Malus sylvestris* subsp. *mitis* Wallr) stored for 15 days under different conditions (Saevels *et al*., 2004); pear (*Pyrus communis* L.), in a study conducted to classify four cultivars through their volatile content during postharvest, using principal component analysis and linear discriminant analysis (Benedetti *et al*., 2008); mango (*Mangifera indica* L.), where volatile compounds were analyzed during postharvest (Lebrun, 2008); and tangerine cv. China (*Citrus reticulata* Blanco), assessed for volatiles in fruits harvested at different times (Hernández, 2006). Also, this instrument has been used in apple and pear as nondestructive analysis technique to evaluate postharvest quality and classify the fruits according to their degree of maturity in unripe, ripe and overripe (Brezmes, 2000).

The objective of this research was to determine the volatile groups present in the fruit pulp of soursop cv. Elita during ripening (unripe, half ripe, ripe and overripe stages), using volatiles measurement instrumental techniques, namely portable EN (E-nose AIRSENSE PEN3®) and gas chromatography coupled to mass spectroscopy, applying headspace solid phase microextraction (HS-SPME/GC-MS).

MATERIALS AND METHODS

Plant material. Elita soursop fruits obtained from orchards established in the agribusiness area of the Department of *Valle del Cauca* (Colombia) were employed for the trial. The experimental site is located in the rural area of the municipality of Pradera, *Agrícola Varahonda* (1,070 m.a.s.l.; average temperature of 23 °C; 1,225 mm of annual precipitation; average solar radiation of 4.8 Wm^{-2}day^{-1}; and average relative humidity of 83%). The fruits were harvested during the main production peak, which corresponds to the month of March. The fruits were all collected at the same ripening stage, 16 weeks after floral bud formation. Then, they were transported in styrofoam containers to *Universidad Nacional de Colombia*, Bogota campus, where they were stored at 20 °C and 65% RH in the Food Quality Control Laboratory of the Food Science and Technology Institute (*Instituto de Ciencia y Tecnología de Alimentos* – ICTA).

Determination of volatile compounds by EN. Volatiles were analyzed at the following ripening stages: unripe, half ripe, ripe and overripe, corresponding to postharvest days 1, 3, 6 and 9, respectively. For all evaluations, the experimental unit (EU) was one fruit, with six replications per ripening stage.

The EN equipment was a portable AIRSENSE PEN3® (Win Muster AIRSENSE Analytics Inc.; Schwerin, Germany). It possesses a small (1.8 cm^3 volume) inner chamber containing 10 metal oxide semiconductor sensors that recognize gas molecular patterns and emit corresponding signals, which are received by a computer system and processed by a Win Muster 1.6.2 software package. Figure 1 presents an overview of this equipment.

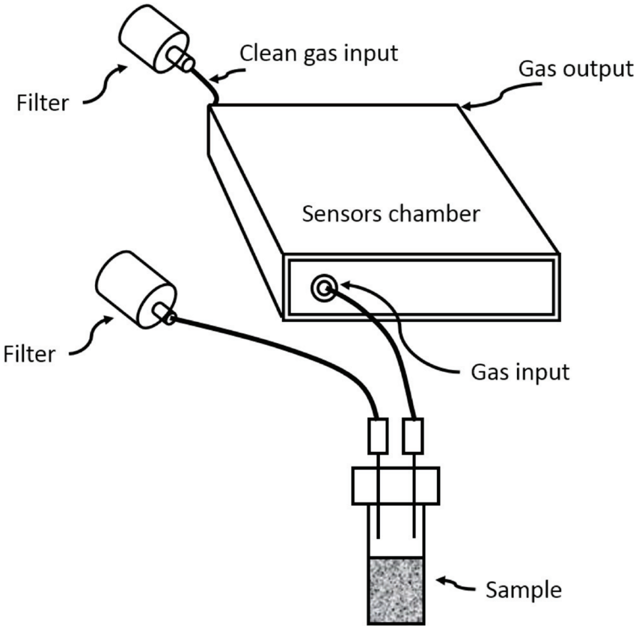

Figure 1. Electronic nose used for the characterization of volatiles in soursop pulp (*Annona muricata* L. cv. Elita) at different ripening stages.

Table 1 shows the 10 sensors used in the EN, their names and position numbers within the chamber and the general description of the gases they detect (Benedetti *et al*., 2008).

Sensor response is expressed in ohms as a resistivity resulting from changes in conductivity occurred by absorption of the volatile molecules in their gas phase. Having a detection limit of 1 ppm, the sensors are heated to 400 °C by a resistor that burns and transforms the volatiles into CO_2 and water, which are evacuated.

Four grams of fruit pulp were extracted from each EU, then homogenized and placed in a 40 mL vial.

Headspace conditioning time was 20 min; gas flow was 200 mL min^{-1}; running time for each sample determination was 100 s; and sensor cleaning air flow time was 10 min. A septum inserted with two 20 gauge needles was hermetically installed on top of the vial. One of these needles led to an activated carbon filter air cleaning system. The other one took the gas with the volatiles to a Teflon duct (3 mm internal diameter) which ran from the headspace to the sensors chamber of the EN. The gas with the volatiles produced by the fruit pulp was sucked by a pump and conducted from the headspace to the sensors chamber. The dilution of the gases was carried out by a second pump which introduced clean air into the chamber. This clean air was also used to purge the system and take it back to baseline conditions for a new sample determination.

Table 1. Description of the sensors used in the AIRSENSE PEN3® electronic nose, together with their applications.

Position number	Sensor name	General description	Reference gas
1	W1C	Aromatic compounds.	Toluene 10 mg kg^{-1}
2	W5S	Broad sensitivity range, reactive with nitrogen oxides, very sensitive with negative signal.	NO_2 1 mg kg^{-1}
3	W3C	Ammonia, used as sensor for aromatic compounds.	Benzene 10 mg kg^{-1}
4	W6S	Mainly hydrogenated compounds; selective for expired gases.	H_2 100 μg kg^{-1}
5	W5C	Alkanes, lower polarity aromatic compounds.	Propane 1 mg kg^{-1}
6	W1S	Sensitive to methane. Broad sensitivity range.	CH_4 100 mg kg^{-1}
7	W1W	Reactive with sulfur compounds; sensitive to some terpenes and organic sulfur compounds which are important to detect limonene and pyrazine.	H_2S 1 mg kg^{-1}
8	W2S	Detects alcohols and a broad range of partially aromatic compounds.	CO 100 mg kg^{-1}
9	W2W	Aromatic and organic sulfur compounds.	H_2S 1 mg kg^{-1}
10	W3S	Highly selective for methane. It reacts at high concentrations (> 100 mg kg^{-1}).	CH_4 10-100 mg kg^{-1}

(Source: Benedetti *et al.*, 2008)

At each measurement, the signals from all the sensors were stored, plotted and statistically analyzed by principal component (PCA), linear discriminant (LDA) and Biplot analyses. PCA is a descriptive dimensionality reduction technique that facilitates assessing interdependence between groups of variables by representing information on a smaller dimensional space (Vivanco, 1999; Rencher, 2002; Brezmes, 2006; Bern, 2010). LDA allows building linear discriminant functions based on which the maximum possible separation between maturity stages is obtained (Bern, 2010). Biplot analysis approximates the distribution of a multivariate sample in a reduced dimensional space (usually a plane) on which it overlaps representations of the variables (Santos *et al.*, 1991; Gower and Hand, 1996). Two software packages, namely Win Muster 1.6.2 (AIRSENSE Analytics GmbH 2006) and Matlab 7.0 were used for data analysis.

Determination of volatile compounds by HS-SPME/GC-MS. Volatile compounds were analyzed in three fruits per each of the target ripening stages (unripe, half ripe, ripe and overripe). Thirty grams of seedless fruit pulp were extracted from each fruit and homogenized for 5 min, to be deposited into a 110 mL vial which was sealed and allowed an equilibrium time of 20 min at 20 °C. Then, for the solid phase microextraction, a 30 μm fiber of the DVB/CAR/PDMS type was introduced into the headspace and left immersed in the vial for 30 min at 20 °C without agitation, so as to extract the volatiles. This fiber was then removed and immediately placed in the injection port of a GC-MS-QP5050 Shimadzu® gas chromatograph with a desorption time of 5 min. The experiment was performed thrice for each ripening stage, using a different fruit in each case, for a total of 12 EU. The operating conditions of the chromatograph were 250 °C for the injection port and the interface; initial oven temperature of 50 °C; heating rate of 4 °C min^{-1} up to 300 °C; RTX-5 chromatographic column (30 m x 0.32 mm x 0.25 µm); helium at 1.5 mL min^{-1} flow as carrier gas; and 30 min run time. HS-SPME and GC-MS conditions had been previously standardized by Vela *et al.* (2005).

The identification of volatiles was done by comparing the mass spectrum data of the sampled compounds with the information of the CLASS-5000 library and by the Kovats Index (KI) as calculated through equation 1.

$$I_x^s = 100N + 100n\left(\frac{\log t_{R,x} - \log t_{R,N}}{\log t_{R,(N+n)} - \log t_{R,N}}\right) \qquad \text{Equation 1}$$

Where:

I_x^s = retention index of component "x" during stationary phase "s"
N = number of carbon atoms of the n-minor alkane
n = difference in number of carbon atoms between the n-alkanes among which the component has eluted
$t_{R,x}$, $t_{R,N}$, $t_{R,(N+n)}$ = retention times of component x and the n-alkanes among which the component has eluted (Mendoza and Amézquita, 2008).

RESULTS AND DISCUSSION

Determination of volatile compounds by EN. The EN response to the volatile compounds in the pulp of unripe soursop fruit was characterized by its resemblance to that obtained with the reference substances nitrogen oxide (NO_2 - sensor 2-W5S), methane (CH_4) and a wide range of organic substances (sensor 6-W1S), and alcohols and partially aromatic compounds (sensor 8-W2S).

The response of the sensors to the half ripe fruit volatiles showed slightly increased levels with respect to those found for the immature fruit pulp. The response to CH_4 and the wide range organic substances of Sensor 6-W1S was very similar to that observed in immature fruit pulp.

In the case of the ripe fruits, there was an increase in the detection of NO_2 by sensor 2-W5S; CH_4 by sensor 6-W1S; and alcohols and partly aromatic compounds, by sensor 8-W2S. The other sensors showed no change in behavior. The observed increase may be related to the respiration shift that is proper of the climacteric nature of soursop (Pareek *et al.*, 2011).

In turn, the overripe fruits (as compared to the ripe ones) were featured by even higher detected levels of NO_2, CH_4, and alcohols and partially aromatic compounds. These results are certainly useful to classify the ripening stages of this fruit (Gómez *et al.*, 2007).

Figure 2 presents the responses generated by the ten electronic nose sensors.

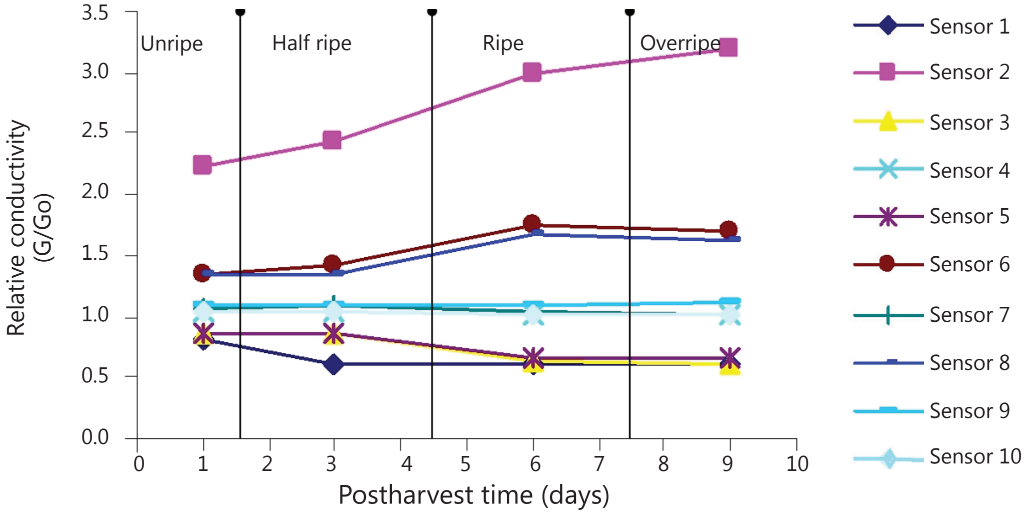

Figure 2. Mean detection values of the electronic nose sensors for the different ripening stages of soursop pulp (*Annona muricata* L. cv. Elita) stored at 20 °C and 65% RH.

Figure 2 shows how the impact of fruit ripeness on pulp olfactory trace is detected by some of the EN sensors (those with the most pronounced slope). The chemical groups associated to such sensors were also detected by Cheong *et al*. (2010), who identified 35 volatile compounds represented by esters, alcohols, terpenes, acids, aromatic ketones and an aldehyde. Although the reports on soursop pulp volatiles reveal chemical group similarities, this does not necessarily cover the specific volatile compounds themselves. In this regard, some authors suggest that the lack of agreement in the results on the specific volatile composition of these groups may be due to evaluation methodology contrasts and to differences among cultivars and regions of origin (Franco and Janzantti, 2005). However, according to Gómez *et al*. (2007) and Hernández *et al*. (2007), EN data can be used to establish a plant material's origin, facilitate taxonomic identification and determine postharvest (ripening) stages. Furthermore, it should be noted that volatile component contributions to a plant's aroma are not necessarily related to the quantitative expression of these products (Mahattanatawee *et al*., 2005).

Principal component analysis (PCA). After subjecting the results of the 10 EN sensors (as obtained across ripening stages) to PCA, it can be observed how the first two principal components collect 98.87% of total variability. In Figure 3, the average results of the sampling dates are displayed on the main plane, where colors identify the ripening stage.

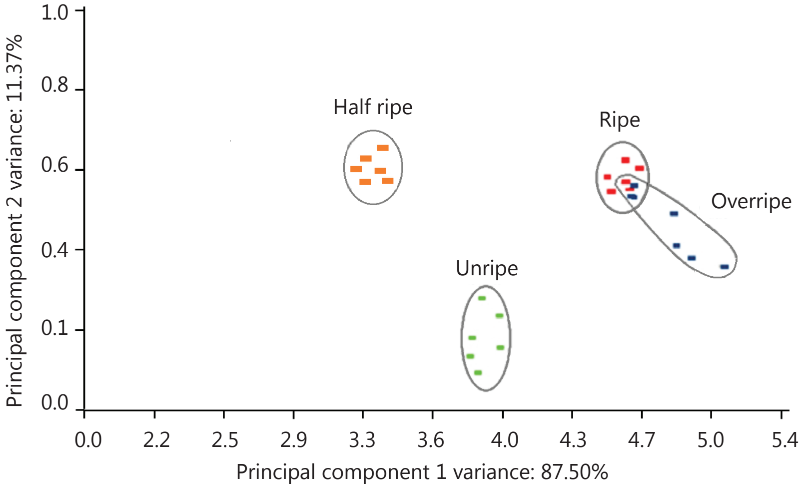

Figure 3. PCA first main plane for electronic nose readings of soursop (*Annona muricata* L. cv. Elita) pulp stored at 20 °C and 65% RH.

Figure 3 shows a good level of separation between almost all ripening stages, except for ripe and overripe fruits, indicating that in terms of volatile compounds, these two would be the least differentiated groups.

In addition to the main separation between groups given on the first dimension, the unripe stage is separated from the other groups on the second dimension, suggesting that this fruit condition has a clearly distinct volatile composition.

Linear discriminant analysis (LDA). Figure 4 illustrates the positioning of the ripening stage sample data on the plotting of the two first discriminant functions.

Figure 4 shows that the first linear discriminant function is enough to separate the samples according to the four predefined ripening stages. The second function could be used to discriminate between ripe and overripe stages, thus confirming the statement by Cantillo *et al.* (2011) in the sense that the formation of volatile compounds during ripening is characterized by a dynamic process wherein the concentration of the constituents changes both qualitatively and quantitatively. Moreover, the usefulness of the EN appears as a rapid instrumental alternative to evaluate quality attributes such as volatiles, some of them responsible for aroma in whole or processed fruits, which can be advantageous to define storage conditions (Quicazán *et al*., 2011).

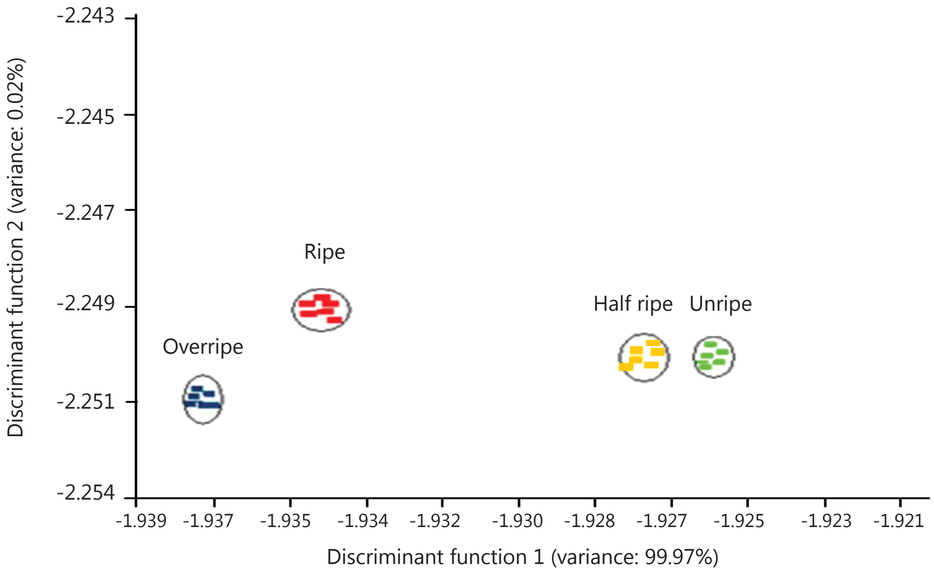

Figure 4. Linear discriminant analysis (LDA) of soursop (*Annona muricata* L. cv. Elita) pulp stored at 20 °C and 65% RH.

Biplot Analysis. Figure 5 shows the first principal plane with the different soursop ripening stages represented by their corresponding EN sensor readings.

Figure 5 shows that the ripening stages are distributed along the first dimension, with the early stages (half ripe and unripe) on the left, and the final states (ripe and overripe) on the right. The sensors that contribute the most to that dimension are 2-W5S, 8-W2S, 1-W1C, 3-W3C, 5-W5C and 4-W6S.

Among the active sensors we can count those sensitive to NO_2 (sensor 2 - W5S), methane and a wide range

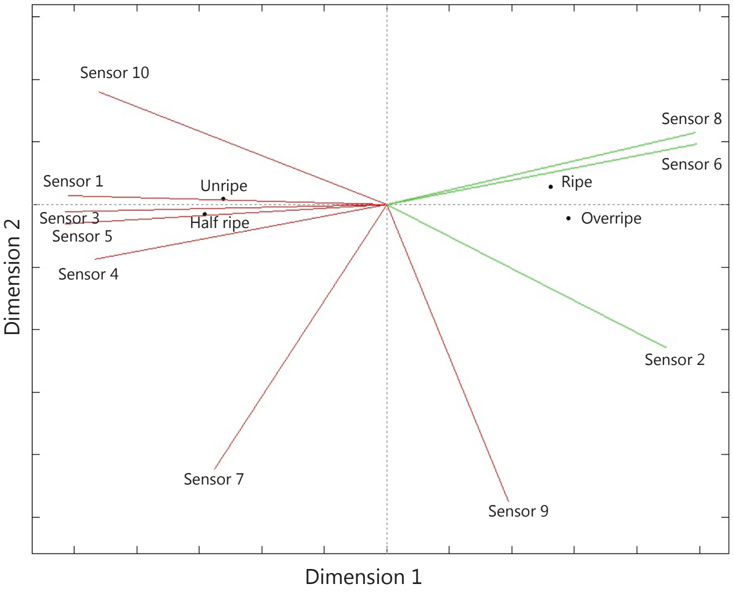

Figure 5. Biplot representation of four electronic nose reading data sets taken from soursop pulp samples at different ripening stages (*Annona muricata* L. cv. Elita) stored at 20 °C and 65% RH.

of organic substances (sensor 6 – W1S), and partially aromatic substances (sensor 8 - W2S), all of which exhibit a strong negative correlation with the group of aromatic compound detecting sensors (sensor 1-W1C and sensor 3-W3C), together with those sensitive to hydrogenated compounds (sensor 4 - W6S) and alkanes and lower polarity aromatic substances (sensor 5 - W5C).

The major contributions on the second dimension are due to the sensors detecting sulfur compounds, terpenes and some organic sulfur substances (sensor 7-W1W); and aromatic and organic sulfur compounds (sensor 9-W2W); none of which has been observed to have a considerable impact on the analysis of volatiles.

From the above, it can be deduced that the early ripening stages (unripe and half ripe) are characterized by elevated aromatic, hydrogenated and lower polarity aromatic compound contents. As aging progresses, these substances decrease, to be replaced by methane and a range of organic and partially aromatic compounds.

Determination of volatiles by HS-SPME/GC-MS. The HS-SPME/GC-MS results of the volatile compound separation analysis applied to soursop pulp samples at four different ripening stages are shown in Table 2. The Kovats Index (KI) was calculated from the application of equation 1, and the relative abundance was found as a function of gas chromatography percentage areas.

Table 2. Volatile compounds found by GC-MS/HS-SPME in soursop pulp (*Annona muricata* L. cv. Elita) at four ripening stages.

No	Compound	KI	Ripening stages[a]/Relative abundance[b]			
			I	II	III	IV
1	Ethyl acetate	<803	+++	+	-	-
2	Methyl butanoate	<803	+	+	+++	++
3	2-Methyl butanoate	<803	-	+++	-	+
4	2-Hydroxypropyl-2-methyl propenoate	<803	-	-	+++	-
5	2-Methyl-4-pentenal	803	++++	+	-	-
6	(*E*)-2-Hexenal	844	+	-	-	-
7	3-Hexenol	854	+++	-	-	-
8	2-Butoxyethanol	908	-	-	-	+
9	2,4-Hexadienal	913	+	-	-	-
10	Butyrolactone	915	-	-	-	+
11	Methyl hexanoate	926	++	++++	++++	++++
12	Methyl hexanoate	927	-	++++	-	-
13	3-Methyl hexanoate	934	++	-	-	-
14	2-Methyl hexanoate	967	+	+++	+++	+++
15	Ethyl hexenoate	1002	-	-	+	+
16	Ethyl hexenoate	1003	-	-	-	+
17	Hexenyl acetate	1009	+	-	-	-
18	Acetate 3-hexenol	1010	-	+	+	-
19	2- Ethyl hexenoate	1047	-	-	+	-
20	1,4-Cycloheptadiene	1048	-	+	-	-
21	Linalool	1050	-	-	+	-
22	Methyl octanoate	1101	-	+	+	-
23	α-Terpinolene	1103	-	+	-	-
24	Nonanal	1106	-	-	-	+
25	Methyl 2-octanoate	1172	-	-	+	+
26	2-(2-Butoxyethanol)	1192	-	-	-	+
27	2-Phenoxyethanol	1249	-	-	-	++
28	2-Oxanone	1640	-	-	-	++

[a] Ripening stages: I-unripe, II-half ripe, III-ripe, IV-overripe
[b] Relative abundance: + : <5%; ++ : 5-10%; +++ : 10-40%; ++++ : 40-70%

The compounds detected through the different studied ripeness stages (pooled data) correspond to esters, aldehydes, alcohols, terpenes and ketones, esters being the most abundant ones and showing an increasing trend along postharvest time, except for the overripe stage. The unripe fruit pulp contained 60% esters, predominantly Ethyl acetate; 30% aldehydes, mostly 2-Methyl-4-pentenal; and 10% alcohols, mainly 3-Hexenol.

The half ripe fruit pulp contained 70% esters (predominantly Ethyl hexenoate, Methyl hexanoate and 2-Methyl butanoate) and 10% aldehydes, alkenes and terpenes (mostly 2-Methyl-4-pentenal, 1,4-Cycloheptadiene and α-Terpinolene).

The highest amount of esters was found in the ripe fruit pulp (90%), mainly corresponding to Methyl hexanoate and 10% Linalool. The overripe fruit pulp showed a general decrease in ester content, which went down to 62%. However, within this group there was an increment in the relative abundance of Methyl hexanoate. In turn, alcohol levels rose to 23%, dominated by 2-phenoxyethanol; whereas aldehyde content (majorly Nonanal) was 8%. Belonging to the group of ketones, a new compound (2-oxanone) appeared at this ripening stage.

The ripe fruit pulp composition coincided with a previous report on other soursop cultivars by MacLeod and Pieris (1981), who found that 80% of the volatiles corresponded to esters, out of which 31% was Methyl hexanoate and 27% was 2-Methyl hexanoate. In turn, Vela *et al.* (2005) reported 58.6% of esters in the volatile composition of fresh soursop fruit, the most representative compounds being Methyl butanoate, (E) 2-Methyl butanoate and Methyl hexanoate.

Besides the mentioned esters, this same fruit has been found to contain Ethyl acetate, 3-methyl hexanoate, 2-methyl octanoate and Linalool (Chong *et al.*, 2011; Lemos *et al.*, 2011). In connection with the volatile compounds which make up the aroma of exotic fruits, Lasekan and Abbas (2012) state that esters and terpenes are the most abundant components in crops like durian (*Durio zibethinus* L.), mangosteen (*Garcinia mangostana* L.), rambutan (*Nephelium lappaceum* L.), langsat (*Lansium domesticum* Corr.) and sapodilla (*Manilkara zapota* van Royer) (Laohakunjit *et al.*, 2007). Ripening determines the emergence of new compounds and changes in the concentrations of the existing ones. This situation can be used as a physiological indicator of the ripening of soursop and other fruits of commercial interest (Sampaio and Nogueira, 2006; Nunes *et al.*, 2008).

At ripeness, the pulp presents alcoholic compounds, mainly butoxyethanol, 2 - (2-butoxyethanol) and 2-phenoxyethanol, probably indicating the beginning of the fermentative stage. This coincides with the EN results, which detected alcohols and a range of aromatic compounds (sensor 8-W2S) in the overripe fruit pulp, facilitating in this way plant material identification through its olfactory trace during postharvest. In general, some esters can serve as precursors, thus participating in the formation of alcohols, which explains the decrease of these compounds at this stage (Villatoro *et al.*, 2008).

For the other ripening stages no relation was found between the compounds detected by the EN and the evaluation of volatile compounds by HS-SPME/GC-MS, which corroborates the statement of Correa *et al.* (2004), who studied the aroma of apple, emphasizing the difficulty to find any correlation between EN and HS-SPME/GC-MS techniques. This sets a contrast with previous research by Lebrun *et al.* (2008), who conducted a study on the volatiles produced during mango fruit ripening and observed high coincidence between the results obtained with both methods.

CONCLUSIONS

The analysis of volatiles by EN allowed classifying the studied soursop fruit groups according to their ripening stages (unripe, half ripe, ripe and overripe), the most active sensors being 2-W5S (sensitive to nitrogen oxides), 6 - W1S (sensitive to methane) and 8 - W2S (sensitive to alcohols and partially aromatic compounds).

The EN data were processed through principal component analysis (PCA) and linear discriminant analysis (LDA), which allowed separating the different stages of maturity for the postharvest period of soursop cv. Elita.

The Biplot representation analysis allowed the visualization of the main changes in volatile components taking place during the ripening process. The unripe and half ripe stages are characterized by elevated levels of aromatic, hydrogenated and lower polarity aromatic compounds. As aging progresses, these substances decrease, to be replaced by methane, partially aromatic compounds and a range of organic products.

Out of the observed volatiles, the major group corresponded to esters, predominantly Methyl hexanoate. Likewise, changes in the relative abundance of volatiles were accompanied by the disappearance of certain compounds and the appearance of some new ones. The current EN assessment detected alcohols and a wide range of aromatic compounds in overripe fruits.

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