Application of Photoacoustic Spectroscopy in Monitoring Emission of C_2H_4 and CO_2 in Passion Fruit Stored under Different Atmospheres

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Abstract

The present work shows the application of the photoacoustic spectrometer in the monitoring of the ethylene emission rate in passion fruit submitted to different types of atmosphere storage. Three types of modified atmosphere were applied: 1) 100% N_2 and 0% O_2 (MA1), 2) 97% N_2 and 3% O_2 (MA2) and 3) 94% N_2 and 6% O_2 (MA3). The respiratory rate and parameters of the skin color as CIE *a*, *b* and angle *hue* were monitored and correlated with the ethylene emission rate. The loss of mass was also evaluated. Results indicated that atmospheres with oxygen concentrations below 3% cause fruit damage, evident as fermentation and presence of fungus in the skin, while 6% oxygen led to a 2 day increased in shelf life.

INTRODUCTION

The passion fruit (*Passiflora edulis*) is one of the main fruits produced and consumed in Brazil. According to IBRAF (2009), the production of these fruit in Brazil was 664,286 tons in 2007. Rich in vitamins, C, B2 and B3, passion fruit is also rich in staple fiber and minerals, such as calcium, iron and phosphous. Its shelf life after-harvest is short due its great loss of mass (Durigan et al., 2004). This justifies the studies in the conservation of this fruit aiming, thus, to prolong its shelf life. One of the alternatives is the use of controlled or modified atmosphere.

In order to evaluate the response of the fruits conditioned under A it is necessary to monitor the ethylene and carbon dioxide emission rates. The ethylene, hormone related to the development of fruits (Abeles et al., 1992), and the carbon dioxide, resultant of fruit respiration, are excellent indicators of the stage of maturation of climactic fruits (Wachowicz and Carvalho, 2002). Some reports have used photoacoustic spectroscopy in the monitoring of ethylene and carbon dioxide emission in tropical fruits (Da Silva et al., 2001, 2003; Corrêa et al., 2005). This technique bases itself on the photoacoustic effect of gases, which consists of light conversion into sound through the incidence of a modulated radiation in a gaseous mixture.

This work has as objective the monitoring of ethylene and carbon dioxide emission rates in passion fruit while being held in different modified atmospheres.

MATERIALS AND METHODS

Fruit Material and Storage Treatments

This work used passion fruit (*P. edulis*) from State Agricultural Antonio Sarlo Technique School, in Campos of the Goytacazes city, RJ, Brazil, located in the geographic coordinates of 21°42'49"S and 41°20'33"W. The fruit at the moment of the harvest presented 90% of green color and 10% of yellow color in the skin and with approximately 65 days after anthesis.

The passion fruit were held in three types of modified atmospheres over 144 h. Each modified atmosphere was generated varying the composition of the oxygen (O_2) and nitrogen (N_2) gases by the use of mass controller. Thirty fruit of yellow passion fruit were used, on a non-destructive form, in the total of the experiment. Three experiments were made, where in each experiment a control group of five passion fruit were exposed

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continuously in a chamber to an atmosphere with flow of 2 L h^{-1} of air and another group of five passion fruit in another chamber to one specific modified atmosphere, also daily. In the first experiment a flow of 2 L h^{-1} of 100% N_2 and 0% O_2 was used as a modified atmosphere (MA1). In the second experiment, a flow of 2 L h^{-1} of 97% N_2 and 3% O_2 was used (MA2). In the third experiment the same flow of 2 L h^{-1} of 94% N_2 and 6% O_2 was used as a modified atmosphere (MA3). The pressure inside the chambers was 1 atm, with a temperature of 25±2°C and 92±4% relative humidity. The modified atmosphere specified is just concerning the initial gas composition.

CO_2 and ethylene emission rates were monitored daily, during 2 hours for each group. Measures of skin color by loss of mass were monitored every two days, removing the fruit of its respective chambers for a period of 30 minutes.

Monitoring of C_2H_4 and CO_2 Emission Rates

The ethylene production by the fruit was determined by using a photoacoustic spectrometer (da Silva et al., 2003; Azevedo et al., 2008), which has a sensitivity of about 0.30 nl L^{-1} for ethylene (Fig. 1). The emitted ethylene was continuously transferred into a photoacoustic cell using air (or modified atmosphere) as pushing gas. The laser light is in amplitude modulated at the resonant frequency of the photoacoustic cell cavity, resulting in amplified acoustic signal, which is detected by a microphone located inside the cavity of the detector. During the measurement, the flow of the gaseous sample was kept constant at a value of approximately 2 L h^{-1}, by an electronic mass flow controller (model 5850S, Brooks Instruments). In order to remove CO_2 and H_2O from the gaseous sample, chemical filters assembled in series were used. First, CO_2 was removed by a potassium hydroxide (KOH) filter and, after that, H_2O molecules were extracted using a calcium chloride ($CaCl_2$) filter. Finally, the rest of water and also small hydrocarbon molecules were condensed in a cryogenic nitrogen trap, avoiding the influence of the rest of those chemical species on the ethylene measurement. The photoacoustic spectrometer was calibrated daily using a standard mixture of 1 ppm of ethylene diluted in synthetic air.

CO_2 emission rates were monitored by a commercial gas analyzer (ABB, model URAS 14) based on infrared absorption (Harren et al., 2000; da Silva et al., 2003). In the experimental set-up, the CO_2 analyzer was built in-line to the photoacoustic spectrometer, being set before the CO_2 filter. This experimental set-up allows simultaneous measurement in real time of the concentration of ethylene and CO_2 emitted by the fruit during the ripening process on a fruit fresh weight basis.

Fruit Skin Color

Fruit skin color change was monitored daily using a portable digital colorimeter (Chroma Meter, model CR-300, Minolta). Measurements were carried out in three equidistant points in the equatorial region of the fruit and the results were expressed by the color or hue angle and the a* and b* parameters of CIELAB measurement. In this scale, a* value varies from green color (negative) to red (positive) and b* from blue (negative) to yellow (positive). When values of a* and b* equal zero, this corresponds to the gray color. The hue angle (h°) defines the basic color, where 0°=red, 90°=yellow, 180°=green and 270°=blue (Coultate, 2004).

Measurement of Mass

In order to normalize the ethylene emission rate with the mass of the fresh substance of the fruit, the mass of each fruit was measured every two days before and after the determination of the ethylene emission rate. A commercial balance, Coleman model JB-1500, was used for this mean. The average value of the two measures was used in the normalization. The loss of mass of the fruit was also monitored throughout the experiment.

RESULTS AND DISCUSSION

Figure 1-1A shows the ethylene emission rate for fruit submitted to MA1 (100%

N_2 and 0% O_2) compared to the control fruits. Figure 1-1B shows the respiratory rate for the same fruit.

The passion fruit submitted to the MA1 presented a very low ethylene emission rate compared with fruit of the control group. While the control group's fruit presented a maximum ethylene emission rate of 1,056.07 µl h^{-1} kg^{-1} after 96 h, the fruit in MA1 presented an emission rate of 0.38 µl h^{-1} kg^{-1}. After 144 h, the fruit in MA were similar in production rates to the control group and presented an increase of ethylene emission. At this time, 3 of the 5 fruit in MA were in senescence stage presenting aspects of fermentation and presence of fungus. It was observed that after 216 h that all the fruit in MA1 were found with aspects of fermentation and presence of fungus on the skin, while none of the fruit from the control group was affected.

The respiratory rate of fruit in MA1 decreased until 144 h (113.41 ml h^{-1} kg^{-1} in time 0 and 61.99 ml h^{-1} kg^{-1} in 144 h). The carbon dioxide emission rate presented a maximum value of 249.87 ml h^{-1} kg^{-1} at 192 h, while the fruit of the control group presented a maximum of 297.21 ml h^{-1} kg^{-1}.

The low ethylene and carbon dioxide emission rate can be explained by the lack of oxygen in the environment, harming, thus, the respiratory metabolism of the fruit resulting in decay and fermentation (Kende, 1993).

Figure 1-2A shows the results of the ethylene emission rate for fruit in MA2 (97% N_2 and 3% O_2), compared with control groups and Figure 1-2B shows the respiratory rate for the same fruit.

The passion fruit in MA2 also showed a low ethylene emission rate compared with control group's fruit. At the same time the fruit of the control group presented two points of high ethylene emission (568.4 µl h^{-1} kg^{-1} in the time of 96 h and 568.41 µl h^{-1} kg^{-1} in 168 h), the fruit in MA2 presented a rate of 104.77 µl of ethylene h^{-1} kg^{-1} in 96 h. After 144 h of experiment, the MA2 fruit had also been under the same conditions of the control group, so that they could suffer the same experimental procedure from the submitted fruit to MA1. At 144 h, just one fruit of the MA2 group presented signs of fungus on the skin. Under the air atmosphere, the fruit previously treated by the MA2 had an increase in the ethylene emission rate from the value of 357.96 µl h^{-1} kg^{-1}. In the end of the experiment (time of 216 h) 4 of the 5 of the fruit treated initially on MA2 had a similar behavior to the fruit treated under the MA2, having presented aspects of fermentation and presence of fungus. However, such aspects were not present in control group's fruit. The respiratory activity for the submitted fruit at MA2 was practically constant between the 24 h and 144 h of measures (90.71 ml h^{-1} kg^{-1} in 144 h). After this period, when the MA2 fruit were in the same atmosphere conditions of the control group, the carbon dioxide emission rate presented a maximum value of 191.01 ml h^{-1} kg^{-1} for the time of 192 h. This behavior indicates that the exposition to the MA with 3% of oxygen was not enough for a well-respiratory fruit standard (Chitarra and Chitarra, 2005).

Figure 1-3A shows the results of the ethylene emission for treated fruit at MA3 (94% N_2 and 6% O_2) compared with control fruit. Figure 1-3B shows the respiratory rate for the same treatment.

The fruit under MA3 had a low ethylene emission compared to the control fruit. However, after being under surrounding air atmosphere for 144 h (the same experiment procedure of submitted fruits to MA1 and MA2), these fruit had an increase on ethylene emission rate, having presented a profile of climactic peak. The fruit under MA3 had a low rise of the ethylene emission rate, having gotten a value of 51.01 µl h^{-1} kg^{-1} to the end of the exposition of the MA3 in the time of 144 h. After these fruit were exposed to surrounding air, the ethylene emission rate presented a peak in 192 h of the 263.31 µl h^{-1} kg^{-1}. This curve represents a behavior of climactic fruit (Abeles et al., 1992), therefore the fruit of this treatment presented good conditions of consumption without indicating fermentation and fungus in the skin. The fruit of the control treatment in this experiment had a maximum ethylene emission rate at 144 h of the 269.81 µl h^{-1} kg^{-1}, what represents a ripeness 48 h earlier than compared with the fruit on MA3. The fruit of the control group had also not presented aspects of fermentation and fungus in the skin in the end of the experiment.

While the fruit of the control group had a practically constant carbon dioxide emission rate from 48 h experiment, the fruit under MA3 had a linear rise to 144 h, and after this period (under surrounding air atmosphere) the respiratory rate continued to go up until 192 h (115.37 ml h^{-1} kg^{-1}). This indicates that the passion fruit had a high tolerance under atmosphere with 6% O_2, therefore they were in good condition of consumption at the end of the experiment.

The color's parameters (a*, b* and the angle hue) had been used for validation of the visual description of the skin color evolution. Figure 2-4, 2-5 and 2-6 show the dependence of these parameters with time on the three modified atmosphere conditions.

It can be observed that the values of the parameters a* and b* for the fruit submitted to MA1 and MA2 had a fast increase in values in 144 h, exactly when the fruit had left the MA conditions and had been stored in air. The values of hue angle for fruit at MA1 and MA2 also presented a similar behavior. They also had a rapid fall of its values after 144 h of experiment. This significant alteration of a*, b* and hue values after 144 h for both experiments represent a fast yellowing of the skin due to the fermentation process and of the appearance of fungus in some fruit after leaving its respective MA.

The results for the fruit submitted to MA3 presented a different behavior of that submitted to MA1 and MA2. After the withdrawal of the fruit under MA3 and put under surrounding air atmosphere, these fruit had not presented no significant alteration in parameters a*, b* and the hue angle. The alterations on fruit skin color parameters treated with MA3 indicate that these fruit had a yellowishness after the control group's fruit. This can be seen since the average of a* and b* of the MA fruit were lower compared with the one of the control group's fruit. The hue angle values for MA fruit were bigger compared with the control fruit (at 216 h° the hue equal 104.24 h° for MA fruit and 98.94 h° to control fruit). The results of the CIELab parameters of skin color presented here are compatible with the physiological description of harvested passion fruit (Vianna-Silva et al., 2010).

Table 1 shows the loss of mass of the fruit of each treatment. The statistical analysis, using Tukey's test with 0.1% level of probability, showed that there was not a significant variation in loss of mass among treated (MA) fruit and control fruits. These results show that the reduction of the respiratory activity did not affect loss of mass of the passion fruit.

The results demonstrate that passion fruit storage with low level of oxygen induced the fruit fermentation. The low oxygen concentration interferes directly in the respiratory process of the fruit, causing physiological damages as the fermentation (Brackman and Chitarra, 1998). The obtained results are in agreement with the expected, that is, the high levels of carbon dioxide and low oxygen levels can provoke stress in the fruit (Chitarra and Chitarra, 2005). It was observed that carbon dioxide concentrations above of 5% can provoke off flavor and odor's alteration in oranges (Peretz et al., 2001). Mango and lemon exposed to the carbon dioxide concentrations above of 10% present losses of physiological qualities, while vegetables as cucumber and mushroom do not support concentrations of carbon dioxide above of 50% (Katrodia, 1988; Leguizamon et al., 2001). However, the use of low oxygen concentration and high carbon dioxide concentration also produce good effect in fruit conservation as apple and tomato (Moretti et al., 1998).

Results with banana (Finger et al., 1995) had shown that the use of the high carbon dioxide concentration and low ethylene, with the use of absorbents, resulted in a good effect in the conservation of the fruit. Of similar form, study involving modified atmosphere with ethylene absorber together with low temperature (12°C) showed significant result in the papaya conservation (Pereira, 2008).

CONCLUSIONS

It can be concluded that the monitoring of the ethylene emission rate, through photoacoustic spectroscopy, allowed real time evaluation of the ripening of passion fruit subjected to low oxygen concentrations at 25°C. Oxygen concentrations below 3%

reduced the respiratory activity of the fruit, and impaired the ripening. However, the use of concentration of 6% of O_2 did not present damages to the passion fruit such as fermentation and fungus in the skin, and showed a delay of two days in the climactic peak compared with the fruit stored in air.

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Tables

Table 1. Data of mass loss for the three conditions experienced are compared with the ones of the group has controlled. The values are express in % mass loss.

	MA1 (100% N_2 and 0% O_2)	MA2 (97% N_2 and 3% O_2)	MA3 (94% N_2 and 6% O_2)
Control group (%)*	4,62±0,39% a	3,31±0,16% a	3,05±0,34% a
Treated group (%)*	4,05±0,57% a	3,54±0,23% a	3,53±0,39% a

Data followed by the same letters in a row do not differ at 0.1% probability by Tukey’s test.

Figures

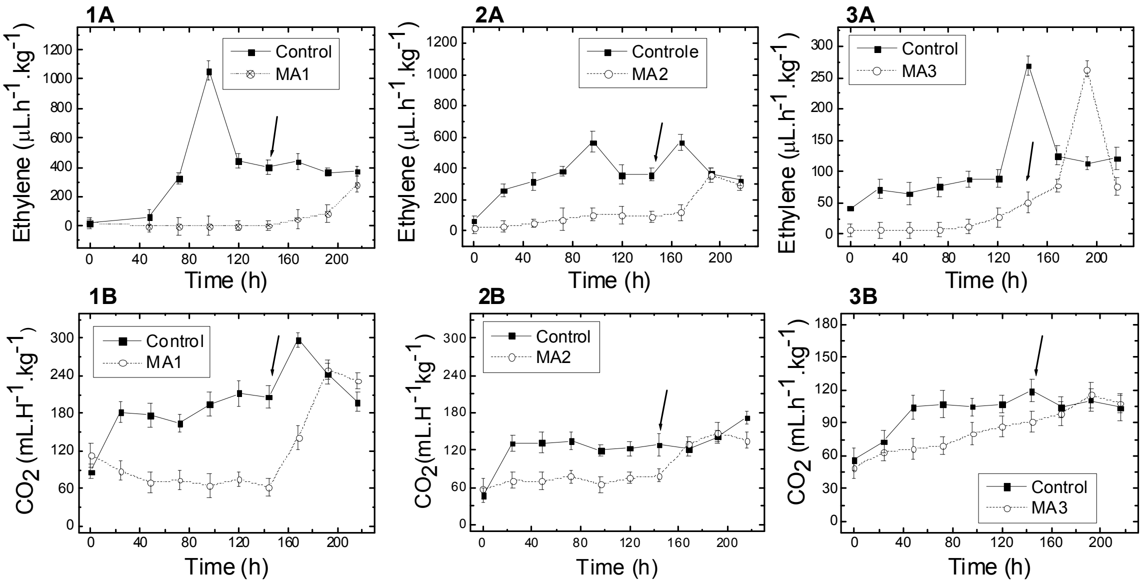

Fig. 1. The graph (1a) shows the ethylene emission and (1b) the respiratory rate for passion fruit held in modified atmosphere [100% N_2 and 0% O_2 (MA1)] and ambient atmosphere [78% N_2 and 21% O_2 (control)] as a function of storage time. The graph (2a) shows the ethylene emission and (2b) the respiratory rate for fruit held in modified atmosphere [97% N_2 and 3% O_2 (MA2)] and the ambient atmosphere (control) in function of the time of storage. The graph (3a) shows the ethylene emission and (3b) the respiratory rate for fruit held modified atmosphere [94% N_2 and 6% O_2 (MA3)] and the ambient atmosphere (control) as a function of storage time. The arrows indicate fruit transfer from modified atmosphere to air and vertical bars indicate the standard error of the average of 5 fruits.

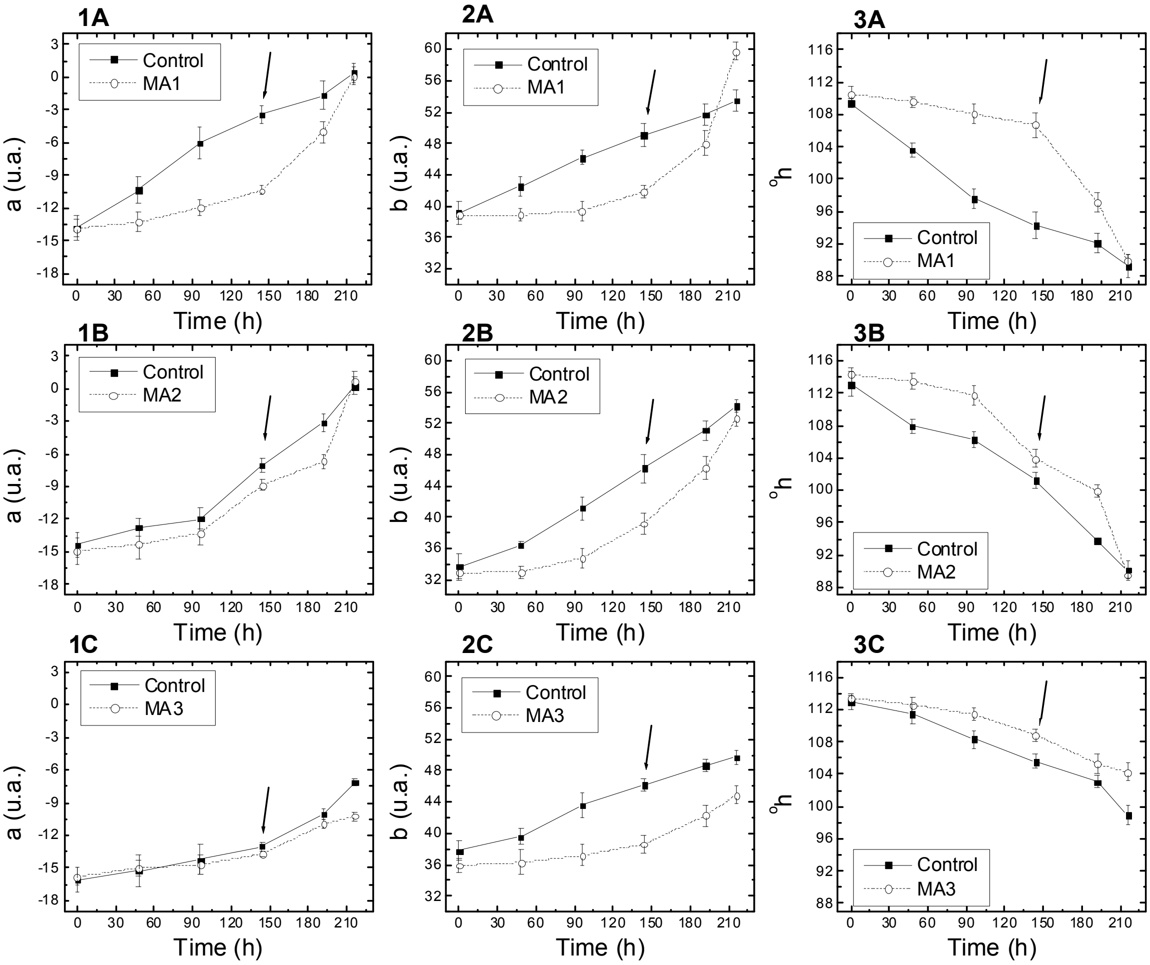

Fig. 2. Changes in color co-ordinates a*, (1) in b* (2), and hue angle (3) of the skin of passion fruit in function of storage period under three modified atmosphere conditions: (A) atmosphere modified with 100% N_2 and 0% O_2 (MA1); (B) atmosphere modified with 97% N_2 and 3% O_2 (MA2); (C) atmosphere modified with 94% N_2 and 6% O_2 (MA3) compared to ambient atmosphere with 78% N_2 and 21% O_2 (control). The arrows indicate fruit transfer from modified atmosphere to air and vertical bars indicate the standard error of the average of 5 fruits.