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To cite this article: G V L Alves et al 2010 J. Phys.: Conf. Ser. 214 012020

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A photoacoustic technique applied to detection of ethylene emissions in edible coated passion fruit

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Abstract. Photoacoustic spectroscopy was applied to study the physiological behavior of passion fruit when coated with edible films. The results have shown a reduction of the ethylene emission rate. Weight loss monitoring has not shown any significant differences between the coated and uncoated passion fruit. On the other hand, slower color changes of coated samples suggest a slowdown of the ripening process in coated passion fruit.

1. Introduction

Photoacoustic spectroscopy has a special advantage to study biological systems: a high detection level in real time. This characteristic allows one to closely follow the changes of biological systems in response to external stimuli like mechanical stress or stress due to changes in the composition of the atmosphere.

It is well known that the composition of the atmosphere in which a fruit is stored can produce favorable results in postharvest applications, such as delaying ripening and controlling some fruit properties. Although the use of controlled and modified atmospheres has been studied for several species of fruits [1,2,3], their application for climacteric fruit is discouraged due to the reduction of the fruit quality [4]. For some fruits, an appropriate combination of high concentration of carbon dioxide (3.0 - 8.0 %) and low concentration of oxygen (1.5 - 3.0 %) reduces the occurrence of physiological disturbance, delaying their senescence. High concentrations of CO₂ reduce the activity of ACC synthase (ACS, 1-amminocyclopropane-1-carboxylate synthase) enzyme, just as low concentrations of O₂ inhibit the activity of ACC oxidase (ACO, 1-amminocyclopropane-1-carboxylate oxidase) enzyme. Both enzymes are very important in the biosynthesis route of the plant hormone ethylene [5]. A reduction of the ethylene action results in an increase of the shelf life for climacteric fruits, creating possibilities for exporting tropical fruits into worldwide markets.

The coating of fruit surfaces, in order to increase the storage time and delay the ripening processes, has been practiced for centuries [6]. The principle of edible coating with polysaccharides involves the interference in the respiratory and ethylene emission processes in fruits. Ethylene is the hormone that promotes the fruit ripening process. Ethylene emission and respiration reduction are determinant factors to retard the fruits’ ripening and delay the senescence process. Polysaccharide edible coatings
prevent, partially or completely, the gaseous exchange, reducing the respiratory rate and increasing the
time it takes to ripen. The permeation selectivity for some gases like O$_2$, CO$_2$, H$_2$O and C$_2$H$_4$, varies
according to the nature of the polysaccharides used for edible coating. Because of this, the gaseous
balance of fruit respiration may be changed according to the selective permeation of each polysaccharide. The respiration changes can result in different rates of ripening in the peel and the
pulp or significant alterations in the consistency or in the flavor and odor of fruits.

One of the advantages of edible coating techniques is the simplicity of necessary equipment for the
coating preparation. Other advantages of these polysaccharides are biodegradability, transparency,
good adhesion to the fruit surface and tastelessness. This work reports the use of chitosan as a coating
film in passion fruit. The emission rate of ethylene, color changes, and mass losses measurements
were carried out in order to study the effects of the edible coating on passion fruit maturation.

2. Material and Methods

Chitosan (medium molecular weight, from Aldrich) was used to coat the passion fruit. The polymeric
films were prepared by immersing the passion fruit in a 1.0 and 1.6 wt% chitosan aqueous solution
with slightly acid pH. After immersion, a polymeric film was formed by drying the surface of the fruit.

The ethylene measurements were carried out using a photoacoustic spectrometer [7]. As an
excitation radiation source for the photoacoustic effect, a CO$_2$ laser was applied. Two CO$_2$ emission
lines (10P12 and 10P14) were used to detect the concentration of ethylene. Ethylene molecules have a
cross section with high absorption for the 10P14, allowing it to be detected at a concentration of some
parts per billion (ppb). A standard mixture of 1 ppm of ethylene in nitrogen [8] was used to calibrate
the photoacoustic detector. The fruit respiration rates (CO$_2$ emissions) were monitored by the use of a
commercial infrared detector (URAS14, ABB), connected to the spectrometer outlet. As a carrier gas,
compressed laboratory air was used to push the emitted gases from the fruits into the photoacoustic
cell at a flow of 2 L/h. The fresh weight of each fruit was measured daily using a precision weight
balance (Gehaka Model BG 1000).

3. Results and discussion

Figure 1 shows the ethylene emission rate for coated and uncoated fruit during ten consecutive days.
Impressive results were found for 1.6 wt% of chitosan in solution, but not for 1.0 wt%, which
presented lower values but not a significant difference from uncoated values. Because of the fact that
passion fruit is a climacteric fruit, an increase of the ethylene emission rate profile is expected. This
feature was observed on the fifth day after harvest with an increase of about 100% in the emission rate
of ethylene. For uncoated fruit, an initial value of about 40 µL h$^{-1}$ Kg$^{-1}$ before the climactic peak and
a peak value of about 130 µL h$^{-1}$ Kg$^{-1}$ were detected. Although a similar behavior was also observed
for the coated fruit, a significant reduction of ethylene emission was measured for 1.6 wt% of
chitosan. This reduction may be related to one of these two hypotheses: either the film works as a
barrier for ethylene diffusion or the film prevents the diffusion of oxygen and CO$_2$ in the gaseous
exchange processes. This second possibility represents an increase in the local concentration of CO$_2$
(originated from respiration) and a decrease of O$_2$ (present in the external environment) in the region
between the film and the fruit. This has the same effect of a modified atmosphere, which could reduce
the action and the biosynthesis of ethylene.
Measurements of the CO₂ emissions in fruit respiration show no significant difference between coated and uncoated fruit. This allows the conclusion that the film is not a barrier against CO₂ diffusion. Weight loss measurements show a similar decrease of weight for both coated and uncoated samples. This means that the film is also not a barrier against water diffusion. Water loss is also a product of respiration.

Visual color changes show a quicker yellowing for uncoated fruits. As yellowing is typically related to the ripening stage of a fruit, the advanced stage is expected when passion fruit is completely yellowed.

Ethylene is an autocatalytic substance. Thus, if the coated film prevents the diffusion of ethylene, a high autocatalytic concentration of ethylene should be present in peel and pulp tissues, promoting an increase of the maturation process. However, instead of this, we observed a slowdown in the ripening of coated fruit. This information allows us to suggest that the low detected concentration of emitted ethylene should be related to a possible reduction of the concentration of oxygen. The reduction of oxygen concentration can inhibit the action of the ACO enzyme, which catalyzes the last step in the biosynthesis of ethylene. Although this concentration is low enough to inhibit the ethylene synthesis, this concentration is not low enough to influence the respiration rate (CO₂ results).

| Days after coating | Uncoated | Chitosan 1 wt% | Chitosan 1.6 wt% |
|-------------------|----------|----------------|-----------------|
| 0                 | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| 4                 | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| 7                 | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| 10                | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |

Figure 1. Ethylene emission as a function of time for uncoated (square symbol) and coated with chitosan 1.0 % wt (circle symbol) and 1.6% wt (triangle symbol) passion fruits.

Figure 2: Scheme of color variation as a function of time for passion fruits uncoated, coated with chitosan 1 wt% and coated with chitosan 1.6 wt%.
4. Acknowledgments
The authors are thankful for the financial support from the Brazilian agencies Capes, CNPq, Finep and Faperj.

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