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Use of passive and active modified atmosphere packaging to prolong the postharvest life of three varieties of apricot (*Prunus armeniaca*, L.)

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Abstract The evolution of the atmospheric composition (O_2 and CO_2 and ethylene) passively produced by three varieties of apricots (Beliana, Rouge de Roussillon and Polonais) stored at $10^\circ C$ under four plastic films of different permeabilities was studied. The results corresponding to respiratory intensity (IR) revealed that, while the IR decreased during the storage period under modified-atmosphere packaging, it increased again with the opening of the bags and the exposure of the fruits to air. The modified atmosphere inside the bags (O_2 and CO_2) and the time necessary to reach equilibrium depended on the IR of the fruits and the permeability of the film. The ethylene concentration decreased from the second day onwards in all the cases studied; this decrease being more pronounced in the films of least permeability due to a combination of its diffusion through the film and the inhibition of its synthesis as the CO_2 concentration increased and O_2 concentration decreased. Partial deviations in the metabolism of the three varieties were detected in the two films of lowest permeability (6060 and 12100 cm^3 of O_2 and $CO_2\text{ m}^{-2}/24\text{ h}^{-1}\text{ atm}^{-1}$ at $25^\circ C$) due to anoxia. The use of the active modified atmosphere, replacing the initial atmosphere of the bags with an atmosphere enriched with CO_2 (20% CO_2 and 80% air), did not modify the gas composition at equilibrium, although it shortened the time necessary for it to be reached. For the Beliana variety a

slight decrease in ethylene concentration was observed inside the bags with an active modified atmosphere in relation to that of the bags with a passive modified atmosphere. The accumulation of ethanol in the tissues was not higher under the active modified atmosphere than under the passive modified atmosphere.

Key words Modified-atmosphere packaging · Post-harvest · Apricot · Ethylene · Ethanol

Introduction

The apricot is a climacteric fruit that displays a pronounced ethylene crisis of very short duration. The time period from commercial ripening to the degradation processes characteristic of senescence ranges between 3 and 5 days, depending on the variety [1]. This aspect forces harvesting of the fruits in a pre-climacteric state, which does not permit their acquisition, during storage and marketing, of the sensory characteristics demanded by the consumer. In order to achieve fruits of suitable quality, they must be harvested at an adequate state of ripeness, and techniques that monitor degradation processes must be used. The use of low temperatures during post-harvesting is an efficient method, but it is not the solution for the preservation of the quality characteristics of apricots during storage and marketing [2, 3]. Therefore, other techniques were tested with the aim of stabilising the ripening process for the longest period possible.

The alteration of the atmosphere around fruits during post-harvesting, decreasing O_2 levels and increasing CO_2 levels, can increase the storage life of different produce [3, 4–6]. Modified-atmosphere packaging involves the use of plastic films, with known permeability to gases, for the packaging of products. The presence of a semi-permeable film causes, inside the package, the formation of an atmosphere resulting from the interaction of the respiration rate of the commodity and the gas permeability of the packaging

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film [6–8]. Inside the bag, and as a consequence of the respiration of the fruit, there is an increase in CO₂ and a decrease in O₂. There is also gas interchange through the film with the external atmosphere, depending on the speed of diffusion through the package [7]. Different atmospheres are achieved according to the film permeability and the respiratory intensity of the fruit, and these affect the physiological activity of the apricots [6, 9, 10].

During the last years, the influence of modified atmospheres on the physiology, biochemistry and quality of a variety of fruits and vegetables has been studied, and there is a wide range of reviews about these works [7, 9, 11–13]. One of the initial physiological effects of a modified atmosphere on fruit metabolism is a decrease in respiratory intensity during the storage period, which involves a decrease in substrate consumption, CO₂ production, O₂ consumption and heat release [7]. In climacteric fruits like apricots, atmospheres rich in CO₂ and low in O₂ inhibit ethylene production [2, 3, 14]. Therefore, the use of modified atmospheres may increase their storage period.

High concentrations of CO₂ have an effect on O₂ consumption rate [7, 15, 16]. They act as antagonists of the ethylene activity [17], preventing autocatalytic ethylene synthesis in some fruits like apple, avocado, pear and fig [18, 19]. In banana, aubergine, cucumber and lettuce, the effect is the opposite [20]. It has been also suggested that CO₂ can have a direct inhibiting effect on the enzymes involved in ethylene synthesis, 1-aminocyclopropane-1-carboxylic acid (ACC) synthase [21] and ACC oxidase [22]. Different studies of apricot tissue have shown that CO₂ concentrations above 80% and O₂ levels above 5% inhibit ethylene metabolism both at the ACC-synthase and ACC-oxidase level [2].

It is worth mentioning that since all kind of species and varieties do not show the same respiratory behaviour, nor the same responses to different concentrations of CO₂ and O₂, it is necessary to establish the correct storage conditions for each [7, 23]. It must be also taken into account that, below a certain O₂ level, a transition from aerobic respiration to anaerobic respiration occurs, together with ethanol production and a significant decline in the sensory quality of the produce [24].

When an internal atmosphere is passively modified by the respiration of a commodity, some days, even weeks, are necessary in order to reach the gas equilibrium concentration. It is assumed that the concentration inside the bag is at equilibrium when the quantity of gas exchanged through the fruit skin is the same as that exchanged through the film. Equilibrium is reached when the gas concentration inside the package stabilises [5, 6, 25, 26]. An active modified atmosphere, obtained by the addition of a certain concentration of gas inside the bag at the moment of fruit packaging, can provide an earlier state of equilibrium and help keep an adequate atmosphere for a longer

period. This contributes to the extension of the shelf life of fruits [6, 25]. Therefore, for some horticultural species with a low IR, which take a long time to reach atmospheric equilibrium when wrapped in modified-atmosphere packaging, the injection of CO₂ at the beginning of the storage period could shorten this period of time.

This work investigated the evolution of the atmospheric composition in passive form (O₂, CO₂ and ethylene) inside packages made with films of different permeability for three apricot varieties (Beliana, Rouge de Rousillon and Polonais) with different respiratory intensities. We also investigated the effect of active modified atmospheres on the internal atmosphere composition at equilibrium. Since certain fruits undergo significant deviations in their metabolism when they are exposed to high concentrations of CO₂, and ethanol may be regarded as the most important volatile caused by anaerobic respiration [10, 27], ethanol accumulation in the tissue under different experimental conditions was also determined.

Materials and methods

Plant material

Beliana, Rouge de Rousillon and Polonais were harvested at their state of commercial ripening, i.e. when they had started to acquire a light coloration characteristic of each variety, but they still preserved in the suture area a light green colour [28].

Packaging material

Danisco Flexible provided the films used in this research. They were micro-perforated films, 30 µm thick. Their specific characteristics were:

1. Film A, 12 micro-pores m⁻²; permeability at 25°C to CO₂ and O₂: 6060 cm³ m⁻² 24 h⁻¹ atm⁻¹.
2. Film B, 24 micro-pores m⁻²; permeability at 25°C to CO₂ and O₂: 12100 cm³ m⁻² 24 h⁻¹ atm⁻¹.
3. Film C, 60 micro-pores m⁻²; permeability at 25°C to CO₂ and O₂: 30000 cm³ m⁻² 24 h⁻¹ atm⁻¹.
4. Film D, 80 micro-pores m⁻²; permeability at 25°C to CO₂ and O₂: 40000 cm³ m⁻² 24 h⁻¹ atm⁻¹.

Sample preparation

Apricots were harvested early in the morning, and sample preparation in the laboratory took place less than 1 h after harvesting. Fruits were chosen according to colour and size in order to obtain homogenous samples. In order to check their ripening state, the ethylene production was determined in three samples of fruits from each variety. Results ranged between 0.97 and 1.75 nl g⁻¹ h⁻¹, confirming that autocatalytic ethylene synthesis had started, and apricots were in their commercial ripening stage with the possibility of evolving to the ripening state at which they are suitable for consumption [1].

Apricots were packed in bags made of plastic film of non-selective permeability with an exchange area of 800 cm²; each bag contained approximately 500 g fruit. They were stored at 10°C. A silicone septum was placed inside the bags in order to take atmospheric samples for analysis. Three bags of each variety were prepared for the different samplings (O₂, CO₂, ethylene inside the bags and ethanol content of tissues).

The determination of the influence of the active modified atmosphere on the equilibrium atmosphere was carried out on Polonais and Beliana varieties. Films C and D were chosen due to their greatest permeability. A mixture of 20% CO₂ and 80% air was obtained with an RDM 280 (Air Liquide). It was injected into the bags at the moment of packaging, replacing the air. Samples were prepared as before, and they were stored at 10 °C for 8 days.

Methods

Respiratory intensity. The IR was analysed with a technique that did not affect the metabolic activity of the fruit [29]. This method involves the placing of a known quantity of plant material inside a hermetically sealed container; in this case, the quantity was Co. 500 g apricot. In order to maintain the initial atmosphere during the measurements, the O₂ consumed as a consequence of fruit respiration was automatically replaced with a known quantity of pure O₂, while the CO₂ released was collected in a 0.1-N NaOH solution. The respiratory intensity was determined in three samples of apricots from each variety, before and after 8 days of storage in films of different permeability at 10 °C.

Analysis of the internal atmosphere of the wrapping: ethylene, O₂ and CO₂. The gas composition inside the bags was measured every day by extracting a gas volume through the silicon septum. The quantification of ethylene was achieved by injecting 1 ml of the atmosphere into a Hewlett-Packard gas chromatograph (model 5890) with a flame ionisation detector and a 3-m stainless-steel column with an inner diameter of one-eighth of an inch containing activated alumina (80/100 mesh). O₂ and CO₂ were quantified by injecting 1 ml of the internal atmosphere into a Shimadzu GL 14 A gas chromatograph with a catarometric detector. The column temperature was 55 °C and the injector and detector temperature 110 °C [2].

Analysis of ethanol in the fruit. The ethanol content was determined at the start and at the end of each experiment from a distillate of 250 ml obtained from a 250-g ground sample of apricot by distillation through a column with water vapour entrainment. Quantification was carried out by injecting 0.1 ml distillate into a Hewlett-Packard gas chromatograph (model 5890), fitted with a flame ionisation detector, and a stainless-steel column packed with activated alumina (80/100 mesh). The temperature of the column was 120 °C and the temperature of the detector and injector was 150 °C [3].

Results and discussion

Influence of the IR and film permeability on the evolution of CO₂ and O₂ inside the wrapping

Table 1 shows the IR of the three varieties of apricot at the beginning of the experiment and after storage for 8 days at 10 °C in packages made of different films.

The results showed that there were differences between the three varieties regarding O₂ consumption. The greatest difference was found between Beliana and Polonais varieties; the former had an IR about 60% greater than the latter at the beginning and at the end of the experiment.

An increase in the IR of the three varieties was observed between the beginning of the experiment and after 8 days under the influence of different modified atmospheres. This was also observed in the controls exposed to air. This increase was the result of the maturation process of the fruit. It showed that the fruits were in a pre-climacteric state and that ethylene levels at the moment of harvesting were sufficient for development of the autocatalytic ethylene synthesis and for the activation of those processes responsible for further ripening [1]. In contrast, there were no differences between controls exposed to air and these apricots after removing the different plastic wrappings. This indicated that the partial inhibition of respiratory activity, due to the high CO₂ concentrations and the low O₂ concentrations, was reversible; after 8 days of storage under a modified atmosphere, apricots quickly recovered to their normal level of IR when they were again exposed to air. However, although the IR was re-established once the normal atmosphere was restored, it has been shown several times that, during storage under modified atmospheres, the IR decreases in fruits like avocado [30] and apple [31], slowing down the rate of substrate consumption. It seems advisable, for apricots, to keep the modified-atmosphere conditions for as long as possible in order to maintain their inhibitory effect on fruit metabolism.

Figures 1, 2 and 3 show the evolution of the internal atmosphere of the bags made with four films of different permeabilities for Beliana, Rouge de Rousillon and Polonais varieties, respectively. Because temperature, fruit weight and exchange area through the film were kept constant, the evolution of the internal atmosphere inside the bag and the time necessary to reach equilibrium were controlled by the permeability of the plastic film and the IR of the fruit.

It was observed that, as the film permeability increased, the CO₂ concentration at equilibrium was lower and the O₂ concentration higher. With the most permeable films (C and D), CO₂ and O₂ values ranged between 6 and 16%, and 11 and 18%, respectively. It was also observed that with the most permeable film (D), there were no significant differences in the O₂

Table 1 Respiratory Intensity (IR) of three varieties of apricot before and after 8 days of storage at 10 °C in films of different permeability (A < B < C < D). Results are means of three bags. MAP Modified-atmosphere packaging

Variety	Day 0	IR (nmol O ₂ kg ⁻¹ h ⁻¹) after 8 days in MAP				
		Control	Film A	Film B	Film C	Film D
Beliana	0.88 ± 0.03	1.19 ± 0.05	1.17 ± 0.04	1.16 ± 0.04	1.18 ± 0.06	1.16 ± 0.05
Rouge de Rousillon	0.78 ± 0.02	1.01 ± 0.03	1.00 ± 0.02	0.99 ± 0.03	1.05 ± 0.04	1.04 ± 0.03
Polonais	0.55 ± 0.01	0.72 ± 0.02	0.75 ± 0.01	0.79 ± 0.02	0.80 ± 0.02	0.79 ± 0.01

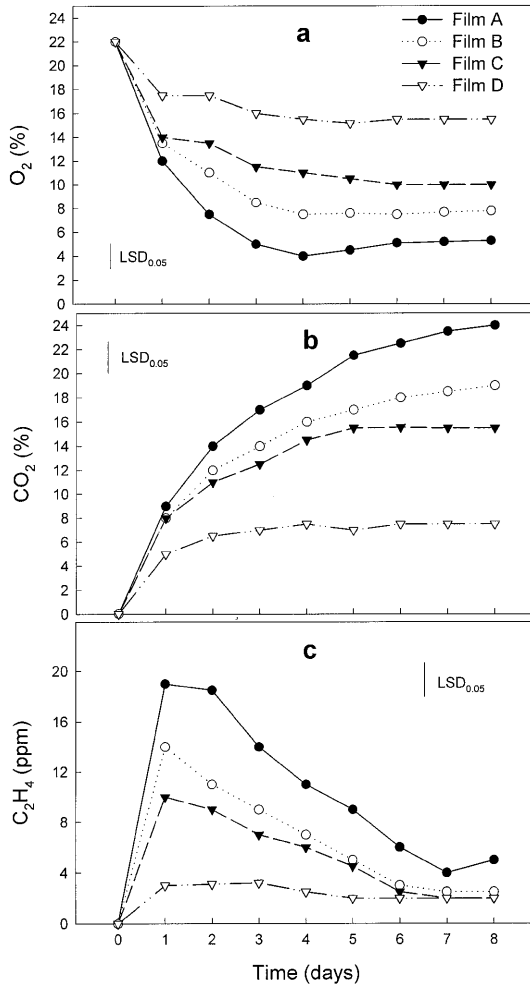


Fig. 1 Internal passive atmosphere: **a** O₂ (%), **b** CO₂ (%) and **c** ethylene (C₂H₄; ppm) inside bags made of films of different degrees of permeability (A<B<C<D) containing apricots cv. Beliana. Storage temperature 10°C. Vertical bars represent least significant difference (LSD) values where $P=0.05\%$

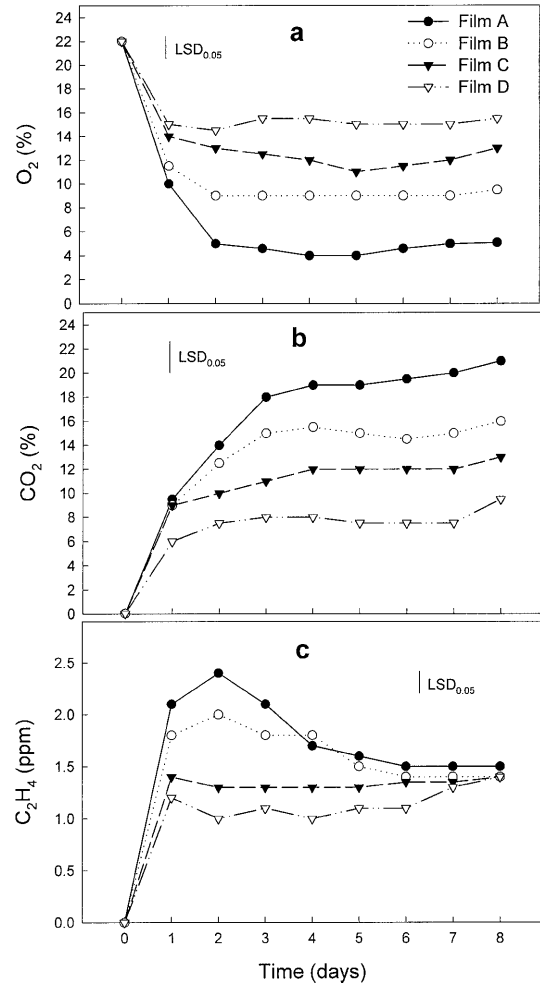


Fig. 2 Internal passive atmosphere: **a** O₂ (%), **b** CO₂ (%) and **c** C₂H₄ (ppm) inside bags made of films of different degrees of permeability (A<B<C<D) containing apricots cv. Rouge de Rousillon. Storage temperature 10°C. Vertical bars represent LSD values where $P=0.05\%$

and CO₂ concentrations at equilibrium between the three varieties. This seemed to indicate that, in these latter cases, the permeability factor was more important than fruit metabolic activity. In contrast, for the other films, the internal atmosphere at equilibrium depended on the variety, because they showed different RIs. In fact, the CO₂ concentration was always higher for Beliana than for Rouge de Rousillon; Polonais always showed the lowest values. For O₂ concentration, the differences were less significant and, therefore, the values were inverted; the maximum was obtained for Polonais, and the minimum for Beliana.

Regarding the time necessary to reach the equilibrium internal atmosphere, there were some differences due to variety and wrapping film. When using the most permeable films (C and D), the CO₂ and O₂ levels become stable from the third or fourth day, regardless of the variety. For the other films (A and B), it seemed that the higher the IR, the sooner the equilib-

rium was reached; for the variety with the lowest IR (Polonais), an atmospheric equilibrium was not attained during the test period.

Influence of the IR and film permeability on the evolution of ethylene inside the wrapping

The evolution of the ethylene concentration produced by the three varieties in the four films tested is shown in Figs. 1c, 2c and 3c. The results showed that the capacity to produce ethylene was different for the three varieties. For all films tested, the values for Beliana were 10 and 50 times higher than those for Rouge de Rousillon and Polonais, respectively, and Rouge de Rousillon produced 5 times more ethylene than Polonais. The concentration of ethylene inside the bags also showed slight differences depending on the film permeability. For Beliana, the levels decreased for the

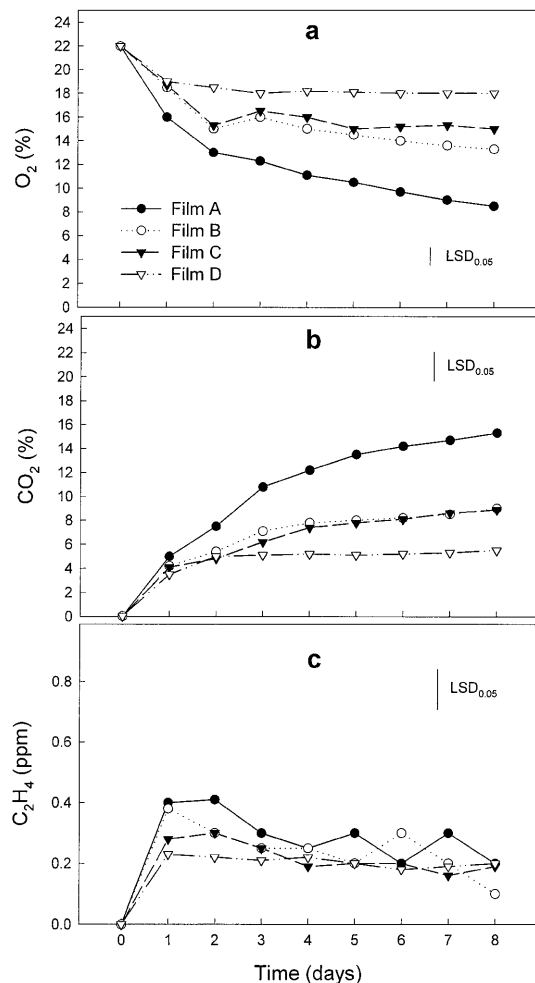


Fig. 3 Internal passive atmosphere: **a** O₂ (%), **b** CO₂ (%) and **c** C₂H₄ (ppm) inside bags made of films of different degrees of permeability (A < B < C < D) containing apricots cv. Polonais. Storage temperature 10 °C. Vertical bars represent LSD values where $P=0.05\%$

four films; the most pronounced decrease was observed for those with lower permeability. For Rouge de Rousillon, this trend was not maintained with the films with the highest permeability (C and D), and ethylene levels remained nearly constant. For Polonais, the fluctuations were not significant. From the second day onwards, for all three varieties, there was an influence of the modified atmosphere on the evolution of the ethylene content inside the bags, with a more or less marked decrease depending on the values for the first day of packaging. Similar results have been found for apricot cv. Búlida [2] and for avocado [6], but the differences between the varieties and the film types were strongly reduced from the fourth day onwards and at the end of the experiment, with values ranging between 1 and 5 ppm for Beliana and Rouge de Rousillon and around 0.2 ppm for Polonais.

The decrease in ethylene emissions could have been due to the effects of O₂ and CO₂ on its biosynthesis, as has been shown for other fruits [7, 32, 33] and for apricot cv. Búlida [2]. On the other hand, the ethylene concentration inside the bags could have been determined by its capacity to pass through the film, since, with the use of plastic micro-perforated films with non-selective permeability, the gas released by fruit will be subjected to exchanges between the fruit-internal microenvironment and between internal microenvironment atmosphere inside the wrapping. In order to verify this possibility, the diffusion kinetics of ethylene through these kinds of film were investigated. For this purpose, bags with the same exchange area (800 cm²) as those used in the tests were made, and fruits were simulated with inert material in order to obtain the same free volume, since the variations in the number of fruits inside the wrapping with the same exchange area affects the atmospheric composition [34]. Two films with different permeability, 12100 cm³ CO₂ and O₂ m⁻² 24 h⁻¹ atm⁻¹ (film B) and 40000 cm³ CO₂ and O₂ m⁻² 24 h⁻¹ atm⁻¹ (film D) were used, and a 10 ppm volume of ethylene was injected into the bags. Figure 4 shows the evolution of the ethylene concentration at 10 °C. These results evidence the diffusion of the gas through both films, with a decrease in the ethylene level by 50% within 9 and 20 h for the films with the highest and the lowest permeabilities, respectively. Concentrations similar to those of the atmosphere in the chamber (0.053 ppm ethylene) were reached after 35 and 80 h. These kinetics seemed to indicate that the ethylene levels inside the wrappings with apricots were regulated more by gas diffusion through the micropores than by the effects of O₂ and CO₂ on the metabolic pathway of ethylene. In fact, the decrease in ethylene observed during the first days of the experiment, especially for the film of the lowest permeability, could have been due to the fact that the ethylene production rate of

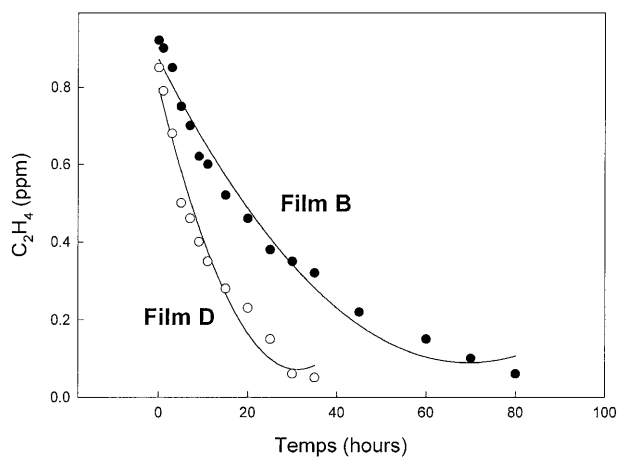


Fig. 4 C₂H₄ evolution inside bags made of films B and D after injecting C₂H₄ (10 ppm) into the bags. Bags contained simulated fruits with inert material

fruit in its pre-climacteric state is not enough to compensate for that lost by diffusion. Moreover, the constant ethylene concentration observed thereafter could have been a consequence of the increase in metabolic activity at the start of the climacteric stage with the increase in ethylene emissions. However, both the evolution of ethylene emissions shown by the apricots wrapped with the film of lowest permeability, and the low ethylene concentrations reached at the end of the experiment (between 0.2 and 5 ppm), lead us to think that, in these varieties and in the equilibrium atmosphere, ethylene was regulated not only by diffusion through the film, but also by the active participation of O₂ and CO₂, as has been shown for the Búlida variety [2, 3].

Influence of the internal atmosphere of the wrappings on the evolution of ethanol in cell tissues

As mentioned before, high concentrations of CO₂ and low ones of O₂, depending on the tolerance of each plant species, bring about some physiological disorders. These leads to fermentative metabolism and, as a consequence, to ethanol formation in fruit tissues [10, 24, 27]. Moreover, in apricots, this situation may become worse due to the possibility of transforming sugars into ethanol, as occurs in grapes when in an atmosphere with a high CO₂ content [35]. Therefore, studying the evolution of the ethanol content in fruit allows the detection of possible deviations from normal metabolism, which are usually associated with off-flavours [27]. To ascertain the maximum capacity for the production of ethanol by apricot under anoxic conditions (0% O₂ and 100% N₂), Beliana was subjected to anoxia for 8 days. It was found that it was capable of producing 7000 µl ethanol kg⁻¹ pulp, which was considered to be a consequence of a total deviation from its normal metabolism.

Table 2 shows the levels of ethanol accumulated in the tissues of the three apricot varieties after 8 days of storage with in each of the tested films. The results showed that only those apricots stored within films with the lowest permeability (A and B) presented metabolic deviations of a relative importance. This

Table 2 Ethanol content in the pulp of apricots after 8 days of storage at 10 °C in films of different permeability. Results are s means of three bags. *TMD* Total metabolic deviation

Film	Ethanol (µl kg ⁻¹ pulp)		
	Beliana	Rouge de Rousillon	Polonais
Control	0	7 ± 0.03	0
TMD	7000 ± 85	–	–
A	1918 ± 21	1015 ± 12	337 ± 35
B	532 ± 6.3	168 ± 12	109 ± 11
C	0	19 ± 2.1	39 ± 4.2
D	0	17 ± 1.2	25 ± 3.5

was especially true for film A, within which Beliana and Rouge de Rousillon accumulated 1918 and 1015 µl ethanol kg⁻¹ pulp, respectively. However, although these concentrations are higher than those causing off-flavours in other fruits, they are lower than those found when apricots are submitted to anoxia, when there is a complete change in metabolism. Significant differences between the three varieties stored in films A and B were observed as a consequence of the different internal atmospheres of the bags at equilibrium, with a direct relationship between ethanol content and both high CO₂ concentrations and low O₂ concentrations, as other authors have already pointed out [3, 10, 19].

According to the equilibrium atmospheres obtained in our experiment, when the CO₂ level is lower than 14% and O₂ level higher than 10%, apricots show an acceptable ethanol level. As observed in other fruits [19, 27] and apricot cv. Búlida [3], these ethanol levels do not affect the organoleptic quality of the fruits. It has been also found that ethanol can inhibit ripening in fruits such as mangoes [36] and apricots cv. Búlida [3]. However, it has also been found that ethanol can have toxic effects on plant cells because of acetaldehyde metabolism [37].

Influence of the active modified atmospheric on the atmosphere composition at equilibrium

In order to study the influence of the active modified atmosphere, the varieties Beliana and Polonais were chosen because they represent the highest and the lowest IR, respectively, and for the same reason, the films with the highest permeability (C and D) were selected. A mixture of 20% CO₂ and 80% air was injected into the bags at the moment of packaging, replacing the initial atmosphere (air). The evolution of the internal atmosphere, recorded in Fig. 5, showed that the injections of CO₂ did not influence the levels of CO₂ and O₂ at equilibrium for either of the two varieties, although an improvement in the time taken to reach equilibrium was observed, as it was established almost from the first day. During the first days of storage, the accumulation of ethylene in the bags containing Beliana was slightly higher with the use of the active modified atmosphere, although there were no significant differences during the last days, of the experiment; a similar result was observed by other authors for mango [6]. In contrast, with the Polonais variety there was no significant deviation in the evolution and concentration of ethylene relative to that found when the initial atmosphere was air, due to the fact that this variety showed a very low production of ethylene. Finally, the production of ethanol was not affected by the treatment, since the values of 63 and 0 µl ethanol kg⁻¹ pulp found for the Beliana and Polonais varieties, respectively, and the values of 91 and 85 µl ethanol kg⁻¹ pulp found for films C and D

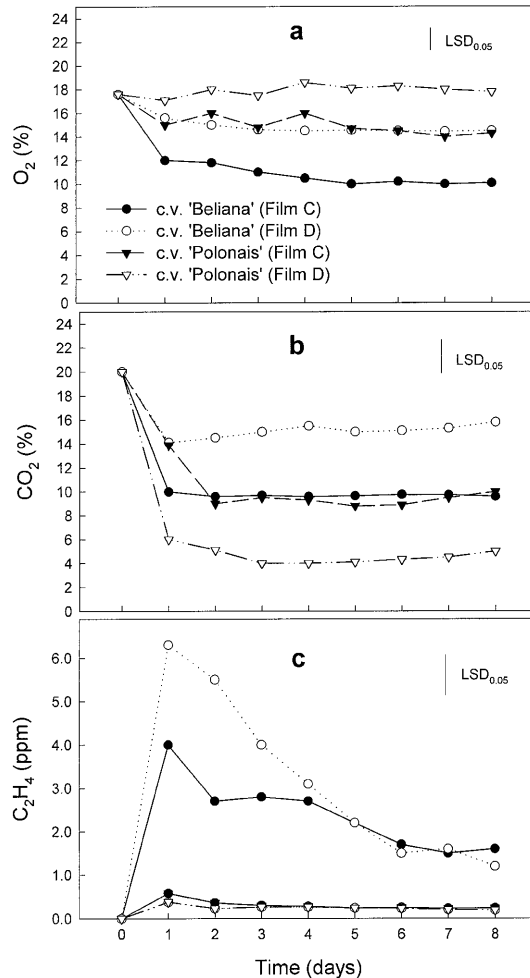


Fig. 5 Internal active atmosphere: **a** O₂ (%), **b** CO₂ (%) and **c** C₂H₄ (ppm) inside bags made of films of different degrees of permeability (A < B < C < D) containing apricots cv. Beliana and cv. Polonais. Initial atmosphere, 20% CO₂ plus 80% air. Storage temperature 10 °C. Vertical bars represent LSD values where $P=0.05\%$

did not seem to indicate any physiological disorder. Therefore, the active modification of the storage atmosphere immediately after packaging could ensure a more desirable atmosphere and thus further prolong the storage life of apricots, as has been already shown for other fruits [6].

Conclusions

It was observed that the IR strongly depended on the variety of apricot and that it was not modified when the fruits were exposed to air after a period of storage under a modified atmosphere. Both apricot variety and film permeability had a great influence on the composition of the internal atmosphere at equilibrium and on the time taken to reach this equilibrium, especially for the most permeable films. Therefore, the establishment of optimal storage conditions for each

species and variety is necessary. Regardless of the ethylene emission capacity of the three varieties under scrutiny, a decrease in ethylene levels when the atmosphere at equilibrium was reached was observed; this was a consequence of the combined action of film permeability and of CO₂ and O₂ concentrations inside the bags. The use of an active modified atmosphere does not change the concentration of gases at equilibrium but it lessens the time necessary to reach this equilibrium.

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