Sorption of carbon dioxide by chickpeas packaged in modified atmospheres

Rey D. Iturralde-García[a], José A. García-Regueiro[b], Cristina Castañé[a], Jordi Riudavets[a],

[a] IRTA, Ctra. Cabrils km 2, E-08348 Cabrils, Barcelona, Spain

[b] IRTA, Finca Camps i Armet, E-17121 Monells, Girona, Spain

Corresponding author:
Jordi Riudavets
IRTA
Ctra. Cabrils km 2
Cabrils, Barcelona, Spain E-08348
Phone: 93 750 75 11 (ext. 1250)
E-mail: jordi.riudavets@irta.cat

Abstract (limit 300 words)

Modified atmospheres (MAs) with high CO_2 concentrations are used for packaging several commodities with different purposes, including as an alternative method for pest control. When used in gas-tight flexible packages, sorption by the commodity produces a vacuum effect that causes the package to adopt a random shape and makes it impossible to reshape it without opening the package. Other than storage problems in retail storehouses, sorption can affect the amount of gas inside the packages needed for pest control. This study reports the amount of CO_2 sorption by chickpeas packaged with different MAs and the negative pressure produced due to the decrease in the partial pressure of the gas. Trials were conducted in 710 mL semi-rigid plastic containers filled up to 24%, 48% and 96% of their capacity (filling ratios). Three MAs (90%, 70% and 50% CO_2 with a residual of 3%, 6% and 10% O_2, respectively, and balanced by N_2) were used during 24 h, 48 h, 240 h and 384 h of exposure at 20°C. The maximum sorption (1.28 g CO_2/kg of chickpea) was obtained with the lower filling ratio (24%) and with an initial concentration of 90%. Sorption decreased with the decline in the initial CO_2 concentration and with the rise in the filling ratio. The time needed to reach the equilibrium sorption varied between 141 h and 27 h, depending on the initial CO_2 concentration and the filling ratio of chickpeas. The vacuum effect produced inside the containers by sorption produced a negative pressure that increased with the increase in the filling ratio and the initial CO_2 concentration. Whether the amount of CO_2 available in packages after gas sorption is still effective for controlling chickpea pests remains to be tested.

Keywords: packaging, legumes, vacuum, equilibrium sorption, pest control

1. Introduction

Chickpea (*Cicer arietinum* L.) is the third most important grown grain legume around the world, after beans and peas. In 2016, there was a worldwide production of 12.1 million tons of chickpea from 12.7 million hectares of harvested areas (FAOSTAT, 2018). Chickpeas are grown in several countries, with the leading exporters being India, Australia and Mexico. After harvesting, chickpea storage can be extended for more than a year due to the seasonal variability in market prices. During this storage period, chickpeas are susceptible to insect attack, particularly by *Callosobruchus maculatus* (Fab.) (Col. Bruchidae). The larvae of *C. maculatus* are internal feeders; the neonate larvae bore holes on the kernels where they develop until the emergence of the adults (CABI, 2018), and they produce qualitative and quantitative losses (weight loss, a decrease in the grain's nutritional value and the failure of seed germination (Ofuya and Reichmuth, 1992). The control of this species is currently based on fumigation with synthetic insecticides, hydrogen phosphide (PH_3) being the most effective and widely used. However, the long storage period of chickpeas results in a high number of PH_3 fumigations, which promotes the development of resistant populations of the weevil. It also poses a threat to the health of operators handling the fumigant, represents a risk to consumers from the accumulation of chemical residues in the grain legume and pollutes the environment (Garry et al., 1989; Chaudry, 1997; Sousa et al., 2009). Therefore, it is important to develop alternative control methods that are effective and environmentally safe.

Modified atmospheres (MAs) with low oxygen (O_2) and high carbon dioxide (CO_2) are one of the alternatives to synthetic chemicals for the control of legume pests, such as *C. maculatus*, *Acanthoscelides obtectus* (Say), *Zabrotes subfasciatus* (Boheman) and *Rhyzopertha dominica* (Fab.) (Donahaye et al., 1996; Navarro, 2006a, b; Riudavets et al., 2009). MAs with 50%–90% CO_2 are effective for the control of *C. maculatus*, *A. obtectus* and *Z. subfasciatus* at exposure times of 3 d, 5 d, 9 d and 2 d for eggs, larvae, pupae and adults, respectively (Wong-Corral et al., 2013; Iturralde-García et al., 2016). Also, the quality of the grain (water absorption, cooking time, texture, colour and flavour) and the vigour of germination are preserved after exposure to CO_2 (Navarro, 2006b; Carvalho et al., 2012; Iturralde-García et al., 2016).

The application of MAs requires the use of gas-tight structures to maintain gas concentrations during the exposure time necessary to achieve the effective control of pests. One problem with the application of this technique when using high-CO_2 MAs with durable food commodities (legumes, cereals, dried fruits, etc.) in flexible packages is the negative pressure caused by CO_2 sorption in the commodity, which gradually decreases the volume of the package. This causes a vacuum effect in the package, which adopts a random shape, and makes it impossible to reshape it without opening the package. Also, the increase of the negative pressure inside the package by sorption eliminates the gas available in the free space of the package, produces a progressive decrease in the gas concentration and, possibly, affects pest control. CO_2 sorption depends on different factors, such as temperature, atmospheric pressure, moisture content, CO_2 initial concentration and the type of commodity (Brunaeur, 1943; Mitsuda et al., 1973; Cofie-Agblor et al., 1995; 1998; Navarro, 1997; Jian et al., 2014). The pattern of CO_2 absorption with different contents of a product within the package (filling ratios) was previously investigated for meat products (Zhao et al., 1995; Jakobsen and Bertelsen, 2004; Rotabakk et al., 2007), but few studies have been conducted on grains (Banks and Annis, 1990; Navarro, 1997).

The present study aimed to measure the sorption of CO_2 by chickpeas and the negative pressure caused by this sorption when they are packaged with different CO_2 MAs and at different filling ratios. Our hypothesis was that sorption by chickpeas and negative pressure inside the package will increase with increasing filling ratios and CO_2 concentrations.

2. Materials and Methods

Chickpeas (cv. Blanco Lechoso) were purchased from Burcol (Guadalajara, Spain) and were all from the same batch. The water activity of the chickpea was 0.600 (Aqualab pre, Labferrer, Cervera, Spain), and the physical properties provided by the supplier were 6.8 % of fat, 57 % of carbohydrates and 23 % of protein.

To assess the sorption of CO_2 by chickpeas, three MAs with different initial CO_2 concentrations were tested: MA1: 90% CO_2, 3% O_2 and 7% N_2; MA2: 70% CO_2, 6% O_2 and 24% N_2; MA3: 50% CO_2, 10% O_2 and 40% N_2. They were previously prepared before starting the experiments using a gas mixer (Witt Km 100-3M/MEM, Witt Gasetechnick, Witten, Germany). The experiments were conducted at room temperature (20 ± 3°C). They consisted of filling a semi-rigid plastic container (710 mL capacity, 500 µm thickness, polyethylene terephthalate [PET]) with 125 g, 250 g or 500 g of chickpeas (bulk density of 0.74 g/cm^3), which occupied filling ratios of 24%, 48% and 96%, respectively. Afterwards, the lid was sealed with hot glue, the desired MA was introduced with a needle in the top of the container and then the gas inlet and outlet holes were sealed with hot glue. The gas concentrations inside the containers were measured with a gas analyser (OXYBABY®, Witt Gasetechnick, Witten, Germany) to verify the CO_2 and O_2 content inside the plastic containers. It was measured at the beginning, without any delay after sealing the container, and at the end of the different periods of exposure tested: 24 h, 48 h, 240 h or 384 h. An aliquot of 6 ml of the headspace gas was collected with a gas analyser using a foam rubber seal (Witt Gasetechnick, Witten, Germany) to avoid the introduction of the exterior atmosphere. A control treatment without chickpeas was also included for each MA concentration, and the exposure time was tested. Ten replicates were done for each combination of initial gas concentration, filling ratio and exposure time.

The gas volume available after introducing the chickpeas was determined by the volume of water displaced when dropping 125 g, 250 g or 500 g of chickpeas into 710 mL water (1.04 g/cm^3 of density) and was calculated as follows:

$$V_{gas} = V_{total} - V_{chickpeas} , \qquad (1)$$

where

V_{gas} = gas volume available in the container (mL);

V_{total} = total volume of the container (mL);

$V_{chickpeas}$ = volume of water displaced after chickpeas were dropped into the water.

2.1. Data Analysis

Assuming the amount of oxygen, nitrogen and water vapour in each container remained constant in each replicate, the volume of CO_2 sorbed at different times was calculated as follows:

$$V_s = (L_{CO2}\, V_{gas}) / 100, \tag{2}$$

where

V_s = volume of CO_2 sorbed by the chickpeas (mL);

L_{CO2} = loss of CO_2 concentration (%) (Initial concentration – final concentration).

Mass (g) of CO_2 sorbed by the chickpeas at different gas volumes, exposure times and initial CO_2 concentrations were calculated using the equation from Jian et al. (2014):

$$S = (\rho_{CO2}\, V_s) / M_{chickpeas}\, , \tag{3}$$

where

S = sorption of CO_2 (g) per tested mass of chickpea (kg);

ρ_{CO2} = CO_2 density of 0.00182952176 g/mL, according to the equation of the density of gases (Chang & College, 2002);

$M_{chickpeas}$ = tested chickpeas mass (kg).

Accumulative CO_2 sorption was fitted to the sorption duration, as proposed by Brunauer (1943):

$$S_C = S_E\, (1- exp\, (-B\Theta^C)), \tag{4}$$

where

S_C = accumulative sorption of CO_2 (g) per mass chickpea (kg);

S_E = equilibrium sorption of CO_2 (g) per mass chickpea (kg);

Θ = sorption duration (h);

B and C = constant.

Equilibrium sorption time (Θ_E), which is the time needed to reach 97% of equilibrium sorption (S_E), was calculated following Jian et al.'s (2014) equation:

$$\Theta_E = - \ln 0.03/B. \quad (5)$$

To evaluate the negative pressure, we first obtained the values of the total mass of CO_2 sorbed in the experiment, calculated as follows:

$$m = S\, M_{chickpeas}, \quad (6)$$

where

m = total mass of CO_2 sorbed in the container (g).

Then, Eq. (5), proposed by Cofie-Agblor et al. (1995), was used to calculate the negative pressure created by the CO_2 sorption:

$$P_f = ((m\, R\, T) / (V_{gas}\, M_{CO2})) - Pi, \quad (7)$$

where

P_f = final pressure (kPa);

R = universal gas constant (8.314472 L kPa/ K mol);

T = temperature (°K);

V_{gas} = gas volume available in the container (L);

M_{CO2} = molar mass of the CO_2 (g/mol);

P_i = initial pressure (Kpa).

Paired t-tests were conducted to compare the percentage of CO_2 sorbed by chickpeas (all pair comparison combinations) for each filling ratio (24, 48 and 96%) at 384 h of exposure. Two-way analyses of variance (ANOVA) followed by a Tukey's multiple range test were used to compare the CO_2 sorption and negative pressure among the different initial CO_2 concentrations and filling ratios for each exposure time. Statistical analyses were done with JMP® 13.1.0 (SAS Institute Inc. 2016). Accumulative sorption was fitted with SigmaPlot curve fitting (SigmaPlot Scientific Graph System, Janel Scientific, 2010).

3. Results

3.1. Analysis of gases

The percentage of CO_2 available in the control treatment showed a maximum reduction of 2% at the end of the test, indicating that the containers were highly gas-tight. The percentages of CO_2 in the containers substantially decreased for all the initial concentrations of CO_2 with all filling ratios, with a greater decrease in the 96% filling ratio (Fig. 1 A-C). As a general pattern, the levels of CO_2 in the sealed plastic containers declined sharply during the first 24 h and continued declining more smoothly until 240 h of exposure, at which time the CO_2 content stopped decreasing and remained at the same level until the last tested exposure period (384 h). The CO_2 treatments were significantly different at the end of the exposure time when comparing the percentage of CO_2 loss in the headspace of containers filled with the same chickpea filling ratio (Table 1), except for the comparison between 70% and 90% with a filling ratio of 24% and the treatments between 50% and 70% with filling ratios of 24% and 48%.

3.2. CO_2 sorption by chickpeas

3.2.1. Volume of CO_2 sorbed (V_s)

The initial gas volume (V_{gas}) available in the 710 mL container with 125 g, 250 g and 500 g of chickpeas (filling ratios of 24%, 48% and 96%, respectively) was 608 ± 0.70 mL, 505 ± 0.98 mL and 300 ± 0.75 mL, respectively. Therefore, true density of chickpeas used was 1.22 g/mL. The volume of CO_2 sorbed after the different exposure times varied with the CO_2 available in the headspace of the containers with the different filling ratios and initial CO_2 concentrations tested (Table 2).

3.2.2. Mass of CO_2 sorbed (S)

Chickpeas sorbed a large quantity of CO_2 that varied according to the initial CO_2 concentration, filling ratio and exposure time. The highest CO_2 sorption (above 50% of the total CO_2 sorption) occurred in the first 24 h of exposure for all the initial CO_2 concentrations and for the different filling ratios tested (Table 3, Fig. 2). The predicted curves of accumulative CO_2 sorption (S_C) from Eq. (4) continued to smoothly increase over time (Fig. 2).

When comparing CO_2 sorption (S) by chickpeas in containers with 24% and 48% filling ratios, significant differences were observed between the initial CO_2 concentrations of 90% and 50% for the all exposure times analysed, with intermediate values for 70% (Fig 2). For the 96% filling ratio, CO_2 sorption was higher in treatments with initial concentrations of 90% and 70% CO_2 compared with 50% during the first 48 h of exposure. Afterwards, no significant differences among all the initial CO_2 concentrations (Fig. 2) were noted.

3.2.3 Equilibrium sorption of CO_2 (S_E)

Sorption gradually stabilised until it reached the equilibrium. For the filling ratios of 24% and 48%, the exposure time to reach equilibrium (Θ_E) tended to decrease as the initial CO_2 concentration increased. However, for the 96% filling ratio, increasing the initial CO_2 concentration increased the exposure time needed to reach the sorption equilibrium (Table 4).

3.3. Negative pressure due to CO_2 sorption (P_f)

Negative pressure depended on the filling ratio and on the initial CO_2 concentration; however, a significant interaction was apparent between both factors at all the exposure times tested (Table 5). Negative pressure due to CO_2 sorption (S) was greater in treatments with a 96% chickpea filling ratio than with 24% at all the initial CO_2 concentrations (50%, 70% and 90%). Similarly, negative pressure was greater in the treatments with 90% than with the 50% CO_2 concentrations at the same filling ratio (Fig. 3).

4. Discussion

Sorption is assumed to be caused by the diffusion of CO_2 into the kernel pores and by the formation of carbamate when reacting with the functional groups of proteins in the kernel. A phenomenon occurs called van der Waals adsorption, in which the CO_2 is quickly absorbed by the carbon atoms on the surface of the grain, forming a layer of CO_2 molecules. This layer attracts more CO_2 molecules, resulting in the accumulation of several layers together at the surface of the grain. Carbamate formation is a weak and reversible interaction (Brunauer, 1943; Yamamoto and Mitsuda, 1980). This interaction is a chemisorption process similar to a reaction between a free radical and a gas molecule, which does not always require activation energies (Hartel and Polanyi, 1930; Eyring, 1931). CO_2 also binds with other molecules of the grain, such as carbohydrates, fatty acids and amino acids, and has a uniform distribution in the kernel (Mitsuda et al., 1973).

The most important decrease in the CO_2 content in the packed chickpeas occurred during the first 24 hours of exposure for all the filling ratios and the initial CO_2 concentrations tested. Afterwards, sorption slowly increased until it reached stability (Fig. 1). Using data from other studies with different commodities and gases (hydrogen, chloropicrin and nitrogen), Brunauer (1943) concluded that gas molecules are sorbed as rapidly as they can reach the surface by van der Waals adsorption followed by a chemisorption reaction.

In this study, CO_2 sorption and negative pressure were influenced by the filling ratios and the initial CO_2 concentrations. In general, the highest CO_2 sorption and negative pressure were obtained at the 90% initial CO_2 concentration. However, the filling ratios differentially affected CO_2 sorption more than negative pressure: the highest CO_2 sorption was obtained at a 24% filling ratio (Fig. 2), and the highest negative pressure occurred at a 96% filling ratio (Fig. 3).

The highest filling ratio was expected to have the highest sorption of CO_2 due to the highest mass of chickpeas. However, our results showed that CO_2 sorption by chickpeas was lower at the 96% filling ratio than at 48%, and both were lower than that at the 24% filling ratio (Fig. 2). This lower sorption observed with the 96% filling ratio was due to the lower amount of gas volume available in the container. At a filling ratio of 48%, the CO_2 volume available was greater, but not enough for the chickpeas to sorb all they could. At a filling ratio of 24%, more gas was available, and the mass of chickpeas was able to sorb more CO_2 than at the other two filling ratios. The sorption of CO_2 was not only affected by the filling ratio of the container but also by the initial CO_2 concentration; a higher sorption of gas with 90% of CO_2 was observed than with the 50% and 70% levels after 384 h of exposure (Fig. 2). This was true for the 24% and 48% filling ratios, while for the 96% filling ratio, no differences could be observed among the initial CO_2 concentrations since the quantity of CO_2 remaining was low. A slightly lower sorption (around 0.33 g of CO_2 at 20°C) was obtained when using wheat at an initial CO_2 concentration of 99.8% in the containers filled up to 93% of their capacity (Navarro, 1997).

CO_2 sorption also depends on temperature, moisture content and type of grain packed. In one study, the CO_2 sorption in canola varied according to temperature from 3 g of CO_2/kg at 10°C to 1.2 g at 30°C and according to moisture content from 2 g of CO_2/kg at 8% to 1.6 g at 14%, with an initial CO_2 concentration of 100% (Jian et al., 2014). Various commodities also absorb CO_2 differently, and oiled seeds absorb more CO_2 than cereals and legumes (Mitsuda et al., 1973). A higher CO_2 sorption was found in 250 g of canola (0.63 g of CO_2/kg of canola) than in cereals (0.38 g of CO_2/kg of wheat and 0.45 g of CO_2/kg of hull-less oats) at a 69% CO_2 initial concentration, 14% moisture content and

20°C (Cofie-Agblor et al., 1998). These different CO_2 sorption amounts, compared with the 0.61 g of CO_2/kg of chickpeas that we obtained at an initial concentration of 70% CO_2 and a filling ratio of 48% (250 g of chickpeas), indicated that chickpeas have a similar CO_2 sorption to canola, and both have a greater CO_2 sorption than cereals.

Equilibrium sorption occurs when the amounts of CO_2 sorbed remain constant over time at a given temperature and pressure. This is specific for the interaction of chickpeas with CO_2 due to the physical structure of the chickpea (the extent of the surface, size, shape and the distribution of pores), its chemical constitution and the physical and chemical properties of the CO_2 (Brunauer, 1943). In our study, the equilibrium sorption was reached at 101 h to 49.5 h at the different filling ratios for a 90% initial CO_2 concentration, which is in agreement with results for wheat, with the equilibrium sorption occurring at 95 h for a filling ratio of 93% (Navarro, 1997). In contrast, the equilibrium time of the sorption occurs quickly at 2 h in oilseeds, such as canola, with 100% CO_2 initial concentration due to the influence of the oil content in the rate and the amount of CO_2 diffusion into the seed (Jian et al., 2014).

Sorption equilibrium time tends to increase with the increasing initial CO_2 concentration at the filling ratio of 96% (Table 4). This is due to the high negative pressures generated by the small amount of CO_2 available in the headspace (Fig. 3). This negative pressure in the package generated a decrease in the multimolecular sorption of CO_2 in the surface of the chickpeas (Mitsuda et al., 1973). Mitsuda et al. (1973) found a negative correlation between the negative pressure and the volume of CO_2 sorbed in brown rice. The same pattern was found in our study; the highest negative pressure (37.3 kPa) was obtained with a filling ratio of 96% of chickpeas at a 90% initial CO_2 concentration. Lower negative pressures were obtained when using wheat: 73 kPa at a filling ratio of 93% at a 100% initial CO_2 concentration (Navarro, 1997). The filling ratio had more influence on the negative pressure than the initial CO_2 concentration (Fig. 3).

In conclusion, and in agreement with our hypothesis, the negative pressure increased with the increasing chickpeas filling ratios and the initial concentrations of CO_2, and the CO_2 sorption increased with the increasing initial concentrations of CO_2. However, the CO_2 sorption by chickpeas did not increase with the increasing filling ratio, which is in disagreement with our hypothesis. This is caused by the lower amount of gas available in the headspace as the filling ratio increases.

This is the first study to evaluate CO_2 sorption by chickpeas when packaged at different filling ratios and to identify the negative pressure produced. Further studies are necessary to test whether the amount of CO_2 that is available in packages after gas sorption occurs at the different filling ratios is required to produce the desired insect mortality. Also, future researchers could determine which conditions can be improved to prevent or reduce the vacuum inside the packages due to CO_2 sorption by the different commodities.

5. Acknowledgements

This work was supported by the Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria projects number RTA2014-00006-C02-01 and RTI2018-095526-R-100 and also by the CERCA Programme (Generalitat de Catalunya). Iturralde-García was supported by Consejo Nacional y Tecnología (CONACYT, Mexico) with a predoctoral grant. We thank the company Air Products for providing the gases with which the experiments were carried out. We are also grateful to the suggestions of three anonymous reviewers, who improved the manuscript.

6. References

Banks, H. J., Annis, P. C., 1990. Comparative advantages of high CO_2 and low O_2 types of controlled atmospheres for grain storage, in *Food Preservation by Modified Atmospheres*, Calderon, M., Barkai-Golan, R., Ed., CRC press, Boca Raton, 93-122.

Brunaeur. S., 1943. The adsorption of gases and vapours-physical adsorption. Princeton University Press, Princeton.

CABI, 2018. *Callosobruchus maculatus*. In: Invasive Species Compendium. Wallingford, UK: CAB International. www.cabi.org/isc.

Carvalho, M. O., Pires, I., Barbosa, A., Barros, G., Riudavets, J., Camara-García, A., Brites, C., Navarro, S., 2012. The use of modified atmosphere to control *Sitophilus zeamais* and *Sitophilus oryzae* on stored rice in Portugal. J. Stored Prod. Res. 50, 49-56. https://doi.org/10.1016/j.jspr.2012.05.001.

Chang, R., College, W., Química, 2002, McGraw-Hill; México.

Chaudhry, M.Q., 1997. A review of the mechanisms involved in the action of phosphine as an insecticide and phosphine resistance in stored-product insects. Pesicide Science 49: 213-228.

Cofie-Agblor, R., Muir, W. E., Sinicio, R., Cenkowski, S., Jayas, D. S., 1995. Characteristics of carbon dioxide sorption by stored wheat. J. Stored Prod. Res. 31, 317-324. https://doi.org/10.1016/0022-474X(95)00022-Y.

Cofie-Agblor, R., Muir, W. E., Jayas, D. S., White, N. D. G., 1998. Carbon dioxide sorption by grains and canola at two CO_2 concentrations. J. Stored Prod. Res. 34, 159-170. https://doi.org/10.1016/S0022-474X(97)00045-3.

Donahaye, E. J., Navarro, S., Rindner, M., Azrieli, A., 1996. The combined influence of temperature and modified atmospheres on *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). J. Stored Prod. Res. 32, 225–232. https://doi.org/10.1016/S0022-474X(96)00018-5.

Eyring, H., 1931. The energy of activation for bimolecular reactions involving hydrogen and the halogens, according to the quantum mechanics. J. Am. Chem. Soc., 53, 2537.

Food and Agriculture Organization of the United Nations Statistics Division (FAOSTAT), 2018. Available at: http://faostat.fao.org/site/567/Desktop (Default.aspx).

Garry, V., Griffith, J., Danzi, T., Nelson, R., Whorton, T., Krueger, L. Y Cervenka, J., 1989. Human genotoxicity: Pesticide applicators and phosphine. Science, Vol. 246:251-255.

Hartel, H. v., Polanyi M., 1930. Atomreaktionen die mit Tragheit behaftet sind. Z. phys. Chem, Abteilung B, B11, 97.

Iturralde-García. R. D., Borboa-Flores, J., Cinco-Moroyoqui, F. J., Riudavets, J., Del Toro-Sánchez, C. L, Rueda-Puente, E. O., Martínez-Cruz, O., Wong-Corral, F. J., 2016.

Effect of controlled atmospheres on the insect *Callosobruchus maculatus* Fab. in stored chickpea. J. Stored Prod. Res. 69, 78-85. https://doi.org/10.1016/j.jspr.2016.06.004.

Jakobsen, M., Bertelsen, G., 2004. Predicting the amount of carbon dioxide absorbed in meat. Meat Science, 68(4), 603–610.

Jian, F., Jayas, D. S., White, N. D. G., Fields, P. G., 2014. Carbon dioxide sorption by stored canola under different storage conditions. J. Stored Prod. Res. 59, 101-107. https://doi.org/10.1016/j.jspr.2014.05.009.

Mitsuda, H., Kawai, F., Kuga, M., Yamamoto, A., 1973. Mechanisms of carbon dioxide gas adsorption by grains and its application to skin-packaging. J. Nutr. Sci. Vitaminol. 19, 71-83.

Navarro, S., 1997. Sorption of carbon dioxide by wheat. In: Donahaye, E. J., Navarro, S., Varnava, A. (Eds.), Proceedings of the International Conference on Controlled Atmosphere and Fumigation in Stored Products, 21-26 April 1996. Printco Ltd., Nicosia, Cyprus, pp. 193-202.

Navarro, S., 2006a. Modified Atmosphere for the Control of Stored Products Insects and Mites. In: Heaps. J. W. (Ed.), Insect Management for Food Storage and Processing. AACC International. St. Paul, Minnesota, USA, pp. 105-145.

Navarro, S., 2006b. New global challenges to the use of gaseous treatments in stored products. In: Lorini, I., Bacaltchuk, B., Beckel, H., Deckers, D., Sundfeld, E., dos Santos, J. P., Biagi, J. D., Celaro, J. C., Faroni, L. R. D.'A., de Bartolinide, L. O. F., Sartori, M. R., Elias, M. C., Guedes, R. N. C., De-Fonseca, R. G., Scussel, V. M.

(Eds.), Proceedings of the 9th International Working Conference on Stored Product Protection. 15–18 October 2006, Campinas, Sa˜o Paulo, Brazil. ABRAPOS, Rodovia, Brazil, pp. 495–509.

Ofuya, T. I., Reichmuth, C., 1992. Mortality of the cowpea bruchid, *Callosobruchus maculatus* (Fabricius) in a highly elevated carbon dioxide atmosphere. In: Proceedings of the First European Conference on Grain Legumes, Angers, France, pp. 365-366.

Riudavets, J., Castañé, C., Alomar, O., Pons, M. J., Gabarra, R., 2009. Modified atmosphere packaging (MAP) as an alternative measure for controlling ten pest that attack processed food products. J. Stored Prod. Res. 45, 91-96. https://doi.org/10.1016/j.jspr.2008.10.001.

Rotabakk, B. T., Lekang O. I., Sivertsvik, M. 2007. Volumetric method to determine carbon dioxide solubility and absorption rate in foods packaged in flexible or semi rigid package. J. Food Eng. 82, 43-50. 10.1016/j.jfoodeng.2007.01.013

Sousa, A., Faroni, L. A., Pimentel, M., Guedes, R., 2009. Developmental and Population Growth Rates of Phosphine-Resistant and Susceptible Populations of Stored Products Insect Pest. J. Stored Prod. Res. 45, 241-246. 10.1016/j.jspr.2009.04.003.

Wong-Corral, F. J., Castañé, C., Riudaviets, J., 2013. Lethal effects of CO_2-modified atmospheres for the control of three Bruchidae species. J. Stored Prod. Res. 55, 62-67. https://doi.org/10.1016/j.jspr.2013.08.005.

Yamamoto, A., Mitsuda, H., 1980. Characteristics of Carbon Dioxide Gas Adsorption by Grain and its Components, in *Controlled Atmosphere Storage of Grains*, Shejbal, J., Ed., Elsevier, Amsterdan, 247–258. https://doi.org/10.1016/B978-0-444-41939-2.50028-0.

Zhao, Y.Y., Wells, J. H., Mcmillin, K. W., 1995. Dynamic changes of headspace gases in CO2 andN2 packaged fresh beef. J. Food Sci. 60 (3), 571-591. 10.1111/j.1365-2621.1995.tb09829.x

Table 1. Paired t-test comparing percentage of CO_2 loss in the headspace of containers filled with different initial CO_2 concentrations after 384 h exposure and for each chickpea filling ratio tested

Filling ratio (%)	Between 50% and 70% initial CO_2		Between 50% and 90% initial CO_2		Between 70% and 90% initial CO_2	
	t	*P*	t	*P*	t	*P*
24	17.2	0.051	2.5	< 0.05	1.4	0.195
48	1.3	0.213	4.3	< 0.001	6.1	< 0.001
96	11.3	< 0.001	17.2	< 0.001	10.1	< 0.001

Degrees of freedom (d.f.) = 1.19

Table 2. Mean volume (± standard deviation) of CO_2 available for 125 g, 250 g and 500 g of chickpeas (filling ratios of 24%, 48% and 96%, respectively) when at a 50, 70 and 90% initial CO_2 concentrations and at different exposure times (h)

Initial CO_2 concentration (%)	Filling ratio (%)	V_s (mL)				
		0 h	24 h	48 h	240 h	384 h
50	24	608	581(9.1)	576 (11.7)	555 (6.3)	558 (10.7)
	48	505	455 (5.6)	465 (9.1)	432 (16.9)	435 (31.1)
	96	300	233 (8.9)	242 (7.3)	225 (4.4)	227 (4.2)
70	24	608	563 (10.7)	569 (10.8)	538 (15.5)	546 (13.7)
	48	505	442 (7.6)	450 (25.5)	417 (11.4)	422 (8.1)
	96	300	210 (5.0)	218 (2.0)	198 (10.0)	203 (5.5)
90	24	608	501 (17.8)	552 (12.9)	524 (16.9)	532 (27.7)
	48	505	421 (10.8)	433 (21.3)	395 (24.8)	391 (14.4)
	96	300	193 (8.3)	187 (11.2)	176 (15.4)	164 (10.6)

Table 3. Factorial tests among CO_2 sorption (*S*) of chickpeas at different chickpea filling ratios and initial CO_2 concentrations

	Statistical parameter	Time of exposure to CO_2 (h)			
		24	48	240	384
	F	40.6	33.3	38.9	30.7
Initial CO_2 concentration (%)	*P*	< 0.001	< 0.001	< 0.001	< 0.001
	df	2	2	2	2
	F	47.7	42.9	137.6	76.0
Filling ratios (%)	*P*	< 0.001	< 0.001	< 0.001	< 0.001
	df	2	2	2	2
	F	3.8	1.4	3.4	1.2
Initial CO_2 concentration × filling ratios	*P*	< 0.01	0.25	< 0.05	0.33
	df	4	4	4	4

The degrees of freedom (d.f.) of the replicates for the factors and their interaction were 89.

Table 4. Equilibrium sorption (S_E) (± standard deviation) and time (Θ_E) under different chickpea filling ratios and initial CO_2 concentrations

Filling ratio (%)	Nominal initial CO_2 (%)	R^2	S_E (g/kg)	Θ_E (h)
24	50	0.98	0.71 (0.061)	141.4
	70	0.91	0.83 (0.159)	98.2
	90	0.96	1.16 (0.145)	101.1
48	50	0.89	0.49 (0.104)	118.5
	70	0.92	0.57 (0.104)	88.8
	90	0.92	0.78 (0.144)	85.7
96	50	0.96	0.25 (0.033)	26.9
	70	0.97	0.33 (0.038)	29.6
	90	0.98	0.47 (0.039)	49.5

The R^2 value for the regression Eq. (4).

Table 5. Factorial test among negative pressure of chickpeas at different chickpea filling ratios and initial CO_2 concentrations

	Statistical parameter	Time of exposure to CO_2 (h)			
		24	48	240	384
Initial CO_2 concentration (%)	*F*	110.7	82.3	70.0	106.1
	P	< 0.001	< 0.001	< 0.001	< 0.001
	df	2	2	2	2
Filling ratios (%)	*F*	861.5	436.8	370.6	415.7
	P	< 0.001	< 0.001	< 0.001	< 0.001
	df	2	2	2	2
initial CO_2 concentration × filling ratios	*F*	13.5	17.1	8.4	16.6
	P	< 0.001	< 0.001	< 0.001	< 0.001
	df	4	4	4	4

The degrees freedom (d.f.) of the replicates for the factors and their interaction were 89.

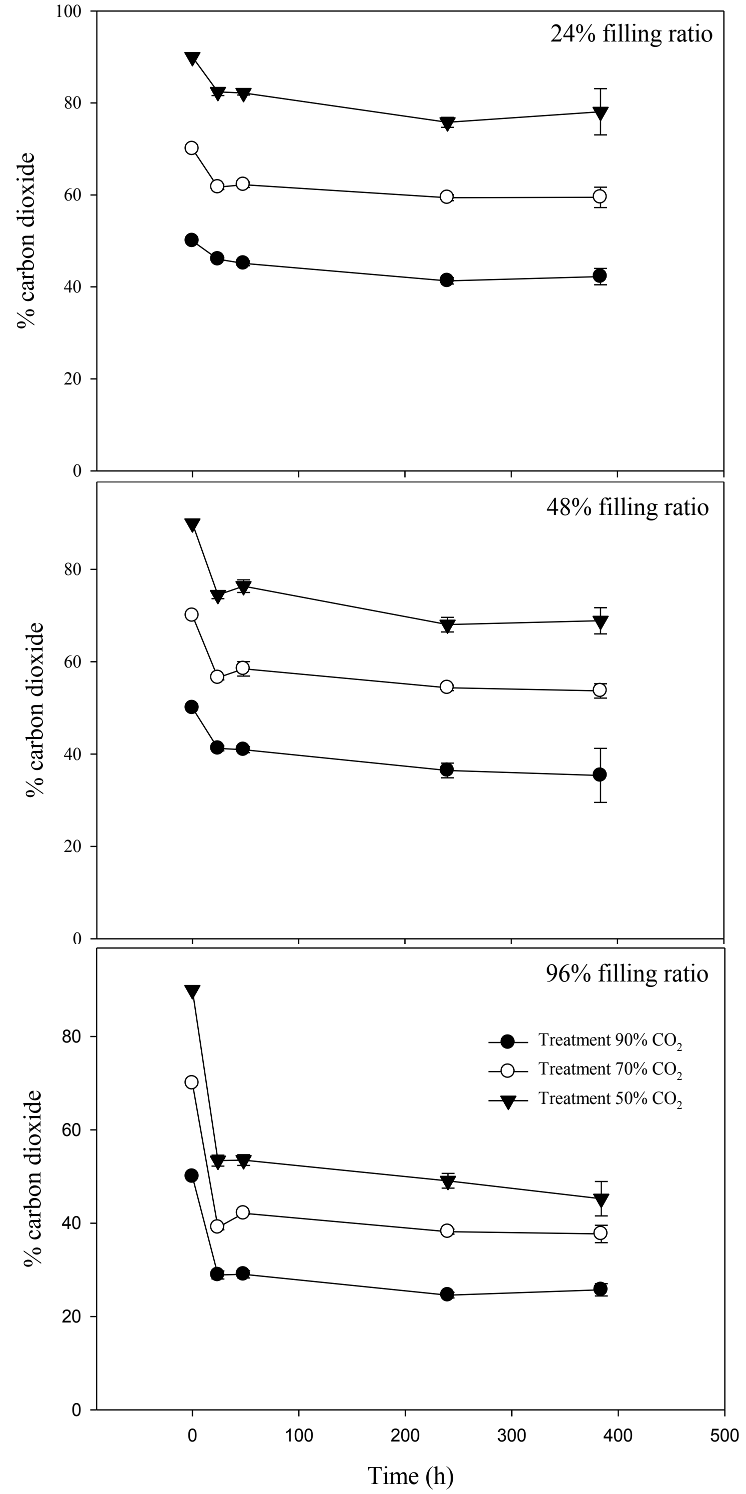

Fig. 1. Changes in carbon dioxide content (means ± standard error) within the sealed plastic containers during exposure to three different modified atmospheres (MA1: 90% CO_2; MA2: 70% CO_2; MA3: 50% CO_2) with different filling ratios of chickpeas at 24 h, 48 h, 240 h and 384 h of exposure time,

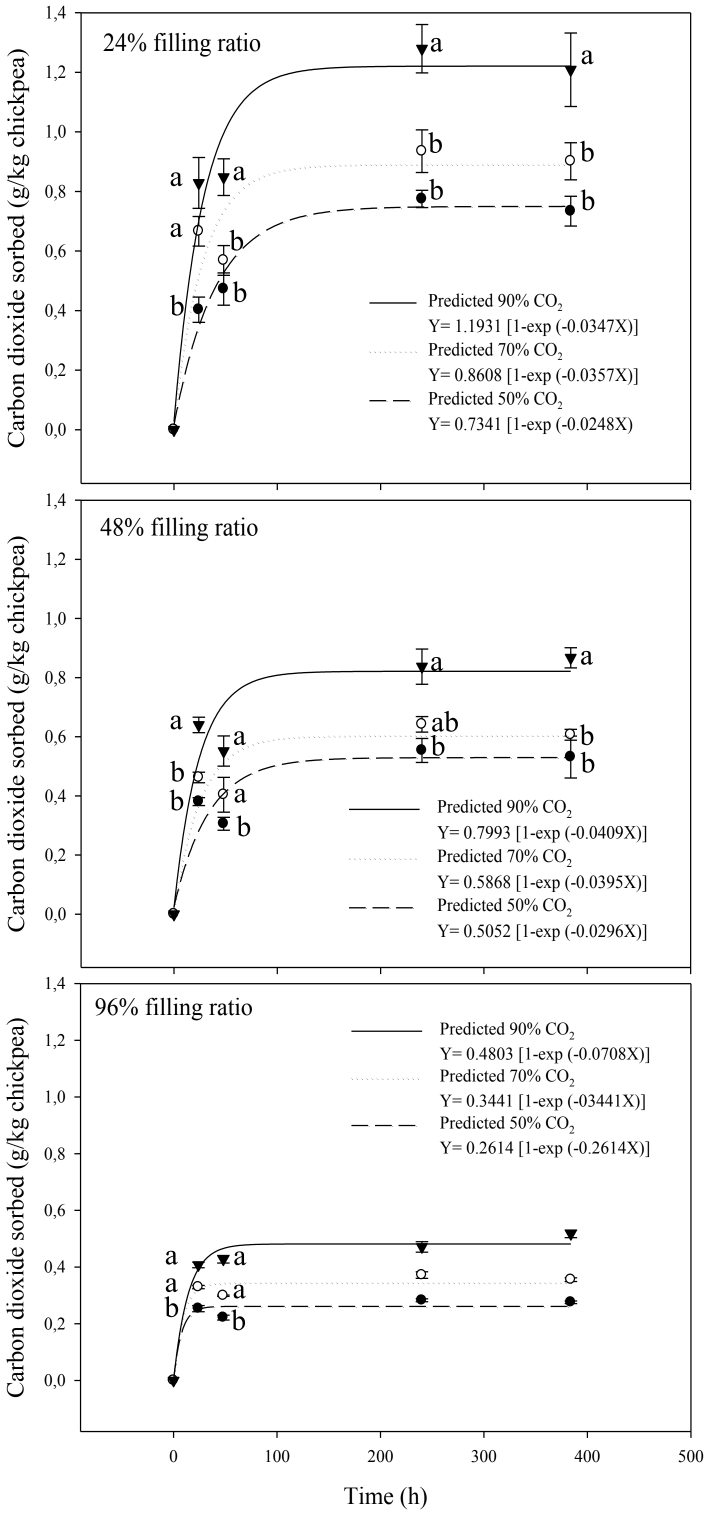

Fig. 2. Carbon dioxide sorption (S) (means ± standard error) at different chickpea filling ratios in 90%, 70% and 50% initial CO_2 concentrations with predicted curves of the amount sorbed (Sc) from Eq. (2). When significant differences were found, means followed by different letters between the initial CO_2 concentrations for each exposure time are shown (P > 0.05, Tukey range test).

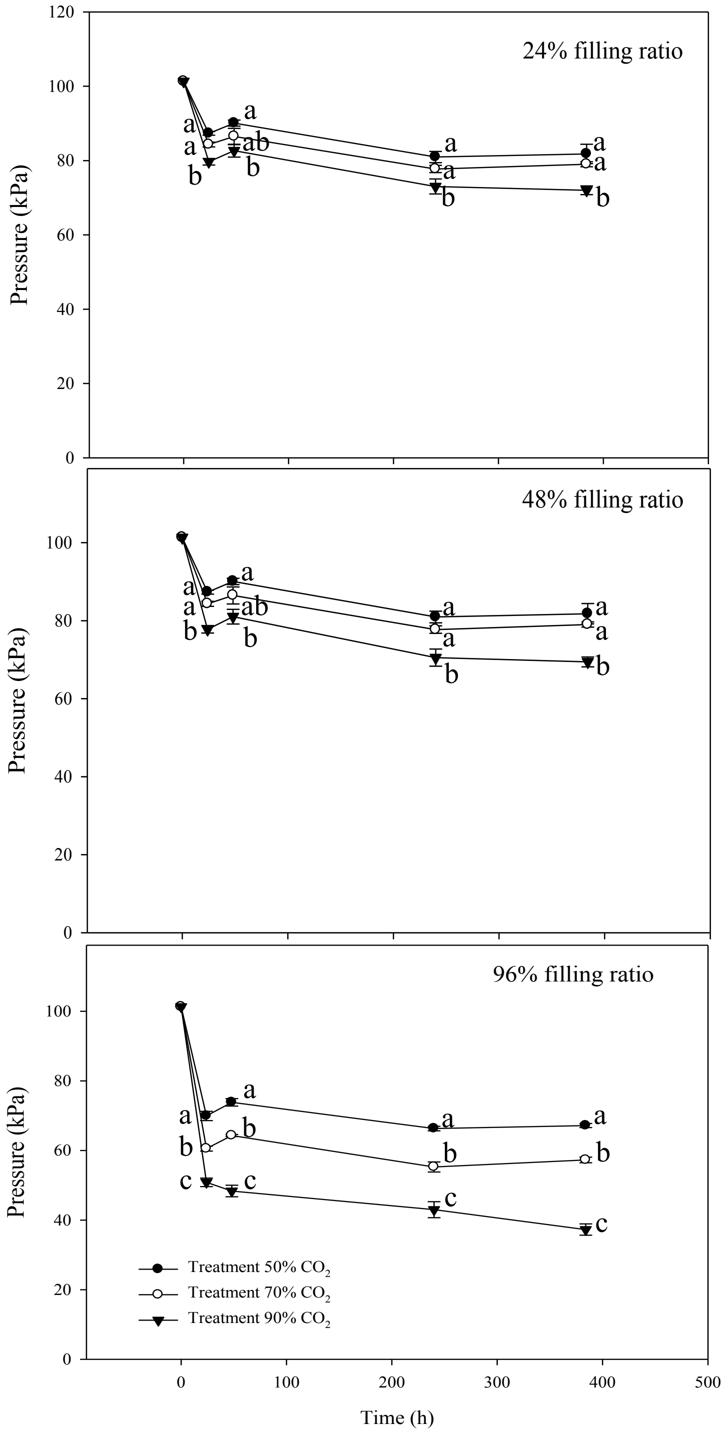

Fig. 3. Negative pressure (means ± standard error) caused by CO_2 sorption at different chickpea filling ratios and different initial CO_2 concentrations. When significant differences were found, means followed by different letters between the initial CO_2 concentrations for each exposure time are shown ($P > 0.05$, Tukey range test).