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Piyush Kumar Jha, Nicolas Chapleau, Pierre-Emmanuel Meyers, Didier Pathier, Alain Le-Bail. Can cryogenic freezing preserve the quality of fruit matrices during long-term storage compared to the mechanical method?. *Applied Food Research*, 2024, 4 (1), pp.100374. 10.1016/j.afres.2023.100374 . hal-04494244

HAL Id: hal-04494244

<https://hal.science/hal-04494244>

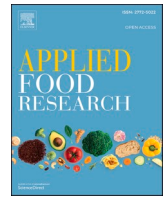
Submitted on 28 May 2024

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Can cryogenic freezing preserve the quality of fruit matrices during long-term storage compared to the mechanical method?

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ARTICLE INFO

Keywords:

Cryogenics
Freezing rate
Storage duration
Physicochemical analysis

ABSTRACT

This study compares cryogenic freezing ($-80\text{ }^{\circ}\text{C}$ and 0.5 m/s air velocity) and mechanical freezing ($-40\text{ }^{\circ}\text{C}$ and 4 m/s air velocity) conditions/methods on the quality of melon and apple tissues during a 90-day storage. Samples were analysed on the 7th, 30th, 60th, and 90th day for various qualities: pH, TSS, titratable acidity, total quality index, enzymology, vitamin C, firmness, colour, exudate, soluble protein, and microstructure. Results show pH, °Brix, titratable acidity, and total quality index changes after freezing. Trends differed between melon and apple. Melon pH increased after freezing, while apple pH decreased. Titratable acidity decreased post-freezing for both. °Brix in melon initially decreased but increased in apples with longer storage. Freezing conditions and storage durations affected total quality index. Melon firmness increased, while apple firmness decreased compared to fresh samples post-freezing. Freezing condition did not affect firmness, but storage duration impacted it. Colour was influenced by both freezing treatment and methods, as well as the duration of frozen storage for melons. The L^* value decreased for both matrices following freezing treatment. The a^* and b^* values of apples increased after post-freezing treatment compared to fresh. The a^* value of fresh and cryogenically frozen melons was similar. Colour differences were more pronounced for mechanically frozen samples, increasing during storage for apples, while a fluctuating trend was observed for melons. Apple samples exhibited a reduction in polyphenol oxidase (PPO) activity post-freezing, while peroxidase activity (POD) displayed some increase in melons. PPO activity was lower for cryogenic freezing, decreasing with storage, while POD activity was storage-duration impacted. Exudation was lower in cryogenic freezing for both matrices. Soluble protein content was higher in cryogenic frozen samples, though fluctuating. Cryogenic freezing slightly reduced pore sizes in apples, preserving microstructure better, unlike mechanical freezing which damaged cellular structure.

1. Introduction

Fruits are a vital component of the human diet, offering both nutrition and promoting health benefits. They supply calories through natural sugars, contain phytochemicals that enhance immune function, prevent cancer, safeguard brain health, and support heart health (Surampudi, 2023). Additionally, their fibre content aids in regularizing bowel movements and health, reducing cholesterol levels, managing blood sugar, and aiding in weight management (Mayo Clinic, 2022). Furthermore, fruits provide essential micronutrients that play a crucial role in metabolism and maintaining tissue function (Shenkin, 2006). The World Health Organization (WHO) has recommended a daily consumption of 400 g of fruits and vegetables, excluding starchy roots,

which is equivalent to five portions. This recommendation aims to reduce the risk of Non-Communicable Diseases (NCDs) such as diabetes, heart disease, stroke, and cancer, while also ensuring the necessary daily intake of dietary fibre (World Health Organization, 2020). Fruits are highly nutritious, but they are also highly perishable, resulting in a shorter shelf life. Moreover, since fruits are seasonal, ensuring their availability year-round, necessitates a certain degree of preservation. Various methods of preservation, including cold temperature preservation, modified atmospheric packaging, drying, and canning are widely used to extend the shelf life of fruits (Jha, Xanthakis, Chevallier, Jury, & Le-Bail, 2019).

Freezing is a cold preservation method that enables long-term storage of food products while preserving nutrients and sensory attributes

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<https://doi.org/10.1016/j.afres.2023.100374>

Received 29 September 2023; Received in revised form 4 December 2023; Accepted 5 December 2023

Available online 6 December 2023

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better than many other methods (Barbosa-Cánovas, Altunakar, & Mejía-Lorío, 2005). It reduces the water activity of the product, leading to decreased enzymatic reactions, reduced microbial activity, and delayed cellular metabolic reactions, ultimately resulting in an extended shelf life (Barbosa-Cánovas et al., 2005; Jha, Le-Bail, & Jun, 2022). The popularity of frozen food is consistently increasing, evident from the rising market value and the wider range of products available on store shelves (Cablevey Blog, 2023). Frozen fruits and vegetables are regarded as next-generation products and are witnessing a significant surge in demand (Cablevey Blog, 2023). Frozen fruits offer advantages such as preserving maximum nutrients, aroma, flavour, and consumer convenience due to their pre-prepared nature, often involving peeling, dicing, or cutting (Barbosa-Cánovas et al., 2005).

Due to the physical changes and chemical alterations that occur during the phase change of water to ice in the freezing process, fresh produce undergoes irreversible quality changes such as textural loss and chemical alterations (Jha, Xanthakis, et al., 2019). Generally, fruit tissues are more susceptible to freezing-related turgidity loss compared to vegetables. This susceptibility is attributed to their delicate tissue, higher moisture content, and lower fibre content (Charoenrein, 2018). Frozen fruits are not only essential for direct consumption but also serve as raw materials for various products like juices, yogurts, candies, cookies, cakes, ice creams, and children's food (Spada et al., 2010). Employing methods that mitigate freeze damage can significantly enhance the value of these products. Traditionally, freezing-induced harm can be reduced by freezing items under conditions that facilitate a higher freezing rate and/or by implementing pretreatment procedures before freezing (Jha et al., 2022). In contemporary times, innovative freezing techniques incorporating physical fields and high-pressure processing have demonstrated the capability to yield superior quality frozen food items (Jha et al., 2022). Ultrarapid freezing, as facilitated by cryogenic fluids, provides exceptionally high freezing rates. This process generates numerous small ice crystals in both intercellular and intracellular domains, thereby minimizing the detrimental effects caused by dehydration and destruction resulting from shrinkage. Consequently, the overall quality of frozen food is effectively preserved. On the contrary, slow freezing rates, as achieved through some of the mechanical freezing, lead to increased freeze damage due to heightened dehydration and shrinkage. This damage is primarily caused by the formation of needle- and spear-shaped ice crystals, predominantly located in the intercellular regions, which pierce through cell walls (Charalambous, Berry, & Leddy, 1989; Xu, Wang, Wang, & Zhang, 2018).

Reports have indicated that cryogenic freezing surpasses conventional methods in terms of preserving the quality of food products after freezing and during their frozen storage. This superior quality preservation is evident through various aspects, including the maintenance of the initial microstructure, reduced exudate loss, improved texture retention, minimized dehydration losses, lower levels of lipid oxidation, and smaller colour changes (Boonsumrej, Chaiwanichsiri, Tantratian, Suzuki, & Takai, 2007; Chassagne-Berces et al., 2009; Chen & Pan, 1997; Mulot, Fatou-toutie, Benkhelifa, Pathier, & Flick, 2019; Pan & Yeh, 1993; Rodezno et al., 2013; Truonghuynh, Li, Zhu, Guo, & Li, 2020). Furthermore, when subjected to cryogenics, an outer layer of ice crust forms on the surface of the product (Agnelli & Mascheroni, 2002). This crust not only enhances the mechanical strength of the product but also acts as a barrier that retains moisture. Importantly, it prevents clumping and the attachment of the product to the conveyor belt—issues commonly encountered when employing slow mechanical freezing methods (Agnelli & Mascheroni, 2002). The moisture retention capability of this crust is likely responsible for the reduced dehydration observed after cryogenic freezing compared to conventional freezing, both during the freezing process and storage (Rodezno et al., 2013). Furthermore, the formation of this crust may serve to encapsulate and safeguard the flavour of the food, offering an added advantage in terms of flavour preservation (Agnelli & Mascheroni, 2002). Apart from these benefits, cryogenic freezing also holds potential to enhance the

microbiological safety of foods (Charalambous et al., 1989). Conversely, there have also been reports indicating a range of outcomes from no discernible difference (Gales, Jones, & Swarts, 2022) to an increased loss of certain quality attributes under cryogenic freezing compared to the conventional method (Anese et al., 2012; Chassagne-Berces et al., 2009). One of the primary reasons cited by researchers is the development of cracks associated with the cryogenic freezing method (Anese et al., 2012; Chassagne-Berces et al., 2009). Other factors that can significantly influence the ability to detect differences include the thawing method employed, the combination of freeze-thawing methods, the temperature utilized in cryogenic freezing, the sample size, the inherent characteristics of the product or species, and the freeze damage assessment method (Agnelli & Mascheroni, 2002; Egelandsdal et al., 2019; Jo et al., 2014; Yang, Hu, Takaki, Yuan, & Yu, 2021).

To the best of our knowledge, most of the studies concerning cryogenic freezing have predominantly centered around meat matrices. However, there are a few studies that have focused on the freezing of fruit matrices. Notable examples include research on apples and mangoes by Chassagne-berces et al. (2010) and Chassagne-Berces et al. (2009), pumpkin by Goncalves et al., (2011a), blueberries by Cao et al. (2018), dates by Alhamdan et al.(2018), raspberries by Gales et al. (2022), durian by Razali et al. (2022), and two others (Mamatov et al. 2020; Otero et al. 2000). Nevertheless, apart from 4 studies (Mamatov et al. 2020; Alhamdan et al., 2018; Gales et al., 2022; Goncalves et al., 2011a) focusing on pumpkin, cherries, raspberries, and cherries, it remains challenging to find research that directly compares the storage quality of cryogenically frozen fruits with those frozen using conventional mechanical methods. Moreover, fruit species display distinct characteristics, and their response to physicochemical changes during freezing and subsequent storage may vary. These differences are noticeable even among various varieties of the same species (González, De Ancos, & Cano, 2002). Consequently, conducting comprehensive studies that compare the long-term storage quality of various cryogenically frozen fruit matrices becomes crucial. Such studies will yield a valuable comparative dataset for cryogenically frozen and traditionally frozen samples stored over the long term. Hence, a study was conducted to assess the impact of freezing methods (cryogenic and mechanical) on the storage quality of two fruit matrices (apple and melon) over a prolonged storage period of 90 days. This study covers a wide range of physicochemical analyses, providing a more comprehensive approach compared to some existing research.

2. Materials and methods

2.1. Sample

Granny Smith apples with standard size and exceptional quality, possessing excellent firmness, were selected. They were then cleaned with cold chlorinated water (30 to 50 ppm). For further processing, the apples were halved vertically, and 15 mm diameter cylinders (nine per half) were created using a cutter, starting from the skin and progressing towards the flesh. The height of the cut cylinders was adjusted to 15 mm using two attached scalpels. Immediately after this step, the cylinders were soaked in a 1 g/l ascorbic acid solution (ice-cold water 2–4 °C) for 5 min. Following this, water was drained and the samples were packed in the plastic bag as such that much of the air was removed prior to freezing.

Melons (Charentais variety) of identical size, shape, and maturity were chosen. Care was taken to select melons that were just red and still quite firm. The cylinders were cut similarly as mentioned for apples. In the end, melon cylinders with a diameter and height of 15 cm each were obtained.

2.2. Freezing, frozen storage, and thawing

The fruit matrices were frozen using an air blast freezer (Servathin,

Poissy, France) and a cabinet cryogenic freezing cell (Air Liquide, France; Supplementary Fig. 1) maintained at $-40\text{ }^{\circ}\text{C}$ and $-80\text{ }^{\circ}\text{C}$, respectively. The air velocity used in the study was representative of that commonly found in industrial equipment, and was 4 m/s in the air blast freezer ($0.4 \times 0.4 \times 0.4\text{ m}^3$) and 0.5 m/s in the cryogenic freezer chamber (dimensions 60 cm long, 30 cm width, and 25 cm height). For all experiments, the freezing conditions were such that the ratio of the freezing zone volume/product quantity was comparable and globally there was no restriction of refrigeration power with respect of the amount of food to freeze (small amount of food being frozen for each test). The air blast freezer was a prototype freezer with an experimental zone of $0.4 \times 0.4 \times 0.4\text{ m}^3$ in which the air velocity (4 m/s) was uniform and parallel to the grids on which the products were installed. The cryogenic fluid (Liquid nitrogen – LN_2) was not sprayed directly on the products; LN_2 was in a Dewar container and was set under pressure (0.5 atm), thanks to gaseous Nitrogen. A control valve was controlling the spraying of LN_2 on a ventilator installed in the freezing setup, located in a section which was separated from the area where the foods were installed. The control valve was actuated when the deviation between the set point temperature and the freezer temperature. The food samples were installed on a grid and were exposed to a gas flow parallel to the grids; a similar installation was ensured in both freezing conditions. In such configuration, direct exposure of LN_2 on the food samples was impossible, thus mitigating any risk of freeze burn. To initiate freezing, the samples were placed on a grid inside the freezing cabinet. To monitor the time-temperature history during freezing, a thermocouple was inserted into the geometric centre of the product, with data recorded every 5 s and 10 s for cryogenic and mechanical freezing methods, respectively. The freezing process was halted once the centre temperature reached $-25\text{ }^{\circ}\text{C}$. Following freezing, the frozen samples were quickly transferred to plastic bags, packed under a partial vacuum, and stored at $-20\text{ }^{\circ}\text{C}$ for 90 days. The samples at different storage durations, namely 7th, 30th, 60th, and 90th day, were subjected to quality analysis. For the physicochemical analysis, the frozen samples had to be thawed overnight (for 12 h) in a refrigerator at $4\text{ }^{\circ}\text{C}$. This timing ensured the complete thawing of the product before conducting the analysis.

2.3. pH, TSS, titratable acidity, and quality index

The pH measurement was performed on the juice obtained after grinding and centrifugation of 50 g of the product. The grinding process was carried out using a vegetable centrifuge (Magimix, France). The pH was measured using a combined redox electrode connected to a pH meter (P107 Consort, Bioblock Scientific).

The brix of the sample was measured using a hand-held refractometer (Optech, Italy) on a strained juice of apple and melon.

The titratable acidity takes into account the organic and inorganic acids present in fruits and vegetables, such as malic acid, tartaric acid, and citric acid. The method used for titration is electrometric titration. To begin, 20 g of the product was weighed after grinding it in a food processor. Then, 100 ml of distilled water was added, and the mixture was homogenized in a Waring Blender at $20,500\text{ rpm}$ for 30 s . The solution was brought to a boil, cooled by adding 50 ml of distilled water, and then centrifuged at $10,000\text{ g}$ for 15 min at $20\text{ }^{\circ}\text{C}$. Subsequently, precisely 100 ml of the solution was taken, and 3 drops of phenolphthalein (pH indicator -1 g in 50 ml ethanol/ 50 ml distilled water) was added. The pH of the sample was then adjusted to 8.1 (the pH at which the colour indicator changes from colourless to pink) by gradually adding 0.1 N sodium hydroxide (NaOH). Titratable acidity is expressed as 1 milliequivalent (meq.) of acid per ml of NaOH added. The results are generally reported for 100 g of the product, and the equivalent value in citric acid (in grams of citric acid per 100 g or as a percentage) was also provided. It should be noted that 10 meq. corresponds to $0.064\text{ g}/100\text{ g}$ of the product. The quality index is referred as to the ratio of the brix to titratable acidity. Three replications were performed for these quality attributes for both fruits.

2.4. Dry matter

Dry matter was measured by placing 5 g of product in the oven maintained at $102\text{ }^{\circ}\text{C}$ until it reached a constant weight. The product weight was measured with an accuracy of $\pm 0.0001\text{ g}$. For the thawed product, care was taken to remove the thawing exudate before the measurements. The dry matter content is given by the following relationship:

$$\text{Dry matter (\%)} = \frac{W_2}{W_1} * 100 \quad (1)$$

where, W_1 and W_2 are the initial and final (dry sample) weights of the product. The mean value for dry matter was calculated based on three samples, each obtained from a different fruit.

2.5. Exudation/drip loss

About 50 g of frozen samples stored in plastic under a partial vacuum were thawed using the procedure mentioned above. Once complete thawing was achieved, the thawed samples were placed on sieves for 15 min to remove any remaining exudate and then reweighed. Thawing exudation is expressed as the difference in weight resulting from freezing/thawing compared to the dry matter weight of the sample ($\text{g exudate/g product dry matter}$). Three replications were performed for this quality attribute.

2.6. Colour

The colour measurement was made on a perfectly smooth sample (obtained using a sharp razor blade) using a spectrophotometer CM-3500d (Minolta, Japan). Different colour parameters, namely L^* , a^* , and b^* values, were obtained. L^* represents the lightness measured on a scale of 0 for black to 100 for white. a^* value represents the colour's position along the green to red axis, while b^* value represents the colour's position along the blue to yellow axis. Red and yellow colours correspond to positive a^* and b^* values, respectively, while green and blue colours are related to negative a^* and b^* values. Furthermore, using Eqs. 2 and 3, other important parameters such as chroma values and total colour difference (ΔE) were also calculated. The chroma value represents the colour's saturation or colour intensity/purity. Higher chroma values indicate more vibrant and intense colours, while lower chroma values indicate less saturated or pastel colours.

$$\text{Chroma} = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (3)$$

where, ΔL^* , Δa^* , Δb^* are the difference in the L^* , a^* , and b^* values of fresh and frozen-thawed samples, respectively. The mean value for the colour parameters was derived from 10 distinct samples.

2.7. Texture

The texture of apple and melon was measured using the instrumental Warner-Bratzler modulus method with a tensile-compression machine (Lloyd Instruments LR5K, UK) on thawed samples at $20\text{ }^{\circ}\text{C}$. The measurements were conducted using a triangular blade, known as the Warner-Bratzler modulus, with a characteristic angle of 30° , in the shape of an inverted V. The blade slid through a 1.1 mm slot at a speed of 20 cm/min . During the measurement, the product was deformed simultaneously by the movement of the blade through the slot and by the V-shape of the blade. The breaking force (N) was determined as the maximum height of the texturogram and was normalized by dividing it by the area of the sample subjected to the blade cut. The mean texture value was obtained from 6 independent measurements.

2.8. Enzymatic analysis

2.8.1. Polyphenol oxidase

Polyphenol oxidase catalyses the initial stage of enzymatic browning by converting phenolic compounds into quinone products, which serve as precursors to coloured melanins. To measure the activity of polyphenol oxidase, spectrophotometry was employed. The first step involved extracting PPO from the apple sample. For this purpose, 30 g of apple was homogenized in 30 ml of 0.2 M McIlvaine buffer (pH 6.5) containing 1 M NaCl and 5 % polyvinylpyrrolidone (PVPP) using a Waring Blender for 10 s at 20,500 rpm. The preparation was then stirred at 4 °C for 30 min and subsequently centrifuged at 15,000 g for 30 min at 4 °C. The supernatant was collected, filtered through paper, and then through a 0.45 µm filter. Next, 0.3 ml of an aliquot of the enzymatic solution, previously prepared was mixed with 2.7 ml of 0.005 M sodium phosphate buffer (pH 6.5) containing 0.11 M catechol. The absorbance was recorded at 420 nm using a spectrophotometer, with the absorbance measurements being taken for 1 min and 30 s to determine the slope of the curve. This slope provides the unit of enzyme activity expressed as the difference in absorbance per min and per gram of fresh product (ΔDO/min/g). This assay was conducted with five replications.

2.8.2. Peroxidase

Peroxidases are hemoproteins that catalyse the oxidation of various substrates. To measure peroxidase activity, 30 g of melon was homogenized using a Waring Blender for 10 s at 20,500 rpm in 30 ml of 0.2 M McIlvaine buffer (pH 6.5) containing 1 % polyvinylpyrrolidone (PVPP). The preparation was then stirred at 4 °C for 30 min and subsequently centrifuged at 15,000 g for 30 min at 4 °C. After that, the supernatant was collected and filtered using filter paper. Next, 2.6 ml of 0.05 M sodium phosphate buffer (pH 6.5) was prepared, and 0.1 ml of 1.5 % hydrogen peroxide and 0.2 ml of 1 % 1,4-phenylenediamine were added to it. Following this, 0.1 ml of the previously prepared protein extract was added to the mixture. The measurement was carried out using a spectrophotometer at 485 nm. The absorbance was monitored for 1 min and 30 s to determine the slope of the curve, which provides the unit of enzyme activity expressed as the difference in absorbance per min per gram of fresh product (ΔDO/min/g). Six replications were performed for this assay.

2.9. Vitamin C

The Vitamin C assay relies on the reducing properties of ascorbic acid with redox indicator dyes, using the dichlorophenolindophenol (DCPIP) titrimetric method. Firstly, 20 g of the product is blended with 90 ml of 2 % oxalic acid, macerated for 15 min, and then centrifuged at 10,000 g for 15 min to obtain the supernatant. The supernatant is then adjusted to 100 ml by adding 2 % oxalic acid. Simultaneously, a stock solution of 1 mg/ml ascorbic acid in 2 % oxalic acid is prepared. Next, the DCPIP solution (50 mg/ml) is calibrated by removing 5 ml of 1 mg/ml ascorbic acid solution, adding 20 ml of distilled water, and titrating with the DCPIP solution until a pinkish coloration appears for 30 s. The quantity of DCPIP required to dose 5 mg of ascorbic acid is noted for calibration. Once calibration is achieved, the vitamin C content in the product is measured by centrifuging and filtering 5 ml of the prepared solution (equivalent to 0.5 g of product), and then adding 20 ml of distilled water. The volume of DCPIP solution required to reach the pinkish coloration endpoint is measured. Using the obtained results, the equivalent concentration expressing the mass of vitamin C in relation to the product quantity is calculated. Finally, the concentration of vitamin C in the sample is established in mg/100 g of the product, based on the data obtained from calibration and the assay. The mean value for vitamin C was derived from three different measurements.

2.10. Soluble proteins

Soluble proteins were quantified in the exudates collected after thawing using the bicinchoninic acid method (BCA, Sigma method N° TPRO-562). The BCA method is a modification of the Lowry method and relies on the reduction of Cu²⁺ ions to Cu⁺ ions by the proteins present. Bicinchoninic acid serves as a highly Cu⁺-specific chromogenic reagent, forming a purple compound, which is then measured spectrophotometrically at 562 nm. The sensitivity of this method ranges from 0.01 % to 0.1 %, allowing for accurate detection of protein concentrations in the samples. The mean soluble protein values were obtained from three replications.

2.11. Microstructure analysis

The size and location of ice crystals in frozen product samples was observed by fixing the samples in their frozen state using the isothermal cryo-fixation technique. Samples approx. 10 × 5 × 5 mm were cut from frozen products using a sharp scalpel or razor blade precooled to -20 °C. Then the samples are fixed in Carnoy's solution (60 % absolute ethanol, 30 % chloroform and 10 % acetic acid (v/v)) for 36 h at -20 °C. After the samples were dehydrated by washing with successive baths of alcohol. The alcohol bath included a 2h absolute ethanol bath, 3 times 2 h, then 12 h in 1-butanol. Following, cleaning of samples was performed using 3 baths of toluene or Bioclear (Microm, France) for 20 min each. Next, the samples were fixed in molten paraffin at 57 °C. This step included an impregnation process through three successive dips of 1 h in molten paraffin, then moulding into a paraffin block using a plastic mould (20 × 15 × 15 mm). A section of 10µm was cut from the fixed sample using a microtome, dewaxed and rehydrated, followed by staining with 3 % light green SF yellowish (C.I. 42095). The stained sample was observed under an optical microscope coupled with an RGB CDD camera (MACC-C71, Sony, Japan). The mean pore size value was obtained by analysing three micrographs.

2.12. Statistical analysis

All values are presented as means with standard deviations. One-way ANOVA analysis, using IBM SPSS software, was conducted on the data, and the Tukey HSD test was employed to determine differences between the means of the fresh and treated conditions. A two-way ANOVA (Multivariate Analysis of Variance - MANOVA) was used to assess the effects of freezing conditions and frozen storage durations. This analysis allowed for the examination of both individual effects and potential interactions between the factors. To evaluate specific differences between the means, Bonferroni analysis was conducted.

3. Results and discussions

3.1. Impact on pH, brix, titratable acidity, and quality index

The initial pH measurement of the fresh melon was 6.02, indicating a slightly acidic nature. After undergoing treatment, it exhibited an increase, approaching a neutral pH (Table 1). It is important to note that both freezing conditions and storage durations had a significant impact on the pH (Table 2). The change in pH was more pronounced with cryogenic freezing compared to mechanical freezing, as shown by the group mean values of 6.60 and 6.43, respectively. In terms of the storage period, a noticeable decreasing trend was observed in the pH values. Over the course of 90 days, the pH value degraded by 6 % compared to its value at 7 days. Notably, samples stored for 7 days and 90 days exhibited significant differences in pH across all storage durations. Conversely, while samples stored for 30 and 60 days did not show significant differences between each other, they remained distinct from samples stored under other durations. There was no interaction effect between freezing conditions and storage durations on the pH of melon

Table 1
Physicochemical analysis of fresh and frozen melon samples. * denotes difference between fresh and treated samples.

Melon (Charentais)	Experimental conditions	Storage at -20 °C Cryogenic freezing				Mechanical freezing				
		Fresh	7 days	30 days	60 days	90 days	7 days	30 days	60 days	90 days
Quality attributes										
pH	6.02 ± 0.07	6.81 ± 0.01*	6.61 ± 0.01*	6.61 ± 0.06*	6.40 ± 0.01*	6.66 ± 0.05*	6.40 ± 0.04*	6.39 ± 0.11*	6.27 ± 0.05*	
°Brix	11.85 ± 0.07	10.4 ± 0.14*	11.45 ± 0.07	11.4 ± 0.71	11.1 ± 0.14	8.95 ± 0.07*	11.25 ± 0.07	12.75 ± 0.07	12.05 ± 0.07	
Titrateable acidity (g citric acid/100g)	0.089 ± 0.001	0.078 ± 0.001*	0.064 ± 0.001*	0.054 ± 0.005*	0.075 ± 0.003*	0.078 ± 0.001*	0.078 ± 0.001*	0.072 ± 0.003*	0.070 ± 0.000*	
Quality index (total sugar/acidity)	133.91 ± 1.87	134.19 ± 0.6	178.96 ± 5.06*	209.74 ± 4.45*	148.96 ± 8.11	115.48 ± 0.14*	145.17 ± 2.24	177.16 ± 4.59*	171.16 ± 1.0*	
Vitamin C (mg/100g)	24.27 ± 0.31	16.07 ± 0.31*	ND	9.90 ± 0.30*	6.89 ± 0.01*	22.93 ± 0.72*	ND	7.23 ± 0.06*	3.56 ± 0.07*	
Colour L*	55.20 ± 1.49	40.45 ± 2.61*	48.41 ± 2.24*	46.37 ± 3.92*	41.38 ± 2.07*	41.43 ± 4.30*	45.65 ± 3.18*	45.89 ± 2.48*	38.94 ± 4.13*	
	a*	12.38 ± 1.23	13.27 ± 1.50	12.51 ± 1.41	10.69 ± 0.87	13.81 ± 1.38	14.24 ± 1.98	9.70 ± 1.39*	9.76 ± 1.18*	12 ± 1.70
	b*	28.37 ± 1.97	31.13 ± 3.47	25.26 ± 2.18	21.56 ± 3.21*	32.70 ± 2.71	32.55 ± 4.05	21.12 ± 3.18*	21.07 ± 3.05*	29.88 ± 3.81
Chroma	30.95 ± 2.25	33.84 ± 3.74	28.19 ± 2.48	24.08 ± 3.17*	35.51 ± 2.94	35.54 ± 4.48	23.26 ± 3.38*	23.23 ± 3.23*	32.20 ± 4.10	
ΔE	-	15.55 ± 1.91	7.71 ± 2.79	11.45 ± 4.70	14.89 ± 1.64	15.41 ± 3.04	12.38 ± 4.42	12.25 ± 3.65	16.93 ± 3.57	
Firmness (N/cm ³)	1.19 ± 0.10	1.41 ± 0.36	1.84 ± 0.22*	2.00 ± 0.24*	2.00 ± 0.31*	1.15 ± 0.22	1.67 ± 0.13*	2.06 ± 0.25*	1.82 ± 0.14*	
Peroxidase (% activity)	100 ± 2.37	128.84 ± 6.61*	105.26 ± 1.72	92.76 ± 3.48	112.28 ± 2.30*	136.95 ± 8.84*	94.24 ± 2.46	96.82 ± 4.43	107.89 ± 3.38	
Exudation (g/100g)	-	4.81 ± 0.43	8.66 ± 0.13	10.03 ± 0.18	12.00 ± 0.79	12.06 ± 0.54	14.65 ± 0.45	14.01 ± 0.30	14.27 ± 1.00	
Soluble proteins (mg/g)	-	2.02 ± 0.07	2.28 ± 0.08	2.00 ± 0.08	2.29 ± 0.10	1.89 ± 0.09	2.06 ± 0.01	1.65 ± 0.03	2.26 ± 0.02	

Table 2
MANOVA results for the different measured physicochemical parameters for melon. ^{a-c} Different small letters within each column indicate significant differences between groups.

P values (individual/interaction effects)	Analysed Parameters						
	pH	°Brix	Total acidity (g citric acid/100g)	Quality index (total sugar/acidity)	Vitamin C (mg/100g)	Firmness (N/cm ³)	Peroxidase (% activity)
Freezing conditions (FC)	0.000	0.256	0.001	0.000	0.100	0.062	0.557
Storage time (ST)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
FC×ST	0.605	0.000	0.001	0.000	0.000	0.428	0.000
Group mean for freezing conditions							
Cryogenic	6.60 ^b	11.09 ^a	0.068 ^a	167.97 ^b	10.95 ^a	1.81 ^a	109.79 ^a
Mechanical	6.43 ^a	11.25 ^a	0.074 ^b	152.24 ^a	11.24 ^a	1.68 ^a	108.98 ^a
Group mean for storage durations							
7 days	6.73 ^c	9.68 ^a	0.078 ^c	124.84 ^a	19.50 ^a	1.28 ^a	132.90 ^c
30 days	6.50 ^b	11.35 ^b	0.071 ^b	162.07 ^b	ND	1.75 ^b	99.75 ^a
60 days	6.50 ^b	12.08 ^c	0.063 ^a	193.45 ^c	8.57 ^b	2.03 ^c	94.79 ^a
90 days	6.33 ^a	11.58 ^{bc}	0.072 ^{bc}	160.06 ^b	5.23 ^c	1.91 ^{bc}	110.09 ^b

(Table 2). Conversely, the pH of fresh apples (i.e., 3.22), which exhibited an acidic nature, decreased after processing, resulting in a more acidic fruit. Significant differences were observed between the fresh samples and those stored for 7 and 90 days, regardless of the freezing conditions (Table 4). The pH of Golden Delicious apples was reported to be in the range of 3.73 to 3.77, depending on the cultivar (organic or conventional) (Neri et al., 2019). The freezing conditions did not have a significant impact on the pH of apples, as the values remained identical (i.e., 3.15 (cryogenic) vs. 3.16 (mechanical)) (Table 5). During the storage of apples, the pH significantly increased from 7 days to 30 days (by 1.60 %), followed by a relatively stable phase up to 60 days. However, the pH decreased significantly upon reaching the 90-day mark (to 3.12), to the point where the sample had an identical pH to that of the 7-day sample (i.e., 3.13). Similarly to melons, no interaction effect was evident for the apple samples (Table 5).

The pH values are of importance as they can cause changes in certain nutrients. For instance, carotenoids are sensitive to acidity, and lower pH levels are considered one of the contributing factors to greater losses

in chlorophyll content (Gunawan & Barringer, 2000; Martínez, Pérez, Carballo, & Franco, 2013; Mínguez-Mosquera & Gandul-Rojas, 1994). The impact of freezing processing conditions (including freezing and storage) has been found to depend on the varieties of fruits. Therefore, it is not surprising to observe different trends in apples and melons, considering they are distinct species. For example, when looking at various raspberry varieties (such as Heritage and Autumn Bliss), the pH after freezing processing (including freezing and frozen storage) consistently appeared lower than that of the fresh sample (González et al., 2002). In contrast, other raspberry varieties (like Zeva and Rubi) either showed a decrease or remained relatively stable in pH up to a certain storage period, followed by an increase later during storage (González et al., 2002). Marin et al. (1992) reported an increase in pH for mangoes after freezing for all studied varieties, but the pH remained stable during storage for up to 120 days at -18 °C. Conversely, in another study, the pH of fresh juices (orange and orange-melon mixed) remained stable after freezing (at -25 °C) and frozen storage (at -20 °C) for 120 days for orange juice and 96 days for orange-melon mixed juice

(Molinari & Silva, 1996). The freezing methods have also been reported to affect the pH of mangoes (Prakobsang & Pornchalermpong, 2018) and tomatoes (Ergün, Gürlek, & Baysal, 2020), but the outcomes were contradictory. For example, a higher freezing rate in the case of mangoes resulted in lower pH values compared to a lower freezing rate, while the opposite results were observed in the case of cherry tomatoes. In another study, cryogenic freezing caused no change in the pH of raspberries, regardless of the variety, while conventional freezing led to a reduction in the pH of fresh raspberries in one of the two varieties (Gales et al., 2022). The pH after freezing and frozen storage has been also found to depend on factors such as blanching time, compounds used (e.g., ascorbic acid, citric acid), and their concentrations during blanching, as well as the combination of compounds and blanching time (Martínez et al., 2013). The changes in pH occurring in fruits due to freezing and frozen storage could be attributed to several factors. These factors include the cryo-concentration effect and the reorganization of cryo-concentrated fluids due to recrystallization, membrane damage causing the release of cellular components and altering pH, enzymatic activity leading to the metabolism of compounds (including organic acids), chemical reactions involving the released or cryo-concentrated compounds, and microbial activity contributing to the metabolism of compounds (Prakobsang & Pornchalermpong, 2018).

The °Brix measurement of fresh melon exhibited a significant difference only with the 7-day stored samples for both freezing conditions. Interestingly, in the case of cryogenically frozen samples, the °Brix value decreased by 12 %, and for mechanically frozen samples, it decreased by 24 %, as indicated in Table 1. Notably, there were no significant differences observed between the two freezing conditions, as revealed by the p-value of 0.256 in Table 2. However, over the storage period, the °Brix value displayed a significant increase up to 60 days (rising by 25 % compared to 7 days); however, beyond that storage duration, no significant changes were observed (at 90 days). An intriguing interaction effect of freezing conditions and storage durations emerged, with a p-values of 0.000 for each analysis, impacting the °Brix value (Table 2). For fresh apples, the initial °Brix value was 9.75. Except for the 7-day samples from both freezing conditions, other storage durations exhibited slightly higher °Brix values (Table 4). A significant increase was noted at and beyond 60 days for cryogenic freezing, and only at the 90th day for mechanical freezing (Table 4). Similar to melon, no discernible impact of freezing conditions on the °Brix value was identified through statistical analysis (Table 5). The brix value saw a significant increase during a certain period of storage (by 12 % from 7 to 30 days), followed by a no significant difference (30 and 60 days), and a slight increase at 90 days, leading to a significant difference from the 30-day storage period (by 6 %) (Table 5). Unlike melons, there was no observed interaction effect for apples, as indicated by a p-value of 0.482.

The °Brix value is directly related to the sugar content of fruits; 1°Brix represents 1 g of sucrose per 100 g of solution. Having knowledge of it is important with respect to the taste, flavour, ripeness, and sweetness of fruits (González et al., 2002; Tajana Mokrović, 2023). The impact of the freezing process on Total Soluble Solids (TSS) depends on factors such as cultivars, fruit species, freezing rate, freezing method, and storage duration. It has been reported that the freezing process significantly increased TSS in the case of early cultivars of raspberries (by 4–16 %), while it reduced the Brix level for late cultivar raspberries (by 4 %) (González et al., 2002). Furthermore, this trend persisted across the cultivars during the 12-month frozen storage at -24°C . These researchers attributed the increase in TSS to the rise in sugar content resulting from cellular disruption that occurs during freezing and frozen storage. Meanwhile, the reduction of TSS in later varieties was attributed to the loss of water-soluble compounds (sugar) due to the drip resulting from the freezing/thawing process. An increase in TSS in frozen raspberries compared to fresh ones was observed by Gales et al. (2022). On the other hand, the freezing process reduced the TSS of cherry tomatoes, and the magnitude of reduction was related to the freezing rate; a higher freezing rate resulted in a significantly lower

decrease in TSS compared to a lower freezing rate (Ergün et al., 2020). In another study (Prakobsang & Pornchalermpong, 2018), it was found that the freezing method, rather than the freezing rate, determined the TSS change in fresh mango upon freezing. For instance, still air freezing (0.2 cm/h) and air blast freezing (1.80 cm/h) caused a reduction in TSS and were not significantly different from each other. In contrast, when air blast freezing was combined with vacuum freezing methods, resulting in freezing rates of 1.64 and 2 cm/h, the samples had TSS levels similar to fresh ones, which were higher than those obtained using still air freezing and air blast freezing conditions (Prakobsang & Pornchalermpong, 2018). When comparing the impact of cryogenic and conventional freezing methods, a similar effect was reported for raspberries, which is consistent with the present findings (Gales et al., 2022). Furthermore, Gales et al. (2022) observed that the TSS levels of raspberries remained consistent between the cryogenic and conventional methods during the storage period. The increase in TSS observed during storage in the present study could be attributed to the release of sugars due to membrane damage caused by the recrystallization of ice. On the other hand, a fluctuating trend in TSS content throughout the storage period, regardless of the variety of raspberries being studied, was reported by González et al. (2002).

The fresh melon sample exhibited the highest titratable acidity value of 0.089, which decreased after processing (freezing and storage) (Table 1). Notably, both individual effects and interaction effects were observed for this parameter, with a p-values of 0.000–0.001 (Table 2). Among the freezing methods, cryogenic freezing led to a more pronounced decline in titratable acidity compared to mechanical condition, with values under cryogenic condition being significantly lower (by 8 %). A noticeable decreasing trend in titratable acidity was observed up to the 60-day mark, after which the acidity increased to a point where no significant differences were observed between the 90th day and the 7th or 30th day (Table 2). The increase in titratable acidity at the 90th day was primarily due to the higher acidity value exhibited by the cryogenic freezing condition at that time (Table 1). Similarly, like melon, the titratable acidity of fresh apples (initially 0.349) also decreased significantly after processing (Table 4). Unlike melon, however, there was no difference in acidity between the two freezing conditions, with a calculated p-value of 0.659 (Table 5). Nevertheless, a significant impact of the storage period (p-value = 0.000) and an interaction effect of freezing conditions and storage durations (p-value = 0.000) were observed on acidity. Compared to the 7-day storage period (acidity value of 0.317), the acidity value significantly decreased at 30th day (by 8 %), beyond which (at 60 days and beyond), the value showed an increasing trend, leading to no significant difference from the 7-day value (Table 5).

Titratable acidity (TA) is a very important quality indicator for assessing fruit product quality, impacting taste, mouthfeel, flavour, ripeness, freshness, and processing (Gales et al., 2022; Grabska, Beć, Ueno, & Huck, 2023; Sadler & Murphy, 2010). A decrease in titratable acidity upon freezing mango was reported by Ergün et al. (2020) and Marin et al. (1992), which aligns with the findings of this study. Conversely, titratable acidity was found to increase upon freezing raspberries compared to the fresh sample, with no significant impact observed between cryogenic and conventional freezing methods or varieties (Gales et al., 2022). Similar to Gales, no impact of freezing rates was found by Ergün et al. (2020). Our results are partially consistent with theirs. We observed no impact of freezing methods on the titratable acidity of apples, but a significant impact was seen in the case of melons. This trend is not surprising, as previous research has shown that the effect on titratable acidity after freezing varies depending on the fruit's cultivar. Three out of four raspberry cultivars showed no significant difference between fresh and just-frozen samples, while one cultivar exhibited a significant increase (González et al., 2002). Additionally, a fluctuating trend was observed during the storage period for all studied cultivars. Overall, the mean titratable acidity during the storage period indicates that, depending on the cultivar, titratable acidity either

increased or decreased compared to the fresh state (González et al., 2002). In the study by Gales et al. (2022), titratable acidity did not change during the storage period (i.e., 2–6 months). Similarly, no change in acidity values of mangoes were observed by Marin et al. (1992) during the frozen storage period of 4 months. Unlike those studies, a specific trend was observed in the present case, as specified above, for both apples and melons.

The quality index, represented as the ratio of °Brix to titratable acidity, of the fresh melon sample was lower than in all other conditions except for the cryogenically frozen samples stored for 7 days and 90 days, as well as the mechanically frozen sample stored for 30 days (which was significantly lower than fresh, i.e., 115.48 ± 0.14 vs. 133.91 ± 1.87) (Table 1). Both individual and interaction effects were found to be significant in melon samples, with p-values of 0.000 for each analysis. The cryogenically frozen sample exhibited a 10 % higher quality index compared to the mechanically frozen sample (Table 2). A notable trend in the quality index value was observed up to 60 days, showing a significant increase of 55 % compared to the 7-day storage, with a value of 124.84. However, beyond that point, the value dipped, resulting in no significant difference between the 90-day and 30-day samples (Table 2). Regarding apples, the quality index of samples stored for 7 days, frozen by both methods, was similar to that of the fresh sample. However, for samples stored for 30 to 90 days from both freezing methods, the quality index was higher than the fresh sample (Table 4). Similar to melon, both individual effects and interaction effects were significant for apples, with p-values ranging from 0.000 to 0.001 (Table 5). The mechanically frozen sample exhibited a significantly higher quality index than the cryogenically frozen sample (33.67 vs. 32.06). The quality index value increased as the storage duration increased from 7 days to 30 days (28.58 vs. 34.67). After 30 days, the value remained stable, as there was no significant difference observed between samples stored under those conditions (Table 5).

According to González et al. (2002), the quality index reflects the theoretical acceptability of fruits concerning taste and flavour (sugars and organic acids). Generally, sweeter and more flavourful/tasteful fruits are associated with higher quality index values. The freezing process, depending on the fruit cultivar, may either increase or have no effect on the quality index (González et al., 2002). In this study, the quality index either increased or remained similar to fresh, depending on the storage duration. While González et al. (2002), observed a fluctuating trend in the quality index during the 12-month storage of raspberries at $-24\text{ }^{\circ}\text{C}$, our results indicated a more stable trend in most cases, except for mechanically frozen apples (as shown in Tables 1 and 3). Additionally, these researchers noted a higher quality index at the end of 12 months for three out of the four studied cultivars. Consistent with their findings, frozen melon and apple samples, with the exception of the cryogenically frozen melon samples, exhibited significantly higher quality index values at the end of the 90-day storage period compared to fresh samples.

3.2. Impact on exudation

Tables 1 and 4 present the exudation data for melon and apple under individual processing conditions, respectively. Meanwhile, Tables 3 and 6 display the results of the MANOVA analysis conducted on the data obtained for various factors for melon and apple, respectively. As evident from Table 3, the exudation was significantly lower (p-value = 0.000) in the case of cryogenically frozen melon samples (with a group mean of 8.87 g/100 g) compared to mechanically frozen melon samples (with a group mean of 13.75 g/100 g). Similarly, the storage duration strongly affected the exudation loss, as indicated by a p-value of 0.000. The obtained data suggest that exudation increased primarily from the 7th day to the 30th day (by 38 %) and from the 30th day to the 90th day (by 9 %) (Table 3). Furthermore, an interaction effect of factors on exudation loss was also observed, as indicated by a p-value of 0.001. For the case of apples, there existed an individual effect of factors (p-value for freezing conditions was 0.002, while for storage durations it was 0.000), but no interaction effect was found (p-value = 0.222). Once again, the cryogenic method resulted in lower exudation compared to the mechanical freezing method (by 9 %), as presented in Table 6. The exudate loss increased significantly up to 60 days; compared to the value on the 7th day (5.90 g/100 g), the value on the 60th day was 131 % higher. Beyond that, it stabilized as no significant change was noted in Table 6.

Exudation or drip loss is a crucial quality indicator that influences the appearance, freshness, texture, nutritive value, and overall appeal of frozen food products (Torres Filho, Cazedey, Fontes, Ramos, & Ramos, 2017). The extent of drip loss in a product is tied to its characteristic freezing time, which refers to the time it takes to transition from -1 to $-7\text{ }^{\circ}\text{C}$. Notably, drip loss tends to be minimal with very short characteristic times, then rises before eventually declining to a consistent value as characteristic freezing times increase (Añón & Calvelo, 1980). The interim increase in drip loss could be attributed to the development of cracks that can form at higher freezing rates (Shi, Datta, & Mukherjee, 1999).

Comparing cryogenic freezing to mechanical freezing for fruits, it is unsurprising that cryogenic freezing yields lower exudation loss. Cryogenic freezing fosters the creation of numerous small, evenly distributed ice crystals throughout the food product, reducing damage to cell structure and preventing water displacement that leads to leaching of cellular content (Jha, Xanthakis, Chevallier, Jury, & Le-Bail, 2018; Le-Bail & Jha, 2019). Additionally, smaller ice crystals possess a larger specific surface area, which aids in water reabsorption during thawing (Bevilacqua, Zaritzky, & Calvelo, 1979). In contrast, elevated drip loss during frozen storage likely stems from the recrystallization phenomenon, which enlarges ice crystals and reorganizes the cryo-concentrated matrix. This process heightens damage to cellular structure, including membrane impairment, biopolymer depolymerization, and protein denaturation, ultimately reducing cell turgidity and water holding capacity (Jha et al., 2018; Mohsen Dalvi-Isfahan et al., 2019). Moreover,

Table 3

MANOVA results for the different measured physicochemical parameters for melon. ^{a-c} Different small letters within each column indicate significant differences between groups.

P values (individual/interaction effects)	Analysed Parameters			Chroma	ΔE	Exudation (g/100g)	Soluble proteins (mg/g)
	L*	a*	b*				
Freezing conditions (FC)	0.107	0.001	0.042	0.020	0.017	0.000	0.000
Storage time (ST)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
FC×ST	0.230	0.001	0.042	0.021	0.135	0.001	0.005
Group mean for freezing conditions							
Cryogenic	44.15 ^a	12.58 ^b	27.66 ^b	30.40 ^b	12.40 ^a	8.87 ^a	2.15 ^b
Mechanical	42.97 ^a	11.43 ^a	26.15 ^a	28.55 ^a	14.24 ^b	13.75 ^b	1.97 ^a
Group mean for storage durations							
7 days	40.94 ^a	13.77 ^b	31.84 ^b	34.68 ^b	15.48 ^b	8.43 ^a	1.95 ^b
30 days	47.03 ^b	11.12 ^a	23.19 ^a	25.72 ^a	10.04 ^a	11.65 ^b	2.17 ^c
60 days	46.13 ^b	10.23 ^a	21.32 ^a	23.65 ^a	11.85 ^a	12.02 ^{bc}	1.82 ^a
90 days	40.16 ^a	12.91 ^b	31.30 ^b	33.86 ^b	15.91 ^b	13.13 ^c	2.28 ^c

Table 4

Physicochemical analysis of fresh and frozen apple samples. *Indicates a difference between fresh and treated samples.

Apple (Granny Smith)	Storage at -20 °C Cryogenic freezing					Mechanical freezing				
	Fresh	7 days	30 days	60 days	90 days	7 days	30 days	60 days	90 days	
Quality attributes										
pH	3.22 ± 0.01	3.11 ± 0.01*	3.18 ± 0.00	3.19 ± 0.02	3.13 ± 0.01*	3.15 ± 0.00*	3.19 ± 0.01	3.21 ± 0.01	3.12 ± 0.02*	
°Brix	9.75 ± 0.21	8.90 ± 0.14	10.15 ± 0.07	10.65 ± 0.07*	10.65 ± 0.07*	9.15 ± 0.07	10.10 ± 0.42	10.40 ± 0.42	10.75 ± 0.07*	
Titrate acidity (g citric acid/100g)	0.349 ± 0.004	0.329 ± 0.004*	0.307 ± 0.000*	0.298 ± 0.005*	0.298 ± 0.005*	0.304 ± 0.004*	0.278 ± 0.005*	0.323 ± 0.005*	0.330 ± 0.005*	
Quality index (total sugar/acid)	27.94 ± 0.27	27.05 ± 0.08	33.06 ± 0.23*	35.79 ± 0.31*	32.32 ± 0.66*	30.11 ± 0.67	36.27 ± 0.93*	32.17 ± 0.86*	36.13 ± 0.79*	
Colour L*	69.01 ± 2.65	55.33 ± 3.55*	53.11 ± 2.24*	54.14 ± 4.49*	50.30 ± 6.58*	55.34 ± 1.59*	51.67 ± 4.71*	51.87 ± 4.38*	47.89 ± 6.03*	
	a*	-1.28 ± 0.52	2.91 ± 1.49*	3.39 ± 1.42*	3.53 ± 2.18*	4.72 ± 3.40*	2.03 ± 1.23*	2.85 ± 2.05*	2.95 ± 1.48*	4.84 ± 1.87*
	b*	11.73 ± 1.49	18.18 ± 3.92*	16.80 ± 1.94*	15.92 ± 2.21*	19.52 ± 3.94*	16.83 ± 2.49*	15.62 ± 2.29	14.86 ± 1.58	20.71 ± 3.55*
Chroma	11.81 ± 1.47	18.43 ± 4.08*	17.17 ± 2.10*	16.39 ± 2.56*	20.19 ± 4.75*	16.98 ± 2.59*	15.95 ± 2.64	15.19 ± 1.81	21.30 ± 3.83*	
	ΔE	-	15.94 ± 4.62	17.41 ± 2.74	16.32 ± 4.97	21.22 ± 8.17	15.12 ± 2.20	18.35 ± 5.23	18.02 ± 4.51	23.88 ± 6.76
Firmness (N/cm ³)	2.98 ± 0.10	1.28 ± 0.30*	1.30 ± 0.25*	1.86 ± 0.37*	1.99 ± 0.45*	1.21 ± 0.35*	1.26 ± 0.16*	1.73 ± 0.23*	1.76 ± 0.34*	
Polyphenol oxidase (% activity)	100 ± 4.58	64.08 ± 2.90*	42.57 ± 0.50*	14.58 ± 4.69*	13.76 ± 5.36*	75.74 ± 3.73*	49.74 ± 1.16*	33.06 ± 3.77*	41.40 ± 4.46*	
Mean pore size (µm)	-	93.43 ± 14.07	-	-	94 ± 0.83	96.93 ± 7.55	-	-	107.17 ± 11.33	
Exudation (g/100g)	-	5.29 ± 0.55	11.94 ± 0.48	13.05 ± 0.02	12.42 ± 0.49	6.51 ± 0.59	12.13 ± 0.67	14.18 ± 0.38	14.11 ± 0.13	
Soluble proteins (mg/g)	-	0.85 ± 0.02	0.61 ± 0.04	0.61 ± 0.04	0.65 ± 0.05	0.63 ± 0.06	0.51 ± 0.01	0.46 ± 0.03	0.58 ± 0.02	

larger crystals, having a greater specific surface area, hinder water reabsorption during thawing. All of these factors contribute to an augmented exudate loss (Mohsen Dalvi-Isfahan et al., 2019).

The trajectory of drip loss during storage depends on factors like storage temperature and duration, temperature stability, initial freezing setpoint temperature, sample size, thawing time, as well as the interplay between freezing rate and thawing method (Egelandsdal et al., 2019; Skrede, 1996). For instance, the drip loss of papaya surged as the storage period advanced (Ayala-Aponte & Sanchez Tamayo, 2017). Similarly, for apples, the drip loss during storage was greater at higher storage temperatures and with larger temperature fluctuations (Vicent, Ndoye, Verboven, Nicolai, & Alvarez, 2018). Likewise, broccoli exhibited more pronounced drip loss at elevated storage temperatures (Goncalves et al., 2011b). Another study spotlighted that rapidly frozen strawberries (at -30 °C with an air velocity of 1.2 m/s) displayed superior drip loss reduction during a 4-month storage period at -25 °C compared to slow frozen strawberries (at -18 °C) (Yanat & Baysal, 2018). Lastly, a quick frozen sample (reaching -20 °C within 1 h) coupled with microwave thawing resulted in the least drip loss from apples and peaches, outperforming other thawing methods (such as air thawing at 4 and 20 °C) and freezing conditions combinations (another tested condition involved slow freezing over 13 h to reach -20 °C) (Phan & Mimault, 1980).

3.3. Impact on firmness

The firmness of the fresh melon sample, measured in N/cm³, was recorded as 1.19. Significantly higher values were observed beyond the 7-day storage period compared to the fresh sample. Particularly noteworthy was the mechanically frozen sample stored for 60 days, which exhibited a substantial increase of approximately 73 % in firmness compared to the fresh sample, as presented in Table 1. The primary influencing factor on firmness was the storage duration (p-value = 0.000), while the impact of freezing conditions was insignificant (p-

value = 0.062), and no interaction effect was found (p-value = 0.428), as indicated in Table 2. However, it is worth noting that the mean firmness value of the mechanically frozen group was less distant from the fresh sample in comparison to the cryogenically frozen sample. Specifically, the mechanically frozen samples were 41 % firmer, whereas the cryogenically frozen samples were 52 % firmer compared to the fresh sample. The increase in firmness during the storage period was evident up to the 60-day mark, where the value rose from 1.28 N/cm³ at 7 days to 1.75 N/cm³ after 30 days, and further to 2.03 N/cm³ after 60 days. Beyond the 60-day threshold, there was a slight dip in the value, but it was not significantly different from the values observed at the 60-day or 30-day storage periods, as shown in Table 2. In contrast to melons, the firmness of fresh apples decreased regardless of the treatment conditions. The most significant degradation of 59 % in firmness compared to the fresh sample was observed for the mechanically frozen sample stored for 7 days (as shown in Table 4). Although not statistically significant, the cryogenically frozen sample exhibited a slightly higher firmness value compared to the mechanically frozen sample (1.61 vs. 1.49 N/cm³), as illustrated in Table 5. These slightly higher values for the cryogenic condition also suggest that the firmness of this condition approached that exhibited by fresh sample. The firmness value remained relatively stable up to 30 days, ranging from 1.25 to 1.28 N/cm³. However, at the 60-day mark, it increased to 1.80 N/cm³ and then stabilized, as indicated by the value at the 90th day, which was 1.88 N/cm³. Intriguingly, no interaction effect was observed for this parameter (Table 5).

Texture is a crucial sensory aspect and quality indicator of fruits, determining consumer preference (Narayana et al., 2023). Generally, fruits tend to experience more texture loss compared to vegetables due to their delicate matrix, higher moisture content, and lower fibre content (Charoenrein, 2018). The firmness of frozen fruits depends on several factors, including cultivar, variety, freezing rates, frozen storage time and temperature, maturity level, and pre-treatments like blanching and calcium impregnation (Alhamdan et al., 2018; Dawson, Al-Jeddawi, &

Table 5

MANOVA results for the different measured physicochemical parameters for apples. ^{a-c} Different small letters in a column for each group indicate significant differences.

P values (individual/ interaction effects)	Analysed Parameters						
	pH	°Brix	Total acidity (g citric acid/100g)	Quality index (total sugar/acidity)	Firmness (N/ cm ³)	Polyphenol oxidase (% activity)	Mean pore size (µm)
Freezing conditions (FC)	0.095	0.914	0.659	0.001	0.219	0.000	0.179
Storage time (ST)	0.000	0.000	0.000	0.000	0.000	0.000	0.367
FC×ST	0.089	0.482	0.000	0.000	0.870	0.000	0.418
Group mean for freezing conditions							
Cryogenic	3.15 ^a	10.09 ^a	0.308 ^a	32.06 ^a	1.61 ^a	33.75 ^a	93.72 ^a
Mechanical	3.16 ^a	10.10 ^a	0.309 ^a	33.67 ^b	1.49 ^a	49.99 ^b	102.05 ^a
Group mean for storage durations							
7 days	3.13 ^a	9.03 ^a	0.317 ^b	28.58 ^a	1.25 ^a	69.91 ^c	95.18 ^a
30 days	3.18 ^b	10.13 ^b	0.293 ^a	34.67 ^b	1.28 ^a	46.15 ^b	
60 days	3.19 ^b	10.53 ^{bc}	0.310 ^b	33.98 ^b	1.80 ^b	23.82 ^a	
90 days	3.12 ^a	10.70 ^c	0.314 ^b	34.22 ^b	1.88 ^b	27.58 ^a	100.59 ^a

Rieck, 2020; González et al., 2002; Skrede, 1996).

Both apples and melons experienced texture changes after freezing. This phenomenon is not unique to these matrices but is observed in many fruit matrices (Chassagne-Berces et al., 2010; Chassagne-Berces et al., 2009; Sirijariyawat & Charoenrein, 2012). The findings of this study regarding apples align well with existing literature, showing a reduction in firmness upon freezing treatment (Chassagne-Berces et al., 2009; Narayana et al., 2023). However, the results for melons contradict the literature (Sirijariyawat & Charoenrein, 2012). The decrease in firmness can be attributed to the loss of turgidity and cellular structure breakage resulting from the freezing process. Conversely, the increase in firmness observed in melons could be linked to an increase in the number of fibres per unit area due to exudation (Jha, Xanthakis, et al., 2019; Le-Bail & Jha, 2019; Mazur, 1984).

It is often difficult to detect differences in the firmness values of fruits and vegetables treated with different freezing rates. For instance, previous reports indicated no significant difference in apple firmness between freezing rates of 8.27 ± 2.01 cm/h and 28 ± 5.25 cm/h (provided by air-blast freezers). However, both of these conditions were significantly different from still air freezing, which had a freezing rate of 0.97 ± 0.10 cm/h (Narayana et al., 2023). Similarly, a study found that freezing at -74 °C resulted in better firmness retention in potatoes compared to freezing at -30 °C, although no significant difference existed between the methods. Nevertheless, a difference was noted between these methods and when freezing was performed at -18 °C in a cold room (Jha, Vidot, et al., 2019). Likewise, air-blast freezing with a freezing rate of 1.80 cm/h reduced texture degradation in mangoes compared to still air freezing (0.2 cm/h), but this difference in freezing rate did not cause a significant impact (Prakobsang & Porncharlernpong, 2018). Notably, freezing method, rather than rate, influenced firmness. For example, air-blast combined with vacuum freezing (freezing rates of 1.64 and 2 cm/h) led to better texture retention than air-blast freezing with a rate of 1.80 cm/h (Prakobsang & Porncharlernpong, 2018). It is worth mentioning that these results were obtained for samples thawed immediately after freezing. In the present case, the lack of significant difference between freezing methods may be attributed to crystal growth during storage and thawing. A well-known fact is that higher freezing rates result in smaller ice crystals in the product, which have higher surface free energy and are more susceptible to recrystallization during storage. Additionally, crystals formed during cryogenic freezing might have grown faster during thawing than those formed during mechanical freezing. As temperature rises during the thawing process, molecular mobility increases, favouring migratory recrystallization, leading to the crystallization of water that was kinetically inhibited during cooling. Hence, the benefits of cryogenic freezing could have been offset by phenomena like recrystallization and volume expansion (Chassagne-berces et al., 2010; Chassagne-Berces et al., 2009; Narayana et al., 2023).

In the literature, a decrease in energy (a textural attribute) was

observed for pumpkins during frozen storage, with the effect being more pronounced at higher storage temperatures. Furthermore, after a certain period, the texture of fruits reached an equilibrium known as the 'frozen storage texture' (Goncalves et al., 2011a). In contrast, our study found that the texture of both fruits increased during the storage period compared to the initial storage period value. In a study on apples, significant firmness loss was noted during the first month of frozen storage, while slight or no difference was observed for up to 10 months (Neri et al., 2019). This suggests that the 'frozen storage texture' of apples was established within one month. In our study, the 'frozen storage texture' of apples and melons was observed at 60 days of the studied storage period (Tables 2 and 5). The increase in fruit firmness observed during frozen storage in the present study may be linked to an increase in the number of fibres per unit area, primarily resulting from increased exudation during the storage period (Le-Bail & Jha, 2019).

3.4. Impact on colour

Table 1 and 4 provide a comparison of the colour parameters between the fresh and all processed conditions for melon and apple, respectively. On the other hand, Tables 3 and 6 present the results of the MANOVA analysis for the processed conditions of melon and apple, respectively.

An evident reduction in the L^* value was observed following processing when compared to the fresh sample. The mechanically frozen sample stored for 90 days exhibited the most notable change in the L^* value, registering a value of 38.94 in contrast to the fresh value of 55.20, as shown in Table 1. The reduction in the L^* value, compared to the fresh sample, was more pronounced in the case of the mechanically frozen sample (group average of 42.97) than in the cryogenically frozen sample (44.15) (illustrated in Table 3). Despite the higher value obtained for the cryogenically frozen samples, a significant difference was not observed when compared to the mechanically frozen samples (p -value = 0.107). In terms of storage duration, the L^* value showed a significant increase after 30 days (rising by $\approx 15\%$) from the initial 7 days (40.94), followed by a stable phase up to 60 days. Subsequently, there was a decrease at the 90-day mark, reaching the lowest value of 40.16. The statistical analysis indicated no interaction effect present (Table 3). Regarding the a^* value, the fresh sample exhibited a value of 12.38, indicating a reddish sample. The a^* value of the fresh sample was not significantly different from most of the processed conditions. However, there were significant differences between fresh and the 30-day and 60-day stored mechanically frozen samples, which showed significantly lower values (of 9.70 and 9.76, respectively), indicating a loss of redness (Table 1). The cryogenically frozen sample exhibited a slightly higher value (12.58, group mean value) than the fresh sample, suggesting increased reddishness. In contrast, the mechanically frozen samples appeared less reddish (11.43) compared to the fresh sample (as depicted in Table 3). In terms of proximity to the fresh sample, the cryogenically frozen samples

Table 6

MANOVA results for the different measured physicochemical parameters for apples. ^{a-c} Different small letters in a column for each group indicate significant differences.

P values (individual/interaction effects)	Analysed Parameters			Chroma	ΔE	Exudation (g/100g)	Soluble proteins (mg/g)
	L*	a*	b*				
Freezing conditions (FC)	0.132	0.298	0.348	0.336	0.341	0.002	0.000
Storage time (ST)	0.001	0.004	0.000	0.000	0.001	0.000	0.000
FC×ST	0.819	0.877	0.459	0.548	0.755	0.222	0.008
Group mean for freezing conditions							
Cryogenic	53.22 ^a	3.64 ^a	17.61 ^a	18.05 ^a	17.72 ^a	10.68 ^a	0.68 ^b
Mechanical	51.70 ^a	3.17 ^a	17 ^a	17.35 ^a	18.84 ^a	11.73 ^b	0.55 ^a
Group mean for storage durations							
7 days	55.35 ^b	2.48 ^a	17.51 ^a	17.71 ^a	15.53 ^a	5.90 ^a	0.74 ^c
30 days	52.39 ^{ab}	3.13 ^{ab}	16.20 ^a	16.56 ^a	17.88 ^a	12.04 ^b	0.56 ^a
60 days	53.01 ^b	3.24 ^{ab}	15.39 ^a	15.79 ^a	17.17 ^a	13.62 ^c	0.54 ^a
90 days	49.09 ^a	4.78 ^b	20.12 ^b	20.74 ^b	22.55 ^b	13.26 ^c	0.62 ^b

showed a 2 % higher value, while the difference between the fresh and mechanically frozen samples was 8 % (as can be perceived from Tables 1 and 3). Significant individual and interaction effects of the studied parameters were found on the a* value (with p-values ranging from 0.000 to 0.001). The tendency of change in the a* value during storage period was similar to that of the L* value, except the values changed in opposite directions (Table 3). The b* and chroma values exhibited a trend similar to that of the a* value when comparing the processed samples to the fresh sample. With a few exceptions, most treatment combinations did not show statistically significant differences compared to the fresh samples ($p > 0.05$) (Table 1). Notable differences were observed in the 60-day stored cryogenically frozen sample and the 30-day and 60-day stored mechanically frozen samples compared to fresh (Table 1). Both the b* and chroma values for the cryogenically and mechanically frozen samples were lower than those for the fresh sample (with b* and chroma values of 28.37 and 30.95, respectively). Interestingly, the cryogenically frozen samples (with group means of 27.66 and 30.40 for b* and chroma values, respectively) exhibited values closer to the fresh sample compared to the mechanically frozen samples (with group means of 26.15 and 28.55 for b* and chroma values, respectively) (as presented in Table 3). Furthermore, the statistical analysis revealed a significant difference between the mechanically and cryogenically frozen samples in terms of b* and chroma values (indicated by p-values of 0.042 and 0.020, respectively) (Table 3). This indicates that the yellowness and purity exhibited by the fresh sample were less affected when freezing was performed under cryogenic condition. The trend of change in the b* and chroma values during frozen storage mirrored that of the a* value. There was a significant decrease in values from the 7-day sample to the 30-day sample (a decrease of 27 % for b* and 26 % for chroma value, respectively), followed by stability up to 60 days, and then a significant increase at 90 days (Table 3). This increase led to values similar to those of the 7-day sample. Table 3 presents the MANOVA analysis for total colour change (ΔE) and confirms that cryogenic freezing led to better colour preservation of melon samples compared to the mechanical freezing method (indicated by a p-value of 0.017), as the group mean value of this condition was 13 % lower than its counterpart. The trend during the storage period was similar to that observed for the a*, b*, and chroma values.

Similar to melon, the whiteness of the fresh sample decreased after undergoing freezing processing, with the most significant reduction (31 %) observed in the mechanically frozen apples stored for 90 days (as indicated in Table 4). The changes caused by the individual freezing methods to the L* value of apples were consistent with the results obtained for melons. Cryogenic freezing resulted in slightly higher L* value compared to the mechanical freezing process (≈ 3 % higher), although a significant difference between the two freezing methods was not observed (p -value = 0.132). Regarding the storage duration, a general decreasing trend was observed as the storage period progressed (as shown in Table 6). The change in the a* value of apples was more pronounced after freezing processing compared to melons, as the fresh

sample exhibited a significantly lower a* value than all other conditions. Based on the obtained values, the fresh sample had a greenish hue (as indicated by a value of -1.28), while processing led to the development of a reddish hue, as indicated by a positive a* value (as shown in Table 4). The redness value increased during the storage period, with the maximum change observed after a 90-day storage period (as indicated in Tables 4 and 6). Compared to the fresh sample, cryogenic freezing caused slightly greater changes in the a* value compared to the mechanical freezing condition, as indicated by a 15 % higher a* value in the case of cryogenically frozen samples than mechanically frozen ones (as shown in Tables 4 and 6). The fresh sample's b* value was 11.73, indicating a yellow hue. Overall, freezing treatment intensified the yellowness hue, except for a few conditions, such as the 30-day and 90-day stored mechanically frozen samples, which exhibited no significant difference compared to the fresh ones (as shown in Table 4). The b* value was not significantly impacted by the freezing method (with a p-value of 0.348), although the mechanical process showed a slightly lower value, as evident in Table 6. During the storage period from 7 days to 60 days, the yellowness hue decreased (from 17.51 to 15.39), but this change was statistically insignificant. Interestingly, the yellowness significantly increased at the 90th day (to 20.12) as illustrated in Table 6. The chroma results mirrored the trend of the b* value (as shown in Tables 4 and 6). This indicates that, in general, the processed samples exhibited a higher purity of colour compared to the fresh sample (as shown in Tables 4 and 6). Unlike melon, where a clear higher ΔE was observed for the mechanical freezing condition, in the case of apples, the ΔE of mechanically frozen samples was marginally higher (by 6 %), but this difference was not significant (as shown in Table 6). Furthermore, the ΔE values were insignificantly different up to 60 days, beyond which a significant spike in ΔE was observed at the 90th day (an increase of 31 % compared to the value at 60 days) (as indicated in Table 6).

Colour is the primary quality indicator perceived by consumers, influencing their decision to purchase and ultimately consume a product. The colour of fruits is shaped by various pigments, including anthocyanins, chlorophylls, flavanols, and carotenoids (Jha, Xanthakis, et al., 2019; Skrede, 1996). Changes in the overall colour of a product result from modifications in these pigments, involving processes such as cis-trans isomerization or epoxidation of carotenoids, polyphenol oxidase activity leading to browning reactions in the presence of oxygen, the conversion of chlorophyll a and b into corresponding pheophytins, chlorophyll bleaching during fat peroxidation, oxidation catalysed by light, enhanced release of membrane-bound pigments (e.g., anthocyanins), and water-soluble pigment loss (e.g., anthocyanins) through leaching due to significant membrane damage, etc. (Jha, Xanthakis, et al., 2019; Skrede, 1996). Browning can also occur through Maillard reactions between free amino acids and reducing sugars (Skrede, 1996). Freezing and frozen storage can modify the colour of fruits and vegetables, either by inducing degradation or by enhancing the extractability of their pigments (Jha, Xanthakis, et al., 2019).

Our results align with some of the findings regarding the decrease in

the L^* value following freezing treatment. It appears that the reduction or increase in the L^* value is dependent on the type of fruit. The reduction in lightness value after freezing may be attributed to chemical reactions such as browning and Maillard reactions, which reduce lightness, or cellular alterations that affect the way light is reflected or absorbed, contributing to changes in the L^* value. In the literature, it was found that the L^* value of mango decreased regardless of the freezing conditions or rates (Prakobsang & Pornchalermpong, 2018). Conversely, in a study, the L^* value of strawberries increased upon freezing, with quick freezing ($-30\text{ }^\circ\text{C}$ and 1.2 m/s air velocity) resulting in greater increases compared to slow freezing (still air freezing at $-18\text{ }^\circ\text{C}$) (Ergün, Yanat, & Baysal, 2021). Meanwhile in another study, González et al. (2002) reported no significant increase in the L^* value after freezing compared to the fresh state. The slightly higher L^* value observed in cryogenic freezing, compared to mechanical freezing in this study, indicates reduced chemical reactions or structural alterations in the former case. Similar to our findings, a study highlighted that fast freezing ($-30\text{ }^\circ\text{C}$ and 1.2 m/s air velocity) significantly resulted in a lower decrease in L^* values of fresh tomatoes compared to slow freezing ($-18\text{ }^\circ\text{C}$ without air blowing) (Ergün et al., 2020). Concerning the storage duration impact, Ergün et al. (2021) reported that a clear decrease in L^* value during a storage period of 4 months at $-25\text{ }^\circ\text{C}$ whatever the freezing conditions were, with quickly frozen sample exhibiting a higher value than slowly frozen sample. In contrast, L^* value of raspberries remained fairly consistent during long-frozen storage (12 months) (González et al., 2002). However, we observed a variable trend in L^* value during the storage period.

A significant decrease observed in the a^* value between the fresh sample and mechanically frozen samples stored for 30 and 60 days signifies the potential deterioration of carotenoid pigments typically found in melons. On the other hand, the increase in the a^* value in the case of apples is a clear indication of enzymatic browning or degradation of chlorophyll to pheophytins, or a combination of both (Jha, Xanthakis, et al., 2019; Skrede, 1996). Significant differences in a^* and b^* values were observed between freezing methods for melons, while for apples, no significant differences were observed. It is worth mentioning that the variation in a^* and b^* values compared to fresh can differ based on the type of fruit and freezing rate. For example, Prakobsang and Pornchalermpong (2018) found that the a^* value increased for a lower freezing rate and decreased for a higher freezing rate compared to fresh mango samples. The b^* value either decreased upon freezing or remained similar to the fresh state, depending on the freezing method applied. In another study, fast freezing (at $-30\text{ }^\circ\text{C}$ with 1.2 m/s air velocity) resulted in a significantly lower degradation of a^* values in fresh tomatoes compared to slow freezing (still air freezing at $-18\text{ }^\circ\text{C}$). Conversely, the b^* value was higher for slow freezing than for fast freezing and the fresh sample (Ergün et al., 2020). Another study (González et al., 2002) highlighted that the a^* value of raspberries (regardless of the cultivar) remained practically unchanged after freezing and during frozen storage. While, the b^* value decreased after freezing but was significant only for 2 out of 4 varieties of raspberries. During storage, the b^* value fluctuated, and at the end of frozen storage (i.e., at $-24\text{ }^\circ\text{C}$ for 12 months), there was no significant difference compared to the fresh state. In a separate study (Ergün et al., 2021), the a^* and b^* values of strawberries increased upon freezing, with quick freezing resulting in higher values compared to slow freezing. Furthermore, both a^* and b^* values decreased during a 4-month storage at $-25\text{ }^\circ\text{C}$ for both freezing conditions, with the quickly frozen samples exhibiting higher a^* and b^* values than the slowly frozen samples. The trend in our case during the storage period concerning the a^* and b^* values varied with no significant difference between both freezing methods for apples. However, similar to them, we observed the effect of freezing methods on melons, but the trend of change in values during storage was different or even opposite.

Regarding chroma values, an increase upon freezing of raspberries was reported by Gales et al. (2022). In the present study, changes in chroma values following freezing treatment compared to the fresh state

were predominantly observed in the case of apples, where an increase was found. However, in the case of melons, the frozen samples showed a slightly lower value compared to fresh. Furthermore, no difference between freezing methods (cryogenic vs. conventional) was found in the study of Gales et al. (2022). The interpretation of these results partly aligns with our study as no difference between the cryogenic and mechanical methods was found for apples, but difference was reported for melons. It is worth mentioning that our data considers group means, while theirs focuses on single means (i.e., just after freezing), so a direct comparison may not be valid.

The significantly lower ΔE for melons, and although lower, yet insignificantly so for apples under cryogenic condition in the present study, reflects better colour preservation. This could be attributed to reduced freeze damage and pigment degradation under cryogenic condition. In contrast to our study, ΔE after freezing and during storage (of strawberries) was higher for quick freezing compared to slow freezing (Ergün et al., 2021). Additionally, they found an almost linear decrease in ΔE during storage, while in the present case, a variable trend was observed for melons. Conversely, a sudden and significant increase after a specific storage duration (60 days) was observed for apples. These differences could stem from variations in fruit matrices. As mentioned earlier, different fruit matrices may respond differently to colour changes induced by freezing treatments.

3.5. Impact on vitamin C

The analysis of vitamin C content in melon revealed that the fresh sample had the highest vitamin C content (24.27 mg/100 g), and its amount significantly decreased after undergoing freezing processing, as shown in Table 1. The most significant reduction was observed in the 90-day stored mechanically frozen sample compared to the fresh sample, with a substantial decrease of 85 %. From Table 1, it also appears that the mechanically frozen sample performed better at 7 days of storage, but as the storage duration increased, the cryogenically frozen sample exhibited better performance. Table 2 shows that the group mean for the mechanically frozen sample was slightly higher than that of the cryogenically frozen sample, primarily due to the higher value observed at the 7th day (as can be seen in Table 1). However, statistical analysis indicated no significant difference between these two methods (with a p-value of 0.001). A clear reduction in vitamin C content with an increase in storage duration was observed, with the vitamin C content decreasing by 73 % at 90 days compared to the content at 7 days (Table 2). Furthermore, the p-value of 0.000 indicated a strong interaction effect between the freezing methods and storage durations on the vitamin C content (Table 2).

The vitamin C assay was among the first to be studied concerning the quality of frozen fruits. Vitamin C, being a reactive compound, serves as an indicator for chemical reactions occurring within the fruits (Skrede, 1996). It is sensitive to factors like oxygen, metal ion catalysts, light, and temperature (Erenturk, Gulaboglu, & Gultekin, 2005; Martí, Mena, Cánovas, Micol, & Saura, 2009; Yin et al., 2022). Reduction of vitamin C during freezing is attributed to irreversible oxidation mechanisms. Given that vitamin C is a water-soluble vitamin, exudate loss can also be linked to its loss (Dawson et al., 2020; Skrede, 1996; Vicent et al., 2018). The tendency for vitamin C reduction after freezing was evident across various vegetables, with different levels of loss observed. Among six different vegetables, the highest loss was recorded in potatoes (56.8 %), followed by okra (45.7 %), spinach (44.8 %), green beans (38.2 %), peas (29.1 %), and broccoli (21.9 %) (Tosun & Yücecan, 2008). However, an increase in vitamin C after freezing (1-day stored sample at $-27\text{ }^\circ\text{C}$) was observed in the case of strawberries and green beans by Bulut et al. (2018). The higher ascorbic acid level obtained in frozen samples was attributed to the easier extraction of ascorbic acid after freezing and thawing. Freezing rate was not a determining factor for loss magnitude, as demonstrated by Ergün et al. (2020) findings with cherry tomatoes. Our results align with this, showing no significant difference between

two freezing methods. However, freezing methods did impact the loss of vitamin C from strawberries and raspberries (Skrede, 1996). Among various methods used, including tunnel freezing, fluidization, freezing in sugar, and liquid nitrogen and carbon dioxide freezing, the greatest losses were observed for tunnel freezing, with values of 3.6 % and 27.6 % for strawberries and raspberries, respectively. The highest retention for strawberries occurred during freezing under sugar, with only a 2.5 % loss, and for raspberries, liquid nitrogen freezing resulted in the lowest loss at just 1.3 % (Skrede, 1996). Different freezing media and rates apply varying forces, potentially causing variations in ascorbic acid separation from the structure, thereby affecting the overall estimation (Yanat & Baysal, 2018).

This is consistent with the general understanding that vitamin C content reduces during frozen storage (Gonalves et al., 2011a; Goncalves et al., 2011b), as observed in this study. Factors such as frozen storage temperature, freezing method, temperature fluctuations, storage duration, oxidase inactivation, and packaging play crucial roles in vitamin C loss (Dawson et al., 2020; Skrede, 1996). Higher storage temperatures and greater temperature fluctuations led to more significant vitamin C loss (Dawson et al., 2020; Goncalves et al., 2011a; Goncalves et al., 2011b; Vicent et al., 2018). However, after a certain storage period, the amplitude of temperature fluctuation's impact diminished at lower storage temperatures (Vicent et al., 2018). In regard to freezing methods, Skrede (1996) reported highest vitamin C loss in raspberries and strawberries (61.3 % and 38.4 %, respectively) after six months of tunnel freezing. In contrast, liquid nitrogen and sugar freezing caused less degradation after six months in raspberries (8.6 %) and strawberries (25 %), respectively. Another study demonstrated less vitamin C degradation (8.19 %) in quickly frozen strawberries compared to slowly frozen ones (16.58 %) after 120 days at -25°C (Yanat & Baysal, 2018). Furthermore, vitamin C loss during storage depends on the specific food matrix. For instance, after six months of storage, vitamin C loss varied among six studied matrices, with the highest loss in potatoes (61.5 %) and the lowest in broccoli (27.6 %) (Tosun & Yücecan, 2008). Different food matrices have distinct compositions, affecting the rate and mechanism of vitamin C degradation. Factors such as water activity, pH, metal ions, sugar content, and bioactive compound states within the food matrix contribute to these variations (Goncalves et al., 2011a).

3.6. Enzymology analysis

3.6.1. Impact on peroxidase

As observed in Table 1, the peroxidase activity in melon increased in the samples stored for the 7th day, whatever the freezing conditions were. Additionally, the 90th day stored sample frozen using the cryogenic method exhibited a significantly higher activity level than the fresh sample. For the remaining conditions, the values either slightly increased or decreased, but no significant differences were observed. Overall, a slight increase in peroxidase activity was noticed after processing compared to the fresh sample. This trend is evident from the data presented in both Tables 1 and 2, where the fresh sample had 100 % activity, while the cryogenic and mechanical conditions had activities of 109.79 % and 108.98 % (based on group mean), respectively. Furthermore, the statistical analysis indicated that freezing conditions had a similar impact on peroxidase activity (as shown by a p-value of 0.557), as depicted in Table 2. However, clear individual effects of storage duration and an interaction effect between the factors were evident, with p-values of 0.000 for each analysis (Table 2). Concerning the impact of storage duration, the peroxidase activity significantly decreased on the 30th day compared to the 7th day (from 132.90 % to 99.75 %), followed by an insignificant decrease up to the 60th day. Subsequently, there was a significant increase in activity at the 90th day (to 110.09 %). However, this increase was not sufficient to reach a value similar to that of the 7th day sample (as indicated in Table 2).

3.6.2. Impact on polyphenol oxidase

The polyphenol activity of all processed conditions was lower than that of the fresh sample, with the highest reduction observed in the cryogenically frozen sample stored for 90 days (by 84 %) (Table 4). Furthermore, the MANOVA analysis presented in Table 5 revealed strong individual and interaction effects of the factors, as indicated by p-values of 0.000 for each analysis. In comparison to the cryogenic freezing process, the mechanical process exhibited significantly higher enzyme activity (49.99 % vs. 33.75 %), indicating less degradation of PPO activity. In terms of the impact of storage duration, the activity reduced significantly up to 60 days (from 69.91 % at 7 days to 23.82 % at 60 days), beyond which no further significant change was observed (Table 5).

Polyphenol oxidase (PPO) and peroxidase (POD) are the two main enzymes involved in the oxidative reactions of phenolic compounds (Vitti, Sasaki, Miguel, Kluge, & Moretti, 2011). Under stressful conditions, PPO and POD activity may increase due to the induction of activity or "de novo synthesis" of these enzymes (Vitti et al., 2011). As mentioned earlier, these enzymes are frequently associated with enzymatic browning reactions. However, there are contradictory claims regarding their activity and subsequent role in the enzymatic browning of fruits and vegetables (Cantos, Espín, & Tomás-Barberán, 2001). The observed increase in POD activity in the present study for melons after freezing treatment could potentially be attributed to either the "de novo synthesis" of peroxidases or the induction of their activity (Cantos et al., 2001; Vitti et al., 2011). In fact, the linear increase in peroxidase activity in lettuce during storage after wounding has been linked to the synthesis of new peroxidase isoenzymes (Cantos et al., 2001). The increase in POD activity might also be connected to the enhanced release of phenolic compounds, which could occur due to the freezing treatment (Çubukçu, Kılıçaslan, & Durak, 2019; Jha, Xanthakis, et al., 2019; Vitti et al., 2011). Conversely, the slight reduction in POD activity during later storage months compared to 7 days could be due to the inactivation of POD enzymes over the storage period. A reduction in POD activity after freezing, without regeneration during frozen storage, were observed in mangoes (Marín, Cano, & Fuster, 1992). On the other hand, the reduction in PPO activity after freezing treatment in apples could be associated with the inactivation of polyphenol oxidase enzymes. The lower polyphenol oxidase activity found for cryogenic condition might be due to higher enzyme inactivation. However, further study is required to confirm this hypothesis. The reduction in PPO activity during the storage period could be linked again to the inactivation of the PPO enzyme. Our results are consistent with those of Marín, who also demonstrated a decrease in PPO activity (>80 % compared to fresh) after 120 days at -18°C in 3 out of 4 studied varieties of mangoes (Marín et al., 1992). Despite the reduced PPO activity, an increase in redness was observed for frozen apples. This could potentially be attributed to the action of PPO on the phenolic compounds that are released as a result of the freezing treatment. It is important also to emphasize that higher POD activity in frozen samples is a significant concern as it can lead to quality deterioration, including off-flavours, colour changes, odours, and other undesirable changes (Burnette, 1970).

3.7. Impact on soluble protein

For both apples and melons, the cryogenic freezing condition exhibited a greater amount of soluble protein compared to mechanical freezing, with the difference being more pronounced in the case of melons. Specifically, cryogenic freezing led to 19 % more soluble protein in melons and 8 % more in apples than the mechanical freezing method, as indicated in Tables 3 and 6 respectively. The impact of storage period and the interaction effect of factors were also significant on soluble protein, with p-values ranging from 0.000 to 0.008. The trend during storage for both studied samples was different; for apples, there was a significant reduction (of 24 %) in soluble protein after a certain storage period (from 7th day to 30th day), followed by no change (from 30th

day to 60th day), and then a significant increase at 90th day (to 0.62 mg/g). On the other hand, for melons, the trend was more fluctuating.

The observed increase in soluble protein content in the case of mechanical freezing could potentially be associated with changes in the cytoplasmic ionic strength resulting from the higher mechanical damage caused by the mechanical freezing condition. The change in ionic strength may have led to a significant increase in the solubility of proteins that were ionically bound to the cell walls of fresh tissue (Antonia Marín et al., 1992). Similarly, frozen storage can exacerbate mechanical damages, which might further enhance the cytoplasmic ionic strength. As a result, this could lead to higher solubility of cell wall-bound proteins, as mentioned previously (Antonia Marín et al., 1992).

3.8. Microstructure

The pore size of apples was assessed on the 7th and 90th day of storage after freezing under both conditions, as presented in Table 4. The results of the statistical analysis are displayed in Table 5. Cryogenic freezing resulted in a slightly lower mean pore size compared to mechanical freezing condition (reduced by 8 %); however, this difference did not reach statistical significance (p -value = 0.179, as shown in Table 5). Moreover, the duration of storage did not appear to have an effect on the pore size distribution (p -value of 0.367). Although no significant differences were observed in the pore size distribution between the freezing methods, clear disruption of cell morphology, as indicated by red arrows in Fig. 1, was evident in the case of mechanical freezing. Image analysis data and representative images suggest that cryogenic freezing maintained the microstructure relatively well, while mechanical freezing slightly enhanced the overall destruction of the microstructure (see Fig. 1 and Tables 4 and 5). It is a well-established fact that ice crystal size and cellular structure damage increase as freezing rate decreases. In this study, direct visualization of ice crystals at the frozen state was not performed, making it inappropriate to comment on the impact of freezing methods and storage durations on ice crystal size based solely on the present results. However, the damage caused by freezing rate to cellular morphology was clearly evident in this study, which is consistent with existing research (Chassagne-Berces et al., 2009; Jha, Vidot, et al., 2019; Narayana et al., 2023).

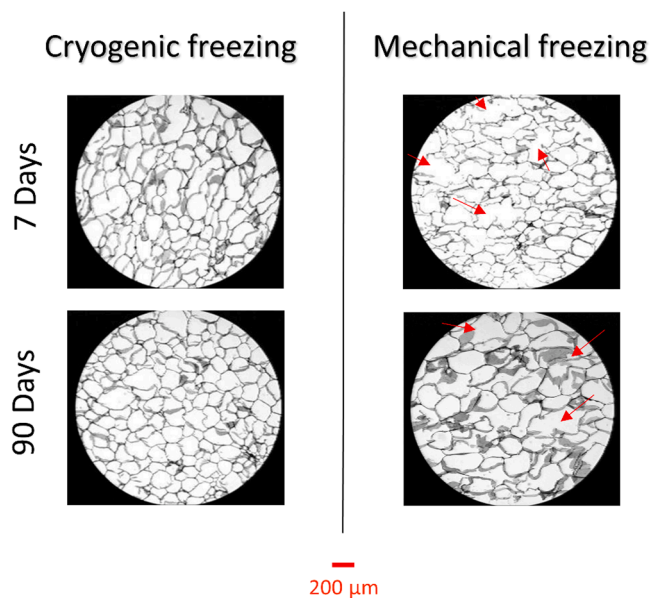


Fig. 1. Microstructure of mechanically and cryogenically frozen apples at various storage periods.

4. Conclusions

In conclusion, both apple and melon exhibited high sensitivity to the freezing process, leading to substantial alterations in most physicochemical parameters when compared to their fresh counterparts. The degree of pH alteration was primarily influenced by the fruit matrix and frozen storage duration, with some impact from the freezing methods. Particularly in the case of melons, cryogenic freezing resulted in a higher pH compared to mechanical freezing. °Brix changes were influenced by both the fruit matrix and storage duration, while showing no significant impact from the freezing methods. The reduction in titratable acidity caused by freezing methods was influenced by the fruit matrix, with a significant difference observed only in the case of melons, where cryogenically frozen samples exhibited lower titratable acidity than mechanically frozen samples. Additionally, frozen storage distinctly impacted the titratable acidity. Quality index improvement was contingent on the combination of freezing condition/method and fruit matrix. Cryogenic freezing resulted in a higher value for melons, whereas the opposite effect was observed for apples. Cryogenic freezing yielded slightly firmer results than mechanical freezing despite a much slower air velocity (0.5 m/s compared to 4 m/s), regardless of the fruit matrix; the gas temperature was much lower in cryogenic than in blast air freezing (-80 °C compared to -40 °C) ensuring a faster freezing. Moreover, firmness alteration was subject to the fruit matrix and the duration of frozen storage. Exudation loss and total colour change were significantly reduced with cryogenic freezing. Cryogenic freezing notably reduced PPO activity in apples. Freezing conditions did not affect POD activity in melons. Enzymatic activity was significantly influenced by storage duration. Mechanical freezing displayed lower soluble protein levels than cryogenic freezing. Lastly, cryogenically frozen apple samples exhibited less microstructure deterioration. As shown in this study, the impact of cryogenic and mechanical freezing on the physicochemical parameters of fruit matrices is influenced by several factors, including the inherent properties of the fruit matrices, the freezing methods employed, and the frozen storage durations. Additionally, the final outcome can be affected by the method used for thawing or the combination of freezing and thawing methods. Furthermore, the sample size and thawing time are crucial parameters that determine the distinguishable differences between cryogenic and mechanical methods. The stability of frozen storage is significantly influenced by storage factors such as time, temperature, and temperature stability during storage. These parameters play a vital role in the overall stability of the frozen product. From our perspective, conducting more studies involving different fruit species, varying sample sizes, thawing methods and times, as well as storage conditions, will enable both industry and academia to develop a more comprehensive understanding of the advantages and disadvantages of cryogenic freezing in fruit matrices.

Funding

This work received no external funding.

Ethical statement

In our research, no studies involving humans or animals were conducted, and no such subjects were used in our experiments.

CRediT authorship contribution statement

Piyush Kumar Jha: Data curation, Formal analysis, Validation, Writing – original draft. **Nicolas Chapleau:** Data curation, Formal analysis, Investigation, Methodology. **Pierre-Emmanuel Meyers:** Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing. **Didier Pathier:** Funding acquisition, Project administration, Writing – review & editing. **Alain Le-Bail:**

Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.afres.2023.100374](https://doi.org/10.1016/j.afres.2023.100374).

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