

Effects of dehydrofreezing conditions on carrot β -carotene and kinetics of β -carotene change in dehydrofrozen carrots during storage

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Abstract

Dehydrofreezing is a food freezing method in which the foods are partially dehydrated before freezing. In this study, carrots were frozen with convective (-30, -35, -40°C and 2 m/s airflow) and cryogenic methods after dehydrating them by different methods (osmotic dehydration, convective and vacuum drying). The effects of dehydration method, freezing conditions and storage time on β -carotene amounts of dehydrofrozen carrots and the changes in β -carotene content of dehydrofrozen carrots during storage for six months at -20°C were investigated. The findings obtained in this study showed that the reaction representing the carotene change in the storage process took place in accordance with the first-degree kinetic model. The reaction rate constants (k) were affected by freezing conditions, and the k value decreased as the freezing temperature decreased. The β -carotene losses were less in the storage process in the cryogenically frozen carrots compared to those frozen by the convective method. As the freezing temperature decreased, the half-life period increased.

Keywords: Carrot, dehydrofreezing, β -carotene, kinetic.

Practical Application: Traditional freezing methods cause serious damage to the vegetables. Dehydrofreezing is a food processing method, which is expected to cause less damage to the vegetal product tissue due to the less amount and size of ice crystals formed during freezing. In conclusion, according to the results, freezing the carrots dehydrated by vacuum drying and osmotic dehydration by the cryogenic method to protect the β -carotene gives better results.

1 Introduction

Carrot is a food item that is willingly consumed by almost everyone. It is known as an important food for human consumption. Its significance is due to its carotenoid content and antioxidant effect (Demiray & Tulek, 2017). Carrots are mostly consumed as fresh in a little period of the year. However, processes, such as drying and freezing, allow this food to be consumed in a longer period. During the application of these processing and preservation methods, some negative effects may occur concerning color, texture and important nutrients (James et al., 2014; Demiray & Tulek, 2017; Muthukumarappan et al., 2019). Thus, the effects of the applied processes on β -carotene, which is an important nutrient element of carrot, has often been investigated (Kamiloglu et al., 2016).

β -carotene, which has been the subject of many studies in recent years, is abundantly found in yellow, orange and dark-green fruits and vegetables. The β -carotene content of carrots varies according to species and growing conditions. Its nutritional importance is well known, and it has biological and medicinal benefits. Moreover, β -carotene is a procurer of vitamin A, and it is also considered important concerning the roles of the vitamins in the organism (James et al., 2014; Demiray & Tulek, 2017). β -carotene is an important carotenoid concerning color and nutritional properties of carrots and is affected by drying and freezing processes. According to the nature of the process applied to food, reactions, such as biosynthesis, degradation and

isomerization, may occur in the structure of food molecules (James et al., 2014; Khattab et al., 2015; Demiray & Tulek, 2017; Muthukumarappan et al., 2019). Therefore, detecting the loss of valuable components, such as β -carotene, lycopene, ascorbic acid and color substances during the processes and storage of foods, can be used as a tool in determining the quality of the products (Dutta et al., 2005).

The freezing process is an important basic food processing method that highly preserves the quality features of fruits and vegetables at a high level and allows them to be processed for a long period in the industry (Demiray & Tulek, 2010; Demiray & Tulek, 2017). Freezing process brings some changes to food product. Because, freezing converts water into ice and the properties of ice and water are quite different. The product quality formed after freezing is associated with the freezing rate and the amount and size of the ice crystals formed. The properties of ice effects the properties of frozen food products (Cemeroglu, 2013; Muthukumarappan et al., 2019). Accordingly, frost damage occurs in the tissue of the food. The tissue damage causes the degradation of important nutritional components by enzymes and other biochemical reactions. Reducing the tissue damage that occurs during the freezing process also ensures that the sensitive nutrient components in the foods like β -carotene are less lost in the storage process. Moreover, degradation of

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β -carotene affects the color, nutritional value and flavor of the carrots (James et al., 2014; Khattab et al., 2015).

Pre-freezing treatment can help reduce the quality loss of foods. Dehydrofreezing is a food freezing method in which the foods are partially dehydrated to specified water content and then frozen with an appropriate freezing method. Removing some of the water in food helps to minimize the formation of large ice crystals (Fan et al., 2020). It is a food processing method, which is expected to cause less damage to the vegetal product tissue due to the less amount and size of ice crystals formed during freezing. Removing some amount of water causes reducing the amount of water to be frozen during the freezing process. Reducing the water to be frozen allows forming ice crystals without damaging the cellular structure of vegetables (Li & Sun, 2002; James et al., 2014). In dehydrofreezing technology, compared to traditional freezing methods, because of the reduction of tissue damage, sensitive nutrients are less affected by process conditions. In an oxygen-containing environment, the losses of sensitive nutrients are due to the activity of enzymes. Moreover, when the damage of vegetative tissue increases, the activity of enzymes increases. The decrease in water content also provides some advantages, such as low freezing time and reducing the freezing start point. In addition, dehydrofreezing technology seems to be more advantageous as it means more weight product for unit volume (Cemeroglu, 2013; James et al., 2014; Demiray & Tulek, 2017)

In the literature, there are some studies about dehydrofreezing of the carrots. In these studies, slow freezing methods are mostly used, and kinetic modeling studies related to the nutritional components of dehydrofrozen products are very limited (James et al., 2014; Schudel et al., 2021).

The present study aimed to investigate the effects of dehydration and freezing methods and storage time on β -carotene amounts of dehydrofrozen carrots. For this purpose, the carrots were frozen using different methods after being dehydrated to a certain extent and then stored at $-20\text{ }^{\circ}\text{C}$ for different periods. Changing the kinetics of β -carotene in dehydrofrozen carrots during storage was also investigated.

2 Materials and methods

2.1 Materials

Fresh carrots (*Daucus carota* L. cv. Nantes) were purchased from a local market (directly from a farmer) in the province of Denizli. Until dehydrofreezing, the products were kept in the refrigerator ($+4\text{ }^{\circ}\text{C}$) in polyethylene bags. The β -carotene standard was obtained from Sigma (St. Luis, MO, USA) and the C18 column (250x4.6 mm ID, 5 μm) was obtained from ACE (Aberdeen, Scotland). Mobile phase chemicals used in extraction and HPLC analysis were obtained from Merck (Darmstadt, Germany). Liquid nitrogen was provided from a nitrogen storage facility in Denizli (Ege Company, Denizli, Turkey).

2.2 Methods

2.2.1 Dehydration Process

The materials to be used in the trials were kept in the refrigerator at $4\text{ }^{\circ}\text{C}$ for 1-2 hour until processing. Then they were subjected to washing and selection. The carrots were sliced into

discs with a thickness of $9 \pm 1\text{ mm}$ and a diameter of $28 \pm 2\text{ mm}$. Sliced carrot samples were subjected to a certain amount of dehydration ($27\% \pm 3$ water loss) with convective (with cabin type dryer), vacuum drying and osmotic dehydration before freezing. The prepared carrot samples were partially dehydrated to the desired dehydration rate ($27\% \pm 3$ water loss) under conditions determined by preliminary trials.

In convective drying, 500 g of carrots were placed in perforated wire trays as a single layer and dried at a rate of 2 m/s airflows at 20% relative humidity, at a temperature of $65\text{ }^{\circ}\text{C}$ for 60 minutes in a cabin type dryer (Yucebas Machine Analytical Equipment Ltd. Inc., Izmir, Turkey).

In vacuum drying, sliced carrot samples were weighed approximately 125 g and subjected to dehydration at $75\text{ }^{\circ}\text{C}$ and 60 mmHg absolute pressure for 90 minutes in vacuum dryer (Model EV 018, Nuve Laboratory Sterilization Technology, Ankara, Turkey).

In osmotic dehydration, 250 g of carrot samples was dehydrated in a 50° Brix sucrose solution for one hour at $35\text{ }^{\circ}\text{C}$ in a shaking water bath (Model ST 30, Nuve Laboratory Sterilization Technology, Ankara, Turkey). In osmotic treatment, the sample/osmotic solution ratio was 1/5.

2.2.2 Freezing process

Fresh (not dehydrated) and partially dried carrot samples were subjected to the freezing process with the air-flow freezing method and cryogenic method. In the convective freezing process performed with the airflow flat type freezer, the partially dried samples were placed in polyethylene containers as 90-100 g after cooling them under room conditions. The containers were tightly closed with polyethylene stretch film. The convective freezing process is performed under an air velocity of 2 m/s at -30 , -35 and $-40\text{ }^{\circ}\text{C}$ temperatures in an airflow flat freezer (Elcold, Altan Industrial and Laboratory Equipment Industry and Trade Corporation, Istanbul, Turkey). A temperature probe (T type) was placed in the center of a product that represented the thermal center of the containers, and the temperature was monitored during freezing. In the cryogenic freezing process, the samples were immersed in cryogenic liquid (liquid nitrogen). After freezing, cryogenically frozen products were placed in polyethylene containers and tightly covered with stretch film. Convective and cryogenic freezing processes were terminated when the central temperature of the product reached to $-20\text{ }^{\circ}\text{C}$. Depending on the ambient freezing temperature, the time needed for the convective freezing process was between 120-200 minutes. The time needed for the cryogenic freezing process was 15-20 seconds. After freezing, the products were taken to a vertical type freezer (Model FT280, Vestel Electronics Industry, and Trade Corporation, Manisa, Turkey), which was operated at $-20\text{ }^{\circ}\text{C}$ for six months storage.

2.2.3 β -carotene Extraction and HPLC (High-Performance Liquid Chromatography) Determination

β -carotene content was determined according to the method of Demiray & Tulek (2017) on both fresh-frozen (without any dehydration process before freezing) and dehydrofrozen carrot

samples. Four grams of carrot samples were homogenized for a minute with 40 mL of ethanol-hexane solution (4:3 v/v) containing 1% butylated hydroxytoluene (w/v) in a polypropylene centrifuge tube. After homogenization, the samples were centrifuged (Universal 30RE, Hettich Zentrifugen, Tuttlingen, Germany) at $9000 \times g$ at 4 °C for 15 min. Then, supernatants were transferred into amber bottles. Before injection into the HPLC, the supernatants were filtered through 0.45 µm membrane filters (Minisart, Sartorius, Germany).

The HPLC system consisted of a pump and a controller (Shimadzu LC-20AD, Shimadzu Corporation, Kyoto, Japan), a photodiode array detector (SPD-M20A), a degasser (DGU-20A) and a column oven (CTO-20A). The mobile phase included a mixture of acetonitrile, methanol, dichloromethane, and hexane (40:20:20:20, v/v/v/v). The flow rate of the mobile phase was 0.45 mL/min at the temperature of 25°C and the analysis time was 20 min. The injection volume was 20 µL and the detection wavelength was 445 nm. The concentration of β-carotene was calculated from the relative peak area of the β-carotene standard curve ($R^2 > 0.99$). Quantification was done by external standardization. The standard curves were constructed with 6 points and 1, 5, 10, 25, 50 and 100 ppm β-carotene standard concentrations were used for standardization.

The dry matter of carrots were measured by the oven method at 105 °C up to constant weight and the β-carotene contents of carrots were calculated based on dry matter (DM).

2.2.4 Determination of the Kinetic Model (reaction degree) of β-carotene Change during the Storage Process

After cryogenic and convective freezing processes, analyzes were performed in 2-month periods to investigate the change of β-carotene in carrot samples frozen at -20 °C thermal center temperature and stored at -20 °C for six months. To determine the model of the changing kinetics of β-carotene during storage, firstly, the graphics were drawn according to the zero degrees kinetic model and then the first-degree kinetic model. The model in which the highest correlation coefficient was obtained in the graphs was defined as the kinetic model representing the change of β-carotene.

2.2.5 Data Analysis and Kinetic Parameters

The β-carotene change during storage of fresh-frozen and dehydrofrozen carrot samples was based on the following first-order reaction kinetics, as given Equation 1 where k is the reaction rate constant, c_0 is the initial ($t=0$) concentration of carrot β-carotene, c is the concentration of carrot β-carotene at time t .

$$C / C_0 = \exp(-kt) \quad (1)$$

The half-life time value ($t_{1/2}$) refers to the time required for the loss of half of the β-carotene concentration in fresh-frozen and dehydrofrozen carrots. It was calculated by the Equation 2 given below;

$$t_{1/2} = \ln(0,5) / k \quad (2)$$

2.2.6 Statistical analysis

Two replicates were taken for each dehydration and freezing treatment. The statistical analysis of results was performed using a univariate analysis of variance based on ANOVA with the software SPSS 16.0. Duncan multiple range tests ($\alpha=0.05$) were used to investigate the significant differences between different process conditions.

3 Results and discussion

β-carotene contents of fresh-frozen and dehydrofrozen carrots were determined based on dry matter (DM) and the β-carotene data were given in Table 1. The samples obtained after freezing (just before storage) are described as the initial sample in text and the storage time of these samples is given as "0 (zero)" in the tables.

In fresh-frozen and dehydrofrozen samples, the β-carotene amounts of the carrots frozen by cryogenic method were higher than the convectively frozen carrots. When the initial β-carotene values of fresh-frozen carrots were examined, it was observed that the lowest β-carotene content was obtained from carrots frozen at -30 °C, and the amount of β-carotene decreased as the freezing temperature increased. In the 6-month storage period, the β-carotene degradation rate of fresh-frozen carrots frozen in the airflow freezer decreased from 39.1% to 32.32% significantly when the freezing temperature decreased from -30 °C to -40 °C ($p < 0.05$). However, the degradation data obtained from the fresh-frozen carrots by cryogenic method were between 1.2% - 7.98% lower than the fresh-frozen carrots in the airflow freezer.

When the initial β-carotene values of dehydrofrozen carrot samples dehydrated by convective drying method were examined, it was observed that the highest amount of β-carotene was obtained in carrots frozen by the cryogenic method and it was statistically different ($p < 0.05$). Depending on the decrease in freezing ambient temperature, the losses in β-carotene decreased in convectively frozen carrots. Similarly, in the 6-month storage period, it was observed that the β-carotene degradation rate of dehydrofrozen carrots dehydrated by convective method gradually decreased significantly when the freezing temperature decreased from -30 °C to -40 °C ($p < 0.05$). However, the β-carotene losses (40.46%) occurred less in cryogenically frozen carrots compared to convective frozen carrots.

In this study, it was seen that the initial β-carotene content of osmodehydrofrozen carrots were remarkably close to the fresh-frozen carrots. Osmotic pretreatment may have negative or positive effects on β-carotene content. β-carotene is bound with proteins in plant tissue, these proteins are dissolved in water. As a result of pretreatment, such as osmotic dehydration, due to the dissolution of bound proteins in water, the carotenes release into water and the loss of β-carotene may be inevitable (Dutta et al., 2005). However, the osmotic dehydration process may reduce oxygen penetration because of covering the carrot surface by the osmotic solution. Therefore, β-carotene oxidation and losses reduce during storage (Dermesonlouoglou et al., 2007). Besides, in osmotic dehydration, as a result of the penetration of the sugar into the carrots, the binding power of β-carotene to the

Table 1. The mean values and standard deviations (Std Dev) of β -carotene contents of fresh-frozen and dehydrofrozen carrots stored at $-20\text{ }^{\circ}\text{C}$ for 6 months (mg/100g DM).

Storage Time (month)	Freezing Conditions							
	-30		-35		-40		Cryogenic	
	Freshly-frozen							
	Mean	Std Dev	Mean	Std Dev	Mean	Std. Dev.	Mean	Std Dev
0	330.00 Ac* ¹	8.64	332.98 Abc	7.32	353.12 Ab	8.40	412.33 Aa	11.12
2	275.04 Bc	16.17	279.90 Bc	8.15	312.27 Bb	9.24	355.00 Ba	14.50
4	249.39 Cc	13.40	264.12 Bbc	4.53	274.98 Cb	8.70	312.00 Ca	12.70
6	200.95 Dc	5.92	211.96 Cc	12.4	238.98 Db	13.80	284.00 Da	11.60
	Dehydrofrozen (Convectively dehydrated)							
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
0	291.62 Ac	16.67	290.36 Ac	13.06	342.86 Ab	8.58	385.24 Aa	7.79
2	236.79 Bb	14.07	231.43 Bb	12.68	244.07 Bb	9.53	325.24 Ba	15.02
4	180.71 Cc	7.35	189.14 Cbc	7.62	208.28 Cb	14.36	296.37 Ca	13.68
6	191.93 Cc	9.64	132.01 Dc	4.29	166.53 Db	8.03	274.26 Ca	12.66
	Dehydrofrozen (Osmotically dehydrated)							
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
0	330.43 Abc	8.13	343.33 Ab	14.80	314.36 Ac	15.30	404.03 Aa	9.89
2	239.87 Bb	9.49	247.99 Bb	12.18	262.78 Bb	15.42	345.54 Ba	14.10
4	192.46 Cc	14.60	201.53 Cbc	8.83	217.95 Cb	4.71	315.24 Ca	12.86
6	166.98 Db	11.54	178.77 Cb	8.71	198.72 Db	12.06	292.25 Da	11.93
	Dehydrofrozen (Vacuum dehydrated)							
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
0	277.83 Ab	14.57	263.24 Ab	12.51	251.54 Ab	9.61	399.25 Aa	8.44
2	236.20 Bb	6.15	225.52 Bb	13.49	217.82 Bb	9.21	345.56 Ba	15.96
4	204.26 Bcb	3.38	201.36 Cb	7.84	196.21 Cb	4.93	315.67 Ba	14.50
6	193.74 Cb	5.71	184.98 Cb	8.17	182.05 Db	5.57	295.65 Ca	7.75

*Levels not connected by the same letter are significantly different ($p < 0.05$).¹Capital letters indicate the difference between storage times, lowercase letters indicate the difference between freezing conditions.

carrot matrix may have increased and its degradation may have been prevented. For these reasons, it has been reported by some researchers that osmotic dehydration can be used to improve the quality characteristics of frozen products (Chiralt et al., 2001; Fito et al., 2001, Dermesonlouoglou et al., 2016, Fan et al., 2020).

Similarly, for each freezing temperature in a convective environment, in the storage period, the highest β -carotene degradation was determined for the products dehydrated by convective drying before freezing. The lowest β -carotene degradation was determined for the carrots frozen after dehydrating in the vacuum dryer. Similar results were seen in carrots frozen by the cryogenic method after dehydration applications. During six month storage, when the β -carotene degradation rates of the cryogenically dehydrofrozen carrots were examined, the highest degradation rate (31.12%) was observed in fresh-frozen carrots and the lowest degradation rate (25.94%) was observed in carrots frozen after dehydrating in the vacuum dryer. Considering the statistical data in the present study, the findings showed that different dehydration methods used in dehydrofrozen process did not affect the initial β -carotene content of products significantly. However, different dehydration treatments had a significant effect on β -carotene loss of dehydrofrozen carrots in the storage period ($p < 0.05$).

For all dehydrofrozen carrot samples, the amount of β -carotene decreased during the 6-month storage period at $-20\text{ }^{\circ}\text{C}$, and the β -carotene was better protected during storage when the freezing temperature decreased. Also, the statistics showed that freezing temperature and storage time has a significant effect on β -carotene losses of all dehydrofrozen products ($p < 0.05$).

It is also revealed by other researchers that there are losses in the amount of β -carotene in the frozen storage process. Indeed, Crivelli & Poleseello (1973) and Howard et al. (1999) determined that there was a significant decrease in the β -carotene content of carrot samples frozen freshly and kept at $-20\text{ }^{\circ}\text{C}$ for one year.

In another study, the fresh carrots were frozen stored at $-18\text{ }^{\circ}\text{C}$. The number of carotenoids equivalent of β -carotene decreased from 1.498 mg/100 g DM to 1.185 mg / 100 g DM as a result of 1-month storage and decreased to 0.99 mg/100 g DM after 2-month storage and decreased to 0.965 mg/100 g DM after 3-month storage. The decrease in these parameters after freezing shows that the effects of storage conditions are important for carrot β -carotene (Al-Dabbas et al., 2014).

In an investigation where carrots were kept frozen, a significant reduction (up to 40%) of β -carotene content has been reported in the later stages of storage. In the study, it was reported that the loss of β -carotene might be due to non-oxidative changes

(isomerization, epoxide formation, cellular tissue disruption by heat effect) or oxidative changes and oxygen upon when exposing to light. It was also seen that the loss of β -carotene decreased with the decrease in storage temperature. With the increase of storage time and temperature, the loss of β -carotene increased and the effects of temperature were faster (Dutta et al., 2005). In another study, it has been also emphasized that β -carotene degradation changes according to the applied temperature, processing time and storage conditions (Kidmose et al., 2004).

It has been reported that the reduction in the number of antioxidant components, such as β -carotene, which has a function of reducing oxidative damage, may be caused by an increase in malonaldehydes caused by lipid peroxidation and oxidative stress in the storage process (Welti et al., 2002; Eraslan et al., 2007; Turfan et al., 2016; Oz & Karatepe, 2017). In this regard, Oz & Karatepe (2017) made a statement that similar antioxidant mechanisms work to suppress lipid peroxidation and radical formation increase because of protein denaturation. Also, some studies have reported that β -carotenes may turn into vitamin A and it may cause a decrease in β -carotene (Gozukara, 2011; Banala & Karnati, 2015; Oz & Karatepe, 2017). In contrast, another study reported that there was no significant change in the amount of β -carotene in blackberry fruit after a three month storage at $-18\text{ }^{\circ}\text{C}$ (Sikora et al., 2013).

It is generally proposed that the properties of β -carotene are preserved in frozen foods. However, many physical, chemical, enzymatic and microbiological changes during processing and storage may affect the quality characteristics of frozen foods to some extent as a function of time and temperature (Dutta et al., 2005).

In this study, the findings suggest that the β -carotene degradation reaction in the storage process of dehydrofrozen carrots was suitable for the first-degree reaction. Similarly, Dutta et al. (2005) reported that the β -carotene degradation reaction in the storage process of dehydrofrozen carrots is suitable for the first-degree reaction.

β -carotene degradation reaction rate constants of fresh-frozen and dehydrofrozen carrots stored at $-20\text{ }^{\circ}\text{C}$ for 6 months were calculated by plotting the natural logarithm of β -carotene concentration against time (Figure 1-4).

Kinetic data (k value and half-life time) related to β -carotene degradation reactions that were carried out in the process of storage of fresh-frozen and dehydrofrozen carrots are given in Table 2.

It was determined that the reaction rate constants (k value) in the storage process of frozen carrots at $-20\text{ }^{\circ}\text{C}$ for six months were affected by freezing conditions, and the k value decreased as the freezing temperature of frozen carrots decreased. The reaction rate constant values of all carrots frozen with the cryogenic method (up to 0.062 month^{-1}) were lower than the frozen carrots by convective freezing methods (up to 0.137 month^{-1}). It was determined that the freezing temperature affects the reaction rate constant, and β -carotene degradation reaction rates during the storage process of frozen carrots were lower when the carrots were frozen at lower temperatures. Desobry et al. (1998) compiled studies on the storage of fresh carrots at different

temperatures in their study. They reported that β -carotene degradation reaction rate constant values were determined as $1.04 \times 10^{-4}\text{ day}^{-1}$ for carrots were stored at $-20\text{ }^{\circ}\text{C}$ 365 days. In another study, Koca et al. (2007) have stored the dried carrot samples. The β -carotene degradation reaction during the storage period was suitable for the first-degree kinetic model. Similar to

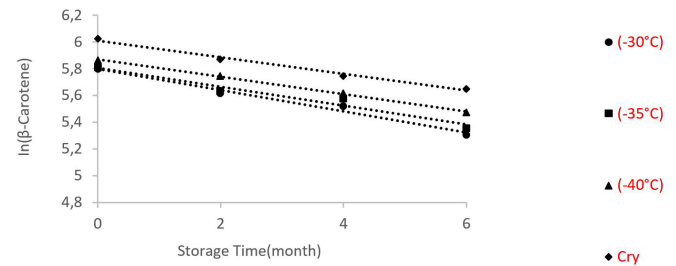


Figure 1. The degradation kinetics of β -carotene in fresh-frozen carrots stored at $-20\text{ }^{\circ}\text{C}$.

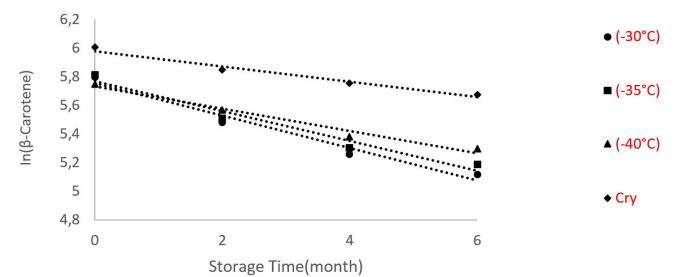


Figure 2. The degradation kinetics of β -carotene in dehydrofrozen carrots (used convective drying) stored at $-20\text{ }^{\circ}\text{C}$.

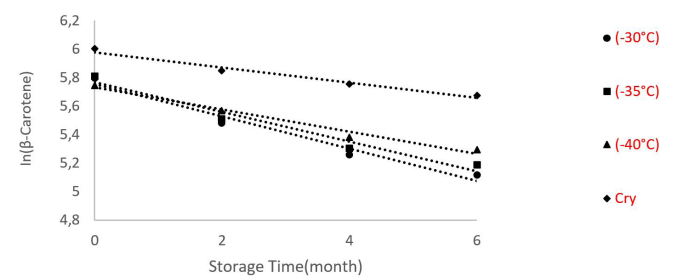


Figure 3. The degradation kinetics of β -carotene in dehydrofrozen carrots (used osmotic dehydration) stored at $-20\text{ }^{\circ}\text{C}$.

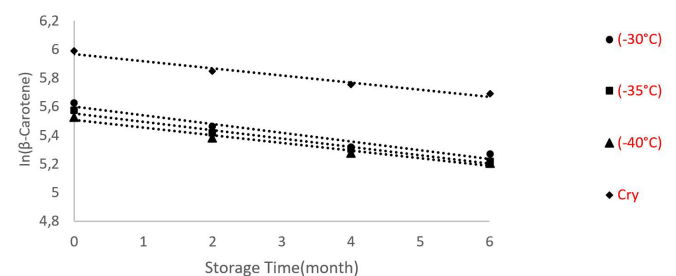


Figure 4. The degradation kinetics of β -carotene in dehydrofrozen carrots (used vacuum drying) stored at $-20\text{ }^{\circ}\text{C}$.

Table 2. The kinetic parameters for β -caroten losses in fresh-frozen/dehydrofrozen carrots during storage.

Freezing Conditions	k (month ⁻¹)	t _{1/2} (month)
Freshly-frozen		
-30°C	0.079	8.77
-35°C	0.070	9.90
-40°C	0.065	10.66
Cryogenic	0.062	11.18
Dehydrofrozen (Convectively dehydrated)		
-30°C	0.137	5.06
-35°C	0.128	5.41
-40°C	0.122	5.68
Cryogenic	0.056	12.38
Dehydrofrozen (osmotically dehydrated)		
-30°C	0.113	6.13
-35°C	0.104	6.66
-40°C	0.078	8.88
Cryogenic	0.053	13.08
Dehydrofrozen (Vaccum dehydrated)		
-30°C	0.061	11.36
-35°C	0.059	11.74
-40°C	0.054	12.83
Cryogenic	0.050	13.86

our study, it was also stated that temperature has an important effect on carotenoid degradation.

Half-life time is the time required for the loss of the concentration of the reactant (β -carotene) to fall half of its initial value. The half-life time is very useful in practice and it helps to predict the amount of β -carotene loss with reference to time. When the degradation reaction rate constant values higher, it represents faster degradation; hence, a lower half-life of β -carotene. In the study, when the half-life times determined for β -carotene exchange reactions in convective freezing were examined, the half-life times increased as the freezing temperature decreased. The highest half-life times obtained from the carrots frozen by cryogenic freezing method. Desobry et al. (1998) reported that in some studies related to the storage of fresh carrots at different temperatures, half-life times of β -carotene degradation reaction were determined as 277 days at -20 °C, 13 days at 5 °C, 7.7 days at 10 °C and 7.4 days at 20 °C.

The results obtained in this study show that the freezing temperature of the carrots has a significant effect on the β -carotene degradation reaction rates ($p < 0.05$). When compared to the traditional freezing methods, especially in the cryogenic freezing method, decreasing the freezing temperature to lower temperatures provides an important advantage in reducing β -carotene losses in the dehydrofreezing and storage process. In addition, the differences between β – carotene losses obtained from different dehydration experiments were significant ($p < 0.05$). The findings also showed that the vacuum and osmotic dehydration applications used in the dehydration part of dehydrofreezing process of carrot samples give better results in terms of protecting β - carotene.

4 Conclusion

Based on the results obtained from the storage process, the degradation kinetics of carrot β -carotene was investigated. It was determined that the reaction representing the β -carotene change in the storage process took place under the first-degree kinetic model. As the freezing temperature decreased, the half-life time increased. It has been determined that the reaction rate constants determined for β -carotene degradation in storage were affected by freezing conditions and it decreased as the temperature decreased. The reaction rate constants of the cryogenically frozen samples were lower than convectively frozen ones. In conclusion, it is thought that freezing the carrots dehydrated by vacuum drying and osmotic dehydration by the cryogenic method to protect the β -carotene gives better results. Pretreated frozen carrots were found to have improved quality stability during subsequent frozen storage. After six months of storage, the dehydrofrozen carrots contained more β -carotene compared with the fresh-frozen carrots. Osmotic and vacuum dehydration were more effective than convective dehydration for protecting β -carotene in dehydrofreezing process and frozen storage.

Cryogenic freezing is successfully applied in the conventional freezing process of foods. As seen in this study, cryogenic freezing was successfully applied in dehydrofreezing of carrots with minimal β -carotene lose. However, as can be seen in the literature, its use in the dehydrofreezing processes is very limited. In this regard, the application of novel advanced freezing methods, which can preserve the quality features of frozen products, such as cryogenic freezing in future studies, can contribute to the development of dehydrofreezing technology.

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References

- Al-Dabbas, M. M., Saleh, M. I., & Al-Ismaïl, K. (2014). Preservation methods impacted phenolic, flavonoid and carotenoid contents and antioxidant activities of carrots (*Daucus Carota L.*). *Journal of Food Processing and Preservation*, 39(6), 1745-4549.
- Banala, R. R., & Karnati, P. R. (2015). Vitamin a deficiency: An oxidative stress marker in sodium fluoride (NaF) induced oxidative damage in developing rat brain. *International Journal of Developmental Neuroscience*, 70(Pt B), 298-303. <http://dx.doi.org/10.1016/j.ijdevneu.2015.08.010>. PMID:26390955.
- Cemeroglu, B. S. (2013). *Basic operations in food engineering* (3. ed.). Turkey: Nobel Publishing.
- Chiralt, A., Martínez-Navarrete, N., Martínez-Monzó, N., Talens, P., Moraga, G., Ayala, A., & Fito, P. (2001). Changes in mechanical properties throughout osmotic processes cryoprotectant effect. *Journal of Food Engineering*, 49(2-3), 129-135. [http://dx.doi.org/10.1016/S0260-8774\(00\)00203-X](http://dx.doi.org/10.1016/S0260-8774(00)00203-X).
- Crivelli, G., & Poleseello, A. (1973). Research on quick-freezing of vegetables. III. Suitability of carrot varieties. *Freddo*, 27, 29-30.
- Demiray, E., & Tulek, Y. (2010). Quality changes in fruits and vegetables during frozen storage. *Academic Food Journal*, 8, 36-44.

- Demiray, E., & Tulek, Y. (2017). Degradation kinetics of β -carotene in carrot slices during convective drying. *International Journal of Food Properties*, 20(1), 151-156. <http://dx.doi.org/10.1080/10942912.2016.1147460>.
- Dermesonlouoglou, E., Giannakourou, M., & Taoukis, P. (2007). Kinetic modelling of the quality degradation of frozen watermelon tissue: effect of the osmotic dehydration as a pre-treatment. *International Journal of Food Science & Technology*, 42(7), 790-798. <http://dx.doi.org/10.1111/j.1365-2621.2006.01280.x>.
- Dermesonlouoglou, E., Giannakourou, M., & Taoukis, P. (2016). Kinetic study of the effect of the osmotic dehydration pre-treatment with alternative osmotic solutes to the shelf life of frozen strawberry. *Food and Bioprocess Processing*, 99, 212-221. <http://dx.doi.org/10.1016/j.fbp.2016.05.006>.
- Desobry, S. A., Netto, F. M., & Labuza, T. P. (1998). Preservation of β -carotene from carrots. *Critical Reviews in Food Science and Nutrition*, 38(5), 381-396. PMID:9704189.
- Dutta, D., Raychaudhuri, U. & Chakraborty, R. (2005). Retention of β -carotene in frozen carrots under varying conditions of temperature and time of storage. *African Journal of Biotechnology*, 4(1), 102-103.
- Eraslan, F., Inal, A., Savastürk, O., & Günes, A. (2007). Changes in antioxidative system and membrane damage of lettuce in response to salinity and boron toxicity. *Scientia Horticulturae*, 114(1), 5-10. <http://dx.doi.org/10.1016/j.scienta.2007.05.002>.
- Fan, K., Zhang, M., Wang, W., & Bhandari, B. (2020). A novel method of osmotic-dehydrofreezing with ultrasound enhancement to improve water status and physicochemical properties of kiwifruit. *International Journal of Refrigeration*, 113, 49-57. <http://dx.doi.org/10.1016/j.ijrefrig.2020.02.013>.
- Fito, P., Chiralt, A., Betoret, N., Gras, M., Cháfer, M., Martínez-Monzó, J., Andrés, A., & Vidal, D. (2001). Vacuum impregnation and osmotic dehydration in matrix engineering, application in functional fresh food development. *Journal of Food Engineering*, 49(2-3), 175-183. [http://dx.doi.org/10.1016/S0260-8774\(00\)00220-X](http://dx.doi.org/10.1016/S0260-8774(00)00220-X).
- Gozukara, E. M. (2011). *Biochemistry. Expanded* (5th ed.). Istanbul, Turkey: Nobel Medicine Bookstores.
- Howard, L. A., Wong, A. D., Perry, A. K., & Klein, B. P. (1999). Carotene and ascorbic acid retention in fresh and processed vegetables. *Journal of Food Science*, 64(5), 929-936. <http://dx.doi.org/10.1111/j.1365-2621.1999.tb15943.x>.
- James, C., Purnell, G., & James, S. J. (2014). A critical review of dehydrofreezing of fruits and vegetables. *Journal of Food Engineering*, 7, 1219-1234.
- Kamiloglu, S., Toydemir, G., Boyacioglu, D., Beekwilder, J., Hall, R. D., & Capanoglu, E. (2016). A review on the effect of drying on antioxidant potential of fruits and vegetables. *Critical Reviews in Food Science and Nutrition*, 56(Suppl. 1), S110-S129. <http://dx.doi.org/10.1080/10408398.2015.1045969>. PMID:26191781.
- Khatab, R., Celli, G. B., Ghanem, A., & Brooks, M. S. (2015). Effect of frozen storage on polyphenol content and antioxidant activity of haskpa berries (*Lonicera caerulea L.*). *Journal of Berry Research*, 5(4), 231-242. <http://dx.doi.org/10.3233/JBR-150105>.
- Kidmose, U., Hansen, S. I., Christensen, L. P., Edelenbos, M., Larsen, E., & Norbaek, R. (2004). Effect of genotype, root size, storage and processing on bioactive compounds in organically grown carrots (*Daucus carota L.*). *Journal of Food Science*, 69(9), 388-394. <http://dx.doi.org/10.1111/j.1365-2621.2004.tb09955.x>.
- Koca, N., Burdurlu, H. S., & Karadeniz, F. (2007). Kinetics of colour changes in dehydrated carrots. *Journal of Food Engineering*, 78(2), 449-455. <http://dx.doi.org/10.1016/j.jfoodeng.2005.10.014>.
- Li, B., & Sun, D. W. (2002). Novel methods for rapid freezing and thawing foods. *Journal of Food Engineering*, 54(3), 175-182. [http://dx.doi.org/10.1016/S0260-8774\(01\)00209-6](http://dx.doi.org/10.1016/S0260-8774(01)00209-6).
- Muthukumarappan, K., Marella, C., & Sunkesula, V. (2019). Food freezing technology. In M. Kutz, *Handbook of farm, dairy and food machinery engineering* (3rd ed., pp. 389-415). London: Academic Press. <https://doi.org/10.1016/C2017-0-01578-1>.
- Oz, O., & Karatepe, M. (2017). Effect of different storage temperatures and durations on vitamin a, β -carotene, astaxanthin and lipid peroxidation level in crayfish fillet. *Journal of Sakarya University Institute of Science*, 21(6), 1537-1543.
- Schudel, S., Prawiranto, K., & Defraeye, T. (2021). Comparison of freezing and convective dehydrofreezing of vegetables for reducing cell damage. *Journal of Food Engineering*, 293, 110376-110387. <http://dx.doi.org/10.1016/j.jfoodeng.2020.110376>.
- Sikora, E., Bieniek, M., & Borczak, B. (2013). Composition and antioxidant properties of fresh and frozen stored blackthorn fruits (*Prunus Spinosa L.*). *Acta Scientiarum Polonorum. Technologia Alimentaria*, 12(4), 365-372.
- Turfan, N., Kurnaz, A., Alay, M., & Sariyıldız, T. (2016). Determination of some chemical properties in taskopru garlic stored under different conditions. *Journal of Kastamonu University Faculty of Forestry*, 16(2), 427-437. <http://dx.doi.org/10.17475/kastorman.289753>.
- Welti, R., Li, W., Li, M., Sang, Y., Biesiada, H., Zhou, H. E., Rajashekar, C. B., Williams, T. D., & Wang, X. (2002). Profiling membrane lipids in plant stress responses. role of phospholipase in freezing induced lipid changes in arabidopsis. *The Journal of Biological Chemistry*, 277(3), 1994-2002. PMID:12077151.