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THE EFFECT OF FREEZING ON THE PHYSICO-CHEMICAL PROPERTIES OF TOMATO FRUITS (*SOLANUM LYCOPERSICUM* L.)

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The modifications of the physico-chemical properties of tomatoes were investigated in case of freezing, applied on two varieties of cherry tomatoes (Flaviola and Ema) cultivated in Buzău, Romania. Preserving by freezing is a common method of keeping the physico-chemical properties for the tomato fruits at home. Fresh fruits and vegetables, when harvested, keep on undergoing chemical modifications likely to bring forth product alteration and damaging. That is the reason why such products must be frozen as soon as possible after harvesting and upon their maximum degree of ripening. The outcomes achieved as a result of the research regarding the content of macroelements (Ca, K, Mg, Na), microelements (Fe, Mn, Ba, Cu, Ni) and also the one in carotenoids (lycopene and β-carotene) after freezing, show that this procedure considerably affected both tomato content as compared to the sample in its fresh condition, which means that there was a certain nutritional value loss. More specifically, in case of the Ema tomato, the content of potassium (K) increased from 141.2 mg L^{-1} to 186.1 mg L^{-1} and for Flaviola from 154.6 mg L^{-1} to 165.53 mg L^{-1}, content of iron (Fe) decreased from 181.37μg L^{-1} to 126.70 μg L^{-1} and the content of copper (Cu) increased for both tomatoes, in case of the Flaviola from 30.1 μg L^{-1} to 35.0 μg L^{-1} and for Ema sample from 31.55 μg L^{-1} to 76.13 μg L^{-1}.

Keywords: lycopene, β-carotene, storing conditions, preservation process.

1. Introduction

Tomato fruit belongs to the genus of *Lycopersicum* of the family Solanaceae, botanically a fruit considered as a berry, but legally a vegetable [1]. The relatively short period of vegetation has led consumers to find and apply certain processes of preservation, with an aim to obtain products than may be successfully consumed even while the tomatoes are not able to provide their natural product, at parameters as close as possible to the natural ones.

By freezing food, people want to preserve its characteristics, expecting to encounter similar characteristics when they eat it again. If these properties have been changed by the preservation process beyond acceptable limits, it means that those foods are no longer good for human consumption [2].

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Water is more than 90 % from the weight of most fruits and vegetables for instance when a tomato fruit is thawed, it becomes soft and aqueous; in addition, it loses its nutritional value, as well. Because of the high level of water content, the rate of degradation reactions in fruits and vegetables is high. This situation increases the significance of preservation techniques [3]. For that, freezing process is a combination of the beneficial effects of low temperatures at which microorganisms cannot grow, chemical reactions are reduced, and cellular metabolic reactions are delayed [4]. According to freezing rate, the foods were collected in 4 main groups. In the first group, the quality of the food is not affected by the freezing rate, for example in the case of peas and greasy meat. For the second group (fish and lean meat), the higher freezing rate does not make the quality better. Instead, for the third group (fruits and vegetables), the quality of the food is protected at an increasing rate. In the case of the tomatoes and cucumbers which belong to the fourth group, the quality is directly affected by the rate of the freezing process [5].

Cherry tomatoes which are in the last group have higher dry matter than tomato fruits and higher levels of soluble solids. Moreover, due to high sugar and organic acid content, cherry tomatoes have a sweeter and more aromatic flavor [6]. It is therefore important to know whether tomatoes preserve their nutritional value by freezing over long periods of time. Preserving food in low temperature (refrigeration, chilling and freezing) has become a popular food processing in food industry after World War II [7].

The purpose of this research was to check if the tomatoes keep their initial characteristics by freezing, and if they are good for human consumption for a longer time (12 months) after thawing. In previous studies, tomatoes were frozen for a maximum period of 6 months. Tomato quality and its potential health benefits are directly related to its chemical composition. The characterization of nutritional properties of this variety of tomatoes is essential to choose suitable donor parents for breeding programs.

2. Materials and Methods

Were studied fruits belonging of 2 varieties of cherry tomatoes (Flaviola and Ema), cultivated in Romania. The tomatoes were grown in March and harvested in July 2021. Approximately two kg of fruits belonging to each variety, all of them in the red ripping stage, were harvested at random from 10 different tomato plants located in the same plantation area**.** The freshly collected fruits were washed three to four times with distilled water to remove foreign materials. Before being transferred into a sealed container and stored, the samples were homogenized by means of a Grindomix blender. They were then frozen, one kg of each variety, for 12 months at -20°C, and analysed right after thawing. Certain samples taken from the fresh tomatoes (one kg) were used as references ones.

2.1. Determination of micro - and macroelements content

Fruit samples (three replicates) were digested in HNO_3 (65% Merck Supra Pure) and H_2O_2 (30% Merck Supra Pure) until a transparent solution was obtained. The micro - (Cu, Fe, Mn, Cu and Ni) and macroelements (Ca, K, Mg and Na) concentrations were determined using by ICP spectroscopy and a Plasma Quant PQ 9000 Elite inductively coupled plasma optical emission spectrometer (ICP-OES). Data are expressed as µg L^{-1} (for microelement) and mg L^{-1} (for macroelement). The determination of the micro- and macroelement content took place by the official method for determining the heavy metals contained in the foodstuff (AOAC's official method - 01.2015) and by the method recommended by Milestone Ethos Up Digestion Apps. The elemental content of fresh tomatoes was compared with that of frozen tomatoes.

2.2. Determination of lycopene and β-carotene content

It was determined using the method proposed by Nagata& Yamashita (1992), with small modifications.

An average sample was made of 5 fruits that were mixed in the Grindomix robot for 10 seconds at a speed of 0.55 rpm. A quantity of 0.5 mL of the obtained tomato juice was homogenized with 8 mL of acetone/hexane solution (4:6 v/v) thus obtaining the supernatant. The solution obtained was read in a spectrophotometer. The beta-carotene and lycopene content were determined using the formula:

$$\beta - carotene\ mg\ (100\ ml)^{-1} = 0.216 \cdot A_{663} - 1.220 \cdot A_{645} - 0.304 \cdot A_{505} + 0.452 \cdot A_{453} \quad (1)$$

$$Lycopene\ mg\ (100\ ml)^{-1} = -0.0458 \cdot A_{663} + 0.204 \cdot A_{645} + 0.372 \cdot A_{505} - 0.0806 \cdot A_{453} \quad (2)$$

3. Results and discussions

Raw materials as control and slow freezing, in home type freezer (-18°C), samples were compared statistically for the physical (pH, humidity (H %) content and dry substance (DS %) content) and chemical (micro and macroelements content, titration acidity, lycopene and β-carotene content) quality properties. Samples were thawed at +4°C in refrigerator before the analyses. All experiments were performed in triplicate**.** The extent to which the micro- and macroelement content was affected by freezing in case of the two varieties under trial is set out in the graphs 1 to 4 and for the other physico–chemical properties (pH, humidity H, titration acidity TA, lycopene, β- carotene) in Table 1.

Table 1

R^2 value from one UV-VIS data set at various analyte concentrations for the macroelements (Ca, Mg, K, Na) and for the microelements (Fe, Mn, Ba, Cu, Ni)

Element	λ (nm)	R^2	$y = a + bx$	
			a	b
Ca	422.673	0.9993	8880.986	67999.897
Mg	279.553	0.9967	1067415.700	5628500.600
K	766.491	0.9935	12282.911	25497.931
Na	589.592	0.9993	96906.702	143051.250
Fe	259.940	0.9998	573.716	352.433
Mn	257.610	0.9992	136.005	1162.741
Ba	455.403	0.9993	6813.999	14702.496
Cu	327.396	0.9975	107.858	158.265
Ni	221.648	0.9962	64.147	62.318

The physical characteristics and chemical composition of tomatoes are influenced by the variety, the age of the fruit and certain external and internal factors [9]. Quality and flavour of the processed products depend upon the chemical composition of the tomatoes which has been reported to vary greatly with the variety [10]. The modifications undergone by the products as a result of freezing are physical ones (water evaporation, colour change, consistency), colloidal ones (juice losses), chemical ones (the catalysation of the enzymes belonging to the peroxidases, oxidases and phenoloxidases group) and nutritional value ones (vitamin losses). Minerals are inorganic solid substances that come up naturally.

The outcomes achieved as a result of the research regarding the content of macro elements after freezing show that this procedure considerably affected the potassium content for both varieties of tomatoes studied, in the sense that, the value increased as compared to the sample in its fresh condition, which means that there was a certain nutritional value loss (Fig. 1).

More specifically, in case of the Ema tomato, the content of potassium (K) increased from 141.2 mg L^{-1} to 186.1 mg L^{-1} and for Flaviola from 154.6 mg L^{-1} to 165.53 mg L^{-1}. Researchers have previously confirmed that mineral concentrations in tomato fruits are strongly influenced by the genotype. Regardless of the variety, K is the prevalent mineral found in tomatoes [11].

According to Rouphael et al. (2017) K was by far the most abundant mineral constituent in two different greenhouse tomato cultivars, followed by Ca, P, Mg, and Na. Similar rezults of macroelements were found by Bonemann et al. (2021), who reported values of K, Mg, and Ca between 217.3 mg/100 g fw and 377.9 mg/100 g fw, 8.0 mg/100 g fw and 10.8 mg/100 g fw, and 4.2 mg/100 g fw and 18.7 mg/100 g fw, respectively, in different tomato cultivars from Brazil.

In the same time, Flaviola sample underwent a significant drop in terms of magnesium (Mg) content, namely from 5.16 mg L^{-1} to 3.83 mg L^{-1} and Ema sample from 4.73 mg L^{-1} to 3.26 mg L^{-1}, respectively; the remaining elements underwent unsignificant reductions.

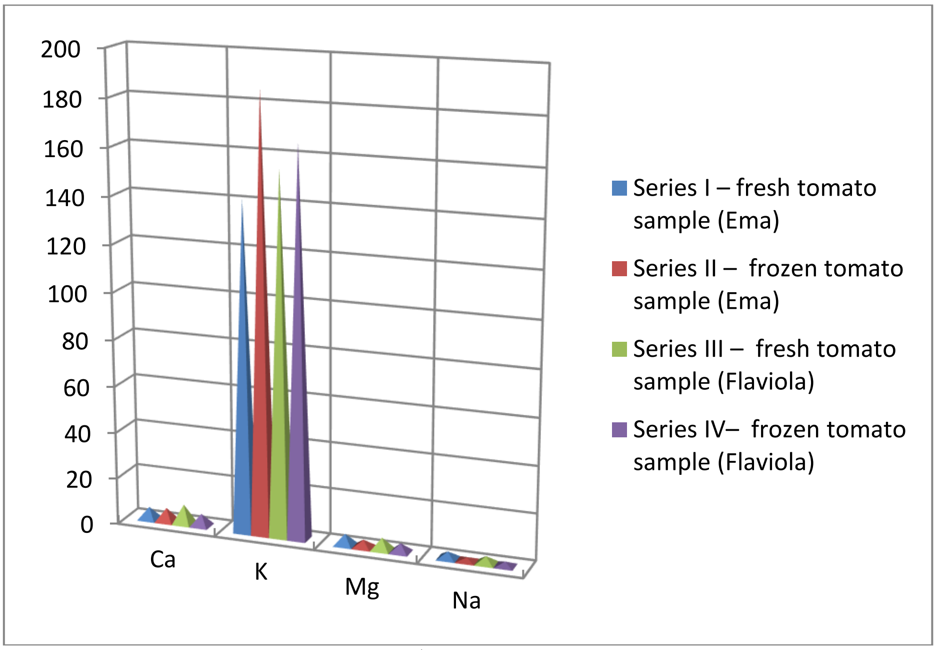

Fig. 1. The macroelement content (mg L^{-1}) of the fresh and frozen, Ema and Flaviola tomato sample

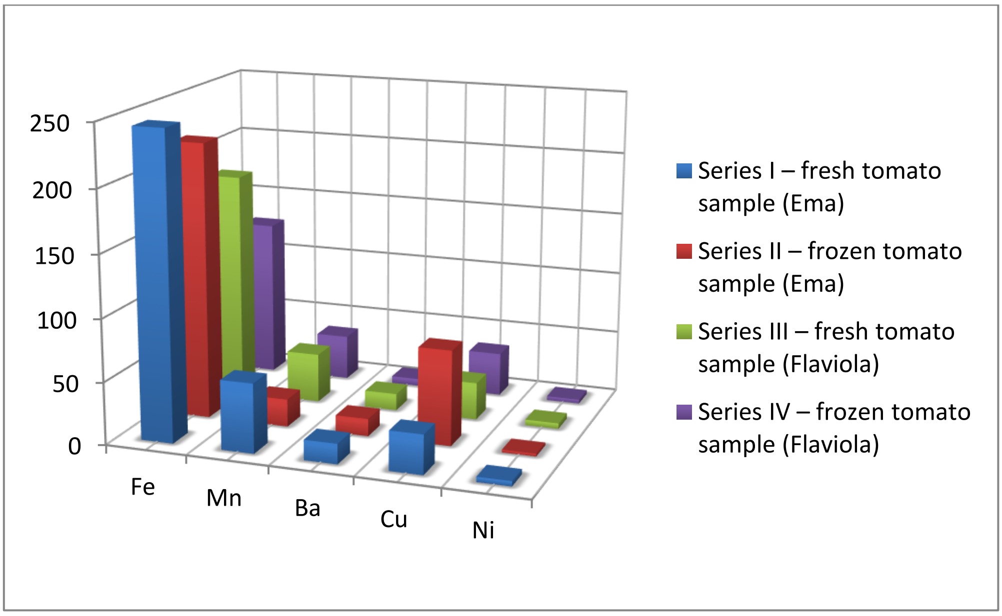

Fig. 2. The microelement content (μg L^{-1}) of the fresh and frozen, Ema and Flaviola tomato sample

Regarding the content in microelements, in case of the Flaviola sample, the content of iron (Fe) decreased from 181.37 µg L^{-1} to 126.70 µg L^{-1}. The content of copper (Cu) increased for both tomatoes, in case of the Flaviola from 30.1 µg L^{-1} to 35.0 µg L^{-1} and for Ema sample from 31.55 µg L^{-1} to 76.13 µg L^{-1} (Fig. 2).

Farooq et. al (2020), investigated the physicochemical and nutraceutical properties of tomato powder as affected by pretreatments, drying methods, and storage period and found similar results to this study.

Also, in the case of the carotenoid content, they suffered significant losses (Table 2).

Table 2

Effect of freezing method on physico-chemical properties of tomatoes (1- fresh sample, 2- frozen sample)

TOMATO TYPE	Lycopene (mg (100 mL)$^{-1}$	β-carotene (mg (100 mL)$^{-1}$
Ema_1 Ema_2	0.76 ±0.01 0.26 ±0.01	0.14±0.04 0.35±0.02
$Flaviola_1$ $Flaviola_2$	0.98±0.03 0.60±0.01	0.11±0.01 0.22±0.02

Values are means of three replications ± standard deviation ($p \leq 5$ ppb)

Initially, the Ema sample had a lycopene content of 0.76 mg (100 mL)$^{-1}$ and Flaviola 0.98 mg (100 mL)$^{-1}$, after freezing it decreased to 0.26 mg (100 mL)$^{-1}$ and 0.60 mg (100 mL)$^{-1}$, respectively. During a 48-week frozen storage of tomatoes, the gradual reduction of carotenoids was accompanied by a change of colour from red to red with a yellow shade. Instead, the β-carotene content increased in the case of the 2 tomato samples as for Ema from 0.14 mg (100 mL)$^{-1}$ to 0.35 mg (100 mL)$^{-1}$ and for Flaviola from 0.01 mg (100 mL)$^{-1}$ to 0.02 mg (100 mL)$^{-1}$. Similar results were reported by Lisiewska and Kmiecik (2000). Freezing does not prevent the degradation of carotenoids is the prevailing opinion. Biacs and Wissgott (1997) affirm that the losses are above-all due to the activity of enzymes, particularly in an oxygen environment. Urbanyi and Horti (1989) in some tomato cultivars observed a significant increase in the contents of carotenoids, betacarotene, and lycopene in relation to the raw material after 1-months' storage of frozen tomatoes, although, after a further 3 and 6 months, the preservation of these compounds was much poorer than that found in the present experiment. Also, they observed that, during a 24-week frozen storage of tomatoes, the gradual reduction of carotenoids was accompanied by a change of colour from red to red with a yellow shade and therefore the colour of fruits seemed increasingly lighter. In this study, organoleptically discernible changes were noted only after 12 months of storing frozen tomatoes at -20℃.

Brovchenko and Golbert (1973) observed preservation of beta-carotene at a level of 90% after 9-months' storage of frozen tomatoes. After 12-months' storage at -20℃, the losses of beta-carotene 51%, and of lycopene 48%.

These modifications of the content may be due to several factors, namely by freezing, water passes from the liquid state directly into the vapour one and in this way the solution gets concentrated, because, generally speaking, thawing takes place slower than freezing.

4. Conclusions

In this study, it was evaluated the nutritional quality of tomatoes if they are subjected to freezing by consumers, in a refrigerator at home. Regarding the studied nutrients, it was observed that the lycopene and beta-carotene were mostly well preserved in the frozen samples compared to the fresh ones. The results obtained indicated that the freezing for a long time, it's a convenient solution if we want also, to preserve the content of micro- , macro elements of tomato fruit.

In conclusion the varieties of tomato analyzed here can be considered as good sources of some mineral elements, some of them with antioxidant properties. These results could help in the conservation of an important part of the agricultural biodiversity, and the high mineral and trace element contents detected in these varieties are potentially useful for tomato breeders working on the development of new varieties with improved composition.

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