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COMPARATIVE ANALYSIS OF FOREST-FRUIT CONSERVATION PROCEDURES BY FREEZING AND LYOPHILIZATION

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Abstract: *The paper presents a parallel between the two conservation modalities of forest fruits, by freezing, respectively by lyophilization. Both conservation procedures share a single purpose, which is, to stop the fruit spoilage phenomena and to preserve their freshness, wholeness, nutritional value and organoleptic features for as long as possible, based on biological and physical processes. Because of their chemical composition, fruits are very little resistant to fresh storage. After the harvest, fruits lose their natural immunity and undergo changes in their chemical composition, to wit they spoil. The main agent of fruit spoilage are microorganisms (bacteria, yeasts and molds), which find therein a favourable environment for their development, made up of water, sugars, starch, nitrogenous substances.*
Keywords: *forest fruit, conservation, freezing, lyophilization.*

1. INTRODUCTION

Conservation is the operation or treatment which stops the spoilage caused by biological, physical, chemical, atmospheric agents on perishables, such as forest fruits, vegetables, and other biological raw materials.
Because of microorganisms and enzymes, numerous raw materials and food products spoil, shortening their storage life, a phenomenon which can be improved by conservation.
Table 1 comparatively shows the essentials of the preservation by freezing, respectively lyophilization.

Table 1: Definition of freezing, respectively lyophilization

Freezing: ✓ Frozen fruits keep part of their vitamins and enzymes still active, which makes them *"almost living"* foods, after defrosting.	***Lyophilization:*** ✓ Lyophilized fruits are the only ones which keep their *"blood"*, even after having been conserved.
= it is a conservation method based on: • cooling foods, down to much lower temperatures than the water solidification point, -18…-45°C, thus increasing the permissible storage life of foods over 5...50 times the preservation by freezing; • the biological principle of anabiosis-physiobiosis, but the preservation method is crioanabiosis.	= it is a conservation method based on: • freezing foods, followed by eliminating almost all water, by vacuum sublimation of ice (water passes directly from the ice into the vapour state) with controlled heat intake, followed by a secondary drying, with a view to removing unfrozen water, thus inhibiting the development of bacterial flora; • biology and physics principles, namely: anabiosis, freezing and sublimation in vacuo.

It is recommended, for freezing, respectively lyophilization, to use only fresh, healthy, ripe, sorted (without foreign bodies) fruits, not attacked by insects, unfermented, not moldy, picked up shortly before freezing. The fruits must meet the specific optimal gustative requirements, being picked up at their optimum harvest maturity.

2. MATERIAL AND METHOD

Table 2 shows some of the most important freezing, respectively lyophilization procedures.

Table 2: Types of freezing, respectively lyophilization

➢ **freezing**, we distinguish:	➢ **lyophilization**, we distinguish:
• *slow freezing* (temperature of -18...-20°C for 80 hours), where the temperature penetration speed and crystal formation speed in the product is very low, the duration being in terms of days. Thus, big crystals take shape, which deform the product tissue. Therefore, slowly frozen products give a greater amount of juice, when defrosted. At the same time, the product is deformed, because the tissue is destroyed; • *fast freezing* (temperature of -30...-35°C, for 24 hours), the process lasts only a few hours, depending on the product volume and on the device resorted to. The freezing time of the fruit in packages is 120 minutes. The crystals which take shape are small, and do not deform the cell tissue. At fast freezing, crystals take shape concomitantly both between fibres and cells, and within the cell; therefore, the amount of juice pushed out from the cell, due to the mechanical action of ice, is very small. This explains why, when defrosting fast frozen products, the quantity of juice which is formed is very small, and the tissue has no significant degradation; • *ultra-fast freezing* (temperature of -35...-40°C), consists in freezing foods in a few tens of seconds, up to one minute, by immersion in liquified nitrogen or nitrous oxide. Following the experimental research, it was found that the transformations undergone by the protoplasm under fast freezing are lower, because its degradation is lower. Nowadays, for fruit freezing, only fast freezing is used, both because it allows obtaining higher-quality products, and because it has a higher productivity.	• *slow lyophilization*, which targets the gradual loss of latent heat, so that the ambient temperature diminishes by 0,5...1^{o}C/minute. During the freezing, ice crystals take shape, the size of which depends on the freezing speed. In the case of slow freezing, these crystals have a size of several microns, and in the case of extremely slow freezing, the crystals reach dimensions of a few millimeters; • *fast lyophilization* targets the heat loss from the material to freeze; in this case, the temperature drops from +20^{o}C to -170^{o}C in 0,5...1 seconds. Fast freezing has the advantage of giving the product a greater porosity, by multiplying the small-sized ice crystals. The rehydration of the product lyophilized in this way is made in better conditions; • *lyophilization in protective substances* supposes the material to freeze to undergo the protective action of colloidal substance.

The stages of the freezing, respectively lyophilization process are shown in figure 1.

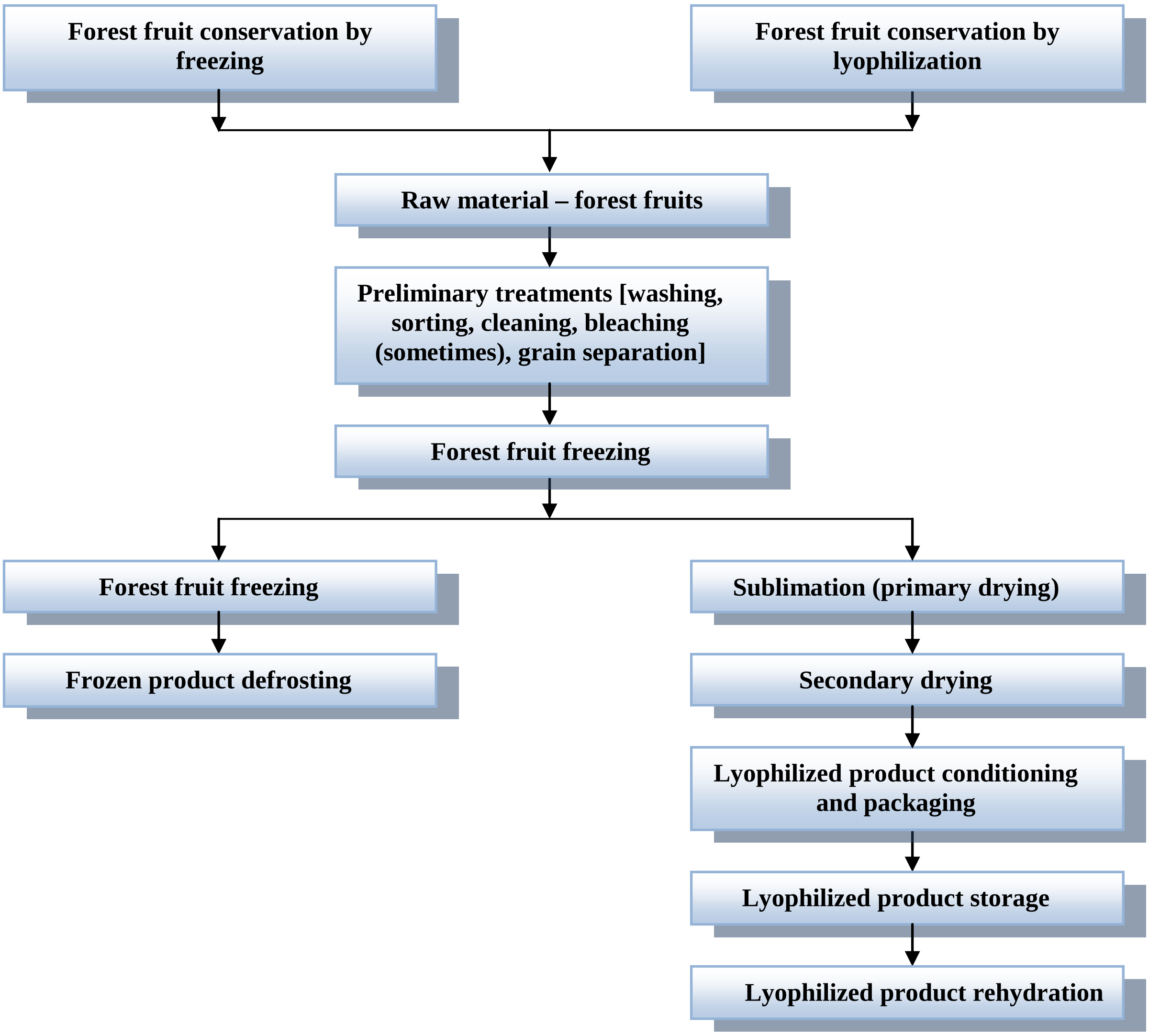


Figure 1: Stages of the freezing/lyophilization process of forest fruits

Table 3 shows a few aspects related to the influence of freezing, respectively lyophilization, on forest fruits:

Table 3: Influence of freezing, respectively lyophilization on forest fruits

➢ **by freezing**, a series of changes occur:	➢ **by lyophilization**, a series of changes occur:
• *physical:* which refer to volume, consistency and weight. By freezing, food volume increases by 6-7%, inasmuch as, by cooling, the water in the product solidifies and increases its volume by 9-10%. By lowering the temperature, food consistency increases and it has a higher hardness, as the freezing temperature is lower. The products to freeze, not packed in water-vapour impermeable material, lose weight by drying, due to the sublimation phenomenon; • *biochemical:* they occur by the oxidation of the product colorants in the presence of artificially ozone air within the freezing spaces. This biochemical process leads to the colour change of	• *physical:* depending on the product, on the freezing mode and on the parameters of the lyophilization process, cryodesiccation leads to a 2…10% reduction in volume compared to the fresh product; at the same time, the mass reduces to 50…90% of the initial value. Lyophilization can cause product colour changes, due to water removal, yet not influencing product quality. As a result of rehydration, the product texture changes from the initial situation; the slower the freezing, the softer the texture of the rehydrated product will be, which can be accentuated in case of over-rehydration. After rehydration of the product, changes in taste and smell from the initial situation can occur; • *chemical and biochemical:* that occur as a

frozen products. The enzymatic activity of vegetal and animal tissues diminishes; • *histological (structural):* they occur in slowly frozen products, because of tissue breakage by large ice crystals. This method has the advantage of keeping the food vitamins almost completely.	result of substitution, oxidation etc. reactions, which make some of the initial constituents disappear at rehydration, and new constituents appear instead. Ultraviolet radiations can catalyse some reactions; • *of the nutritional value:* keeping the nutritional value of lyophilized products, after rehydration, depends on the product type and process parameters. Thus, a slow freezing speed will lead to cell wall destruction; as a result, the active principles are released, and reactions that diminish the nutritional value occur.

3. RESULTS AND DISCUSSIONS

Table 4 shows the saturation curve diagram for freezing, respectively lyophilization.

Table 4: Saturation curve diagram in case of freezing, respectively lyophilization

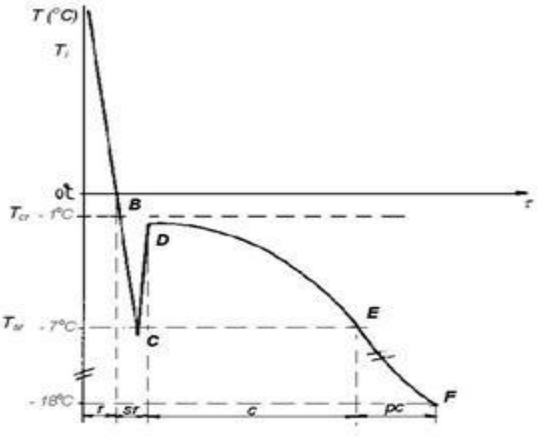
<table>
<tr><th>➢ freezing</th><th>➢ lyophilization</th></tr>
<tr><td>


Figure 2: Curve diagram in case of freezing
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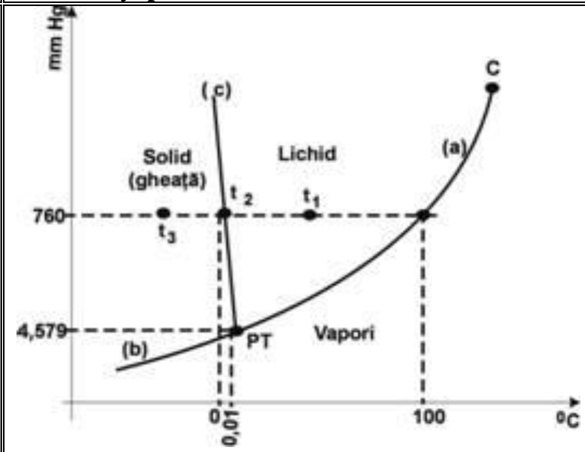

Figure 3: Curve diagram in case of lyophilization
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- **t_1** = critical temp., temp. at which the ice crystals in the cellular liquid emerge = cryoscopic point;

The phenomenon occurs after a preliminary sub-cooling of the cellular juice, at a lower temperature than the freezing point of pure water itself. Therefore, plant products can be kept at lower temperatures than the water freezing point, yet above the sub-cooling point, without their degradation, at slow defrosting.

- **t_2** = temp. which corresponds to biologically and physiologically bound water;

In this case, at defrosting, biological processes are no longer reversible.

- **t_3** = - 25°C is considered the limit temp. down to which freezing can go, and which allows tissue restoration at defrosting, a point below which colloidal substances can no longer absorb the water after defrosting.
- **t_4** = critical temp. which corresponds to the eutectic point, at which the entire amount of water theoretically freezes;

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- **PT** – triple point;
- **C** – critical point.
- **Water sublimation** (the transition from the solid into the vapour state) occurs only if the pressure is below the one corresponding to the triple point (PT), thus being lower than 4,579 mm Hg (0,006 bar).

At constant pressure, the sublimation occurs by temperature increase, hence by heat intake.

The ice sublimation process also occurs at normal atmospheric pressure: at a temperature of -5^{0}C and a relative humidity of 20%, the partial pressure of the water vapour in the air is 0,6 mm Hg (hence lower than the pressure of the triple point), the ice sublimating up to vapour saturation of the environment.

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- $\mathbf{T_i}$ = initial temp. of the product;
- $\mathbf{T_{cr}}$ = temp. of the cryoscopic point, a relatively constant temperature at which ice crystals begin to take shape, having a value ranging between - 1,5...- 5°C;
- $\mathbf{T_{sr}}$ = temp. of sub-cooling which the cellular juice records in the initial phase of the freezing, by thermal inertia, up to the formation of the first ice crystals, being a few degrees lower than T_{cr};
- $\mathbf{T_c}$ = temp. of freezing (- 15°C) at which the freezing of most available water in the product is considered to have occurred (less the constitution water).

In the evolution of the freezing curve (figure 3) the following stages occur over time: *r* -cooling period at refrigeration; *sr*-sub-cooling period; *c*-freezing period; *pc*-post-freezing period.

Table 5 highlights some nutritional values of frozen, respectively lyophilized forest fruits.

Table 5: Nutritional values of some frozen, respectively lyophilized forest fruits

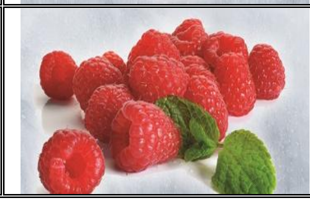
Nutritional values of **FROZEN** fruits		Nutritional values of **LYOPHILIZED** fruits	
	**Strawberries** **Nutritional values** — **per 100g** Energy value: 35 kcal Proteins: 0,4 g Carbohydrates: 9,1 g Fibres: 2,1 g		**Strawberries** **Nutritional values** — **per 100g** Energy value: 289 kcal (1229 kj) Proteins: 7,2 g Glucides: 18,6 g Fibres: 15 g
	**Blackcurrants** **Nutritional values** — **per 100g** Energy value: 50 kcal Proteins: 0,4 g Carbohydrates: 12,1 g Fibres: 2,9 g		**Blackcurrants** **Nutritional values** — **per 100g** Energy value: 190 kcal (810 kj) Proteins: 7,1 g Glucides: 3,8 g Fibres: 42,9 g
	**Redcurrants** **Nutritional values** — **per 100g** Energy value: 33 kcal Proteins: 1,2 g Carbohydrates: 5,3 g Fibres: 2,8 g		**Redcurrants** **Nutritional values** — **per 100g** Energy value: 355 kcal (1480 kj) Proteins: 2,6 g Glucides: 0 g Fibres: 34 g
	**Blueberries** **Nutritional values** — **per 100g** Energy value: 51 kcal Proteins: 0,42 g Carbohydrates: 12,17 g Fibres: 2,7 g		**Blueberries** **Nutritional values** — **per 100g** Energy value: 212 kcal (1157 kj Proteins: 3,8 g Glucides: 4,5 g Fibre s: 15 g
	**Raspberries** **Nutritional values** — **per 100g** Energy value: 45,2 kcal Proteines: 1,1 g Carbohydrates: 10,2 g Fibres: 4,4 g		**Raspberries** **Nutritional values** — **per 100g** Energy value: 192 kcal (814 kj) Proteins: 8,6 g Glucides: 6,6 g Fibres: 44,1 g

Table 6 shows some methods of defrosting, respectively rehydration for forest fruits

Table 6: Methods of defrosting, respectively rehydration for forest fruits

Depending on the nature of the product, on its characteristics and on the purpose of its use, there are several methods for:	
• **defrosting:** Defrosting aims at capitalizing frozen fruits, by means of processing them.	• **rehydration:** Rehydration has the property of introducing moisture back into the fruit, which improves both their aroma and their texture.
• *defrosting in the air*, which is a wide-applicability method, yet with the disadvantage that it takes longer, the products lose weight, and the superficial layers of the products run the risk to oxidize; • *defrosting in the water*, which has the advantage that is defrosts fast, the products do not lose weight, the superficial layers do not oxidize; yet it has the disadvantage that products discolour, nutritional substances are lost, and superficial layers decrease in consistency. Water temperature must be below 20°C and, sometimes, 1-4% salt can be added; • *steam defrosting,* which has the advantage that the duration of the defrosting process is shorter, and fats do not run the risk to oxidize; • *microwave defrosting,* which has the advantages of a very short defrosting time, of the defrosting uniformity in all product mass, and of very small gauges of the appliances.	• *Rehydration process* supposes soaking lyophilised fruits in a hot liquid: water, fruit juice, liqueur, wine etc. *Stage 1:* lyophilized fruits are placed in a bowl with enough space fully cover the fruits with liquid; *Stage 2:* the hot liquid is poured over the fruits: fruits will absorb the aroma from the liquid which was added thereon, which will be reflected in the final product; *Step 3:* fruits are left to soak in the hot liquid for 10-15 minute. Lyophilized fruits will start absorbing liquid from the very first minutes. A change will be noticed, both in their size and in their aspect; *Stage 4:* the liquid will be strained in order to remove excess juice; then, rehydrated fruits will be ready to be eaten. Lyophilized fruits apparently become brighter and bigger, when rehydrated; and they remain so even after they have been removed from the liquid.

Table 7 shows some of the most important advantages, respectively disadvantages of forest fruit conservation by freezing and lyophilisation

Table 7: Strengths and weaknesses of frozen and lyophilized forest fruits

➢ **Strengths** of **frozen** forest fruits:	➢ **Strengths** of **lyophilized** forest fruits**:**
• they contain vitamins, and they are rich in antioxidants, almost equally to the fresh ones; • they keep their properties for a longer period of time, of approximately 6 months-1 year; • no foreign substances are added to them; their chemical components are kept with slight changes and they maintain their organoleptic properties (aroma, taste, colour); • most nutritional substances are well kept throughout the freezing; • freezing decreases the risk of forest-fruit damage during transport.	• lyophilized fruits are a good source of energy; • they quickly offer a feeling of satiety; • they keep an ideal taste, superior to frozen fruits; • they have a low weight; the absence of water does not allow the development of microbes, the aroma and nutrients found in fruits are kept unaltered, they can be stored without refrigeration and they can be easily rehydrated; • after lyophilisation, the fibres, antioxidants and phytonutrients are among those which remain at unchanged levels; • in the case of lyophilisation, water is extracted without destroying the cellular structure of the fruit and without losing the volatile substances in the fruit; • lyophilisation confers superior properties upon food products, by a better conservation and by a greater rehydration capacity; • it keeps sensory properties (texture, taste, smell); the lyophilised product keeps its initial shape and does not contract; • after lyophilisation, over 80% of the

	vitamins remain, a record unmatched yet by any other method currently known; • the aspect of lyophilised fruits is almost the same as the one of the initial fruit; and they are "aired" inasmuch as ice, during sublimation, has left in fruits small channels which maintain their initial aspect; • lyophilisation diminishes fruit weight and volume, inasmuch as water is almost totally removed, the weight of lyophilised products is 1/4...1/10 of the initial weight; • lyophilised fruits are superior to: - candied fruits, as they do not contain excess sugar, they are not rich in carbohydrates and they do not have high calories; - dried fruits, as their nutritional values are not lost, and they do not contain colorants and additives to enrich the fruit aspect; - frozen fruits, as they do not contain excess and can be kept anywhere (not only in the freezer).
➢ **Weaknesses** of **frozen** forest fruits:	➢ **Weaknesses** of **lyophilized** forest fruits**:**
• the consistency of frozen fruits is not the same as that of fresh fruits; • frozen fruits can undergo some physical, chemical and histological changes; • frozen fruits with a high water content can lose their consistency after being defrosted.	• high investment costs (installations about 3 times more expensive than in the case of other methods); • the working technique is relatively complicated, which entails low efficiency (the duration of a cycle is of approximately 24 h); • high energy consumptions; • lyophilized fruits require pre-packaging in vacuo or in inert gas atmosphere, resorting to adequate packaging materials.

3. CONCLUSIONS

Forest fruits are a raw material particularly valuable for alimentation. The aroma of forest fruits grown in spontaneous flora is much stronger than the one of cultivated fruits. Furthermore, they have a high nutritional value rich in sugars, vitamins and mineral substances.
The first condition to obtain frozen, respectively lyophilized forest fruits, of a higher quality, is to use the best-quality raw material, its correct processing, and to pay special attention to the whole process.
Forest fruits are generally more difficult to treat, by means of both freezing and lyophilisation, due to the change in some organoleptic features.

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