

LOW TEMPERATURES IN FOOD TECHNOLOGIES

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Key words:	ABSTRACT
Cryogenous technology Biological activity Freezing Cooling agents Powders Radionuclides Quality Safety	The low-temperature (cryogenous) technology of processing the plant raw materials into biologically active food additives with increased content of vitamins, mineral elements and other precious components important for human organism functioning was designed by the scientists of NUFT, and thereto presented in this article. The technology consisted of two stages — freezing the raw material by liquid nitrogen (first stage) and crystalline water sublimation up to the final humidity of 8...12 % (second stage). The dry products obtained with such a technology were outstanding due to their high quality, positive influence on human organism's organs and functions, the ability to avoid accumulating radionuclides and other toxic substances and, otherwise, to remove those present in the organism. Sublimed products made possible to widen the range of healthy food products, and, consequently, had got the real perspective to be realized on domestic and foreign markets. This could be achieved just thanks to the composition of several indices, including high quality, absolute safety, and moderate prices, in a product. Henceforth, sublimed products were determined as extremely prospective for nutrition of special population categories (such as astronauts, geologists, tourists).
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НИЗЬКІ ТЕМПЕРАТУРИ В ХАРЧОВИХ ТЕХНОЛОГІЯХ

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У роботі представлено особливості низькотемпературної (кріогенної) технології перероблення рослинної сировини на біологічно активні добавки до їжі з підвищеним вмістом вітамінів, мінеральних елементів та інших цінних сполук, важливих для функціонування організму людини. Основними етапами цієї технології є заморожування сировини рідким азотом та сублімація закристилізованої води до залишкової вологості матеріалу 8...12 %. Сублімовані продукти дозволяють розширити асортимент оздоровчих харчових продуктів і відтак отримують перспективу реалізації на внутрішньому й зовнішньому ринках, завдяки поєднанню в продукті кількох показників: високої якості, цілковитої безпеки та помірної ціни.

Ключові слова: кріогенна технологія, біологічна активність, заморожування, холодоагенти, порошки, радіонукліди, якість, безпека.

During the last decade, health of Ukrainian population had sharply worsened by a number of indices. The birth rate had got lower (7.8 percent per 1,000 people), and the death rate had got higher (14.8 percent). It resulted in the negative natural increase of population (–7.0 percent).

One of the main causes of these conditions is the sharp worsening of ecological environment after Chernobyl disaster. More than 90 percent of Ukrainian territory was polluted by radionuclides, and about 2,000,000 people have been living in the area of radiological control. The small doses of ionizing radiation influenced the inhabitants of the large area of Ukraine.

The most realistic, safe, and reliable way to keep good health on the proper degree in such complicated conditions, and to provide the social and intellectual activity is the usage of the new-generation foodstuff with natural radioprotectors and biocomponents that would help increase the immunity level of human organism and its adaptative possibilities.

That is why the work trending on production of such foodstuff from the local cheap plant raw material was extremely actual, socially necessary, and economically expedient.

The scientific innovation of this work was based on the usage of temperatures below zero (by Celsius) to dehydrate the plant raw material. Now the mentioned technology is the only one that makes possible to keep the whole natural biologically-active complex of all of the necessary substances undamaged. Cryogenous technologies were wide-spread in the developed countries of the world, like the USA, England, Japan, France. Generally, there was established the principally new way to preserve the agricultural raw material, which, according to the scientists, would soon replace the traditional ways (like sterilization, high-temperature drying etc.). Talking about Ukraine, the usage of cryogenous technologies in food industry has just begun developing. That is why each way of work in such a trend fills the knowledge sum about the special features of freezing and sublimation of plant materials.

The main objective for these researches were defined as confirming the expedience of low temperatures' usage to preserve the plant raw materials (based on the wide range of fruit and berry raw); studying the specificities of phase transitions «water — ice» and «ice — water» in freezing the biological objects; elucidating the mechanism of water crystallization during freezing the carbohydrate-containing raw materials; establishing the optimal technological parameters of raw's sublimation dehydration; carrying out the biological experiments in the live testing objects to research the radionuclides' de-corporation by sublimed plant powders.

There was well-known that transformation of water into solid phase, accompanied by temperature decrease in the entire system and ice-making warm excretion, was the main physical process characterizing the freezing of any plant raw materials. So, from this viewpoint, the selected research objects allowed the authors of this article setting up the temperature intervals for water crystallization and ice melting in the wide range of indices of materials' initial humidity (from 90 to 20 percent). That was why the obtained data got universal.

The obtained data are presented in table 1. According to the table figures, crystallization of free water during researched samples' freezing began at the significant overcooling, and its initial temperature got lower along with samples' initial humidity decrease.

There is well-known [1] that the presence of stable embryos is necessary for development of crystallization process in the solution. Embryos got created in the certain grade of overcooling in the system; as in our experiments, this grade varied from -7°C to -32°C (particularly, for black currant this index was -14°C). The subsequent growing of ice crystals depended not on temperature, but on time; ice «grew» in the entire volume of liquid.

In thawing the samples with velocity of 4°C per minute, starting melting temperature of crystallized water got also decreased. The consequence in temperature changes got observed in the moment of endothermic peak. The absence of first-grade phase transition on the thermograms of samples with low initial humidity was evidence that all water contained by the researched object was constrained.

Setting up the optimal conditions for carbohydrate-containing raw materials' freezing, based on the studies of the main processes (overcooling, crystallization's start and finish, intensive crystallization), was visually presented on differential-and-thermal analysis thermograms (Fig. 1 – 2), containing the data obtained for black currant [2]. The thermogram showed the freezing process by upper declination of differential curve (Fig. 1). This process might be characterized with several sharp leaps on the differential curve, which corresponded to the certain phase transitions' temperatures: *overcooling* period that went on within the temperature range of

283...272 K; *crystallization start* within the temperature range of 272...271 K; *intensive crystallization zone* within the temperature range of 271...269 K; *subsequent crystallization* within the temperature range of 269...265 K; *crystallization finish*.

Table 1. Experimental data of crystallization / melting of apple water

Relative humidity	Freezing water	Non-freezing water	Starting crystallization temperature, °C	Starting melting temperature, °C	Maximal melting temperature, °C
80.77	76.74	23.26	-23.0	-6.5	-2.5
80.28	80.28	74.05	-23.0	-11.5	-2.0
77.32	70.67	29.33	-26.5	-13.5	-3.5
76.79	65.22	34.78	-24.5	-12.5	-6.5
68.82	62.12	37.88	-26.5	-9.5	-4.5
62.28	54.23	44.60	-26.5	-11.5	-7.5
58.07	46.17	53.83	-26.5	-8.5	-9.5
57.09	40.99	59.01	-26.5	-11.5	-9.5
54.58	35.33	64.67	-26.5	-17.5	-11.5
38.44	—	100.00	—	—	—

Water crystallization process should be continued with the studies of its melting process. The analysis of obtained thermograms could wholly visualize the main picture of water's phase transitions. Figure 2 showed that the ice melting got characterized by the fluent start and it could be proved with almost straight shortcut within the temperature range of 240...258 K. Then it got turned from the maximal melting zone to intensive process zone within 258...260 K. Finally, the temperature range of 260...269 K corresponded to the intensive melting zone with 265 K as a peak on the thermographic curve.

The analysis of melting thermographic curve allowed the authors giving some explanations. First of all, the fluent phase transition was a result of low warm conduciveness of the researched object. The initial melting zone expressed the initial stage of dissipation of molecules which were previously concentrated around the crystallization centers. Then, the amount of dissipated molecules grew up, which caused the destruction of thermodynamic stability of water molecules' crystal grate, and hereinafter disturbed the process of transition into intensive melting zone. This zone was characterized by a 265 K peak on the thermographic curve, whose projection onto the curve of indices obtained with a common thermal measuring device corresponded to the temperature that was close to the critical point.

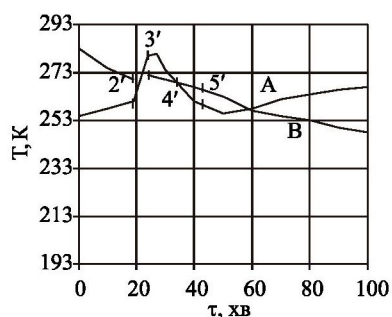


Fig. 1. Thermogram of water freezing in black currant berries (A — differential thermal measuring machine indices; B — thermal measuring machine indices)

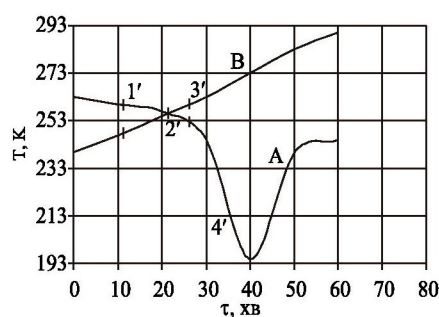


Fig. 2. Thermogram of ice melting in black currant berries (A — differential thermal measuring machine indices; B — thermal measuring machine indices)

The thermogram showed that the complete free water crystallization in black currant berries went on within the temperature range lower than 250 K, which corresponded to eutectic concentrations.

The temperature of water freezing could be considered the maximal temperature of its getting into solid phase. Achievement of this temperature is a necessary and sufficient condition for plant raw materials' freezing before sublimation.

The choice of optimal freezing temperature was based on the fact that the minimal melting temperature for crystallized water, which could be defined experimentally, was significantly higher than the maximal solid-phase temperature. This could be connected with overcooling the transitive eutectic mixtures during the freezing process, which delayed the subsequent crystallization [3], so that the plant raw material was to be cooled to lower temperatures. The index of marginal temperature was determined by the properties of the cooled object and the characteristics of any solid matter which was present at the same environment.

Technological regime for subliming dehydration of plant raw material

Subliming dehydration of fruit and vegetable raw materials can be presented as the sequence of complicated one-direction processes of mass and warm transfer in capillary and porous matters to which the objects of our researches belong [4].

Sublimation drying was carried out according to the optimal parameters which were set up previously (particularly, upon reaching the pressure of 13.3 Pa at the sublimator, we used the regulator on power control device to adjust so high voltage that would allow obtaining the specific potency of warm stream within 800 W per square meter).

Upon reaching the product temperature of 273 K (according to the data of the «tray — products» resistance thermometer), we decreased the specific potency of warm stream to 400 W per square meter, and then the process was carried out until the temperature fell to 298 K. That temperature was kept constant by the voltage regulator with precision of ± 5 K until the pressure in the chamber reached 1.33 Pa.

Sublimation drying was carried out in the following regimes:

- The raw material got frozen by liquid nitrogen irrigation with the velocity of 16...32 K per minute;
- Drying was going on with the initial warm stream of 800 W per square meter;
- The sample temperature in the sublimation period was kept at 268 K;
- The warm stream in 25 minutes was weakened to 400 W per square meter and kept constant for a long time;
- The additional drying temperature was kept at 287 ± 1 K.

The next regime was similar to the previous one; however, it differed from it by the following features:

- The specific warm stream got gradually weakened to 800 to 100 W per square meter;
- The additional drying temperature was 300 ± 3 K;
- The material got self-frozen to 248 K;
- Drying was carried out at the initial warm stream of 800 W per square meter;
- Temperature of the product in sublimation was 268 K;
- The warm stream got gradually weakened;
- The additional drying temperature was 293 ± 3 K.

Sublimation drying was accomplished in direct-radiation warming conduction until the final humidity in the products within 8...10 percent.

There was confirmed that the periods of constant and decreasing energy conduction were expedient to organize the process of sublimation drying, independently of the kind of raw.

Generally, the process of sublimation drying consists of several simple processes:

- Sublimation from mono-molecular layer of the surface whose zone is moving up to down;
- Sublimed particles of migrating water were in the state of diffusion through the capillary and porous skeleton of the partial raw layer from the conditional surface to the free one;
- Water got removed from the free surface to the entire volume of sublimation chamber.

Process of sublimation drying finished with removal of all crystalline water (except constrained) from the raw layer.

The sublimed products that were obtained in the mentioned technological regime practically do not differ from initial raw by their qualitative indices. I.e., the dry products can keep the whole biological compound (for example, the carbohydrate complex).

Conclusions

Based on the results of conducted researches of low-temperature procession of carbohydrate-containing raw materials and on the new scientific notions of quality and ecology of foodstuff, we proved, designed, and realized some of the newest decisions in the technology of production of plant raw materials into sublimed biological additives with high nutritional quality. Those technologies would increase the output of high-quality products; provide the growth of production efficiency; make possible to use the fruit and vegetable raw on the new level as the source of important biocomponents synthesized by nature. Our technologies would allow widening the new generation foodstuff spectrum, and implement some radical changes into Ukrainians' nutrition structure. The mentioned thesis describes the main factor of healthy lifestyle, prevention and medication of different diseases.

Systematic consumption of sublimed food products, made of carbohydrate-containing raw material, helps rising the physical and mental workability, stimulates the work of blood-making organs, strengthens the organism's resistance to destructive environmental factors, and thereto decreases the risk of oncology, heart and vessel diseases, and so on.

Significant decreasing the losses of plant raw materials during harvesting and storage, high quality of final products and their absolute safety for consumer, possibility to widen the range of half-fabricates and final products with increased content of essential and biologically active components through the year, creation of competitive and competition-oriented foodstuff with healthy and preventive destination were the cardinal advantages of using the low temperatures to process and to store fruit and vegetable raw and the products made of it.

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НИЗКИЕ ТЕМПЕРАТУРЫ В ПИЩЕВЫХ ТЕХНОЛОГИЯХ

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В работе представлены особенности низкотемпературной (криогенной) технологии переработки растительного сырья на биологически активные добавки к пище с повышенным содержанием витаминов, минеральных элементов и других ценных соединений, важных для функционирования организма человека. Основными этапами данной технологии являются замораживание сырья жидким азотом и сублимация закristализованной воды до остаточной влажности 8...12 %. Сублимированные продукты позволяют расширить ассортимент оздоровительных пищевых продуктов и, следовательно, получают перспективу реализации на внутреннем и внешнем рынках, благодаря сочетанию в продукте следующих показателей: высокого качества, абсолютной безопасности и умеренной цены.

Ключевые слова: криогенная технология, биологическая активность, замораживание, хладагенты, порошки, радионуклиды, качество, безопасность.