Abstract
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, etc.).

Keywords: cryogenous technology, biological activity, freezing, cooling agents, powders, radionuclides, quality, safety.

Introduction
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 adaptive 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, and 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 tasks of researches in the present article 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.

Materials and methods
2.1. The studied varieties of raw
Fruit (apples, citrus, apricots, peaches), berries (strawberries, raspberries, grapes, black currant), vegetables (potatoes, topinambour, carrot, red beet, sugar beet, sweet pepper), and seeds (parsley seeds, fennel seeds). All of the mentioned materials were grown in Ukraine (except of citrus which was imported from Spain). Selection of those raw materials was based, first of all, on their physical and biological value.

2.2. Total carbohydrates analysis in plant raw materials
Total carbohydrates were determined by a colorimetric method based on Phenol reaction with glucose (See Daniels, Hanson, & Phyllips, 1994).

2.3. Determination of vitamin C concentration
Vitamin C content was determined by potentiometric titration by sodium 2,6-dichlorophenolindophenolate according to USSR State Standard No. 24556-89.

2.4. Determination of mineral contents in plant raw materials
Micro and macro elements’ contents were determined by SPECORD UV VS spectrophotometer (Bulatov, Kalinkin, 1992).

2.5. Evaluation of water state in freezing-thawing the plant raw material
Kinetics of the processes that take place in thawing the biological objects was investigated by the method of differential scanning microcalorimetry (See Mychaylyk, Davydova, 1990).

2.6. Analysis of carbohydrate complex in fresh and sublimed topinambour
The researches were carried out by liquid gel-chromatography on Dionex HRAEC-Pad chromatographer (Ashoor, Monte, Welty, 1984).

2.7. Laboratory aggregate for plant raw sublimation dehydration
The low-temperature dehydration of plant raw materials and setting up the optimal technological parameters of sublimation for every kind of raw material was carried out on the experimental laboratory aggregate (See Fig. 1). This aggregate was designed in Physical and Technical Institute of Low Temperatures (Ukraine, 1990).

Fig. 1. Experimental Sublimation Aggregate
1 – sublimation device; 2 – control system; 3 – vacuuming system; 4 – transition pipe with cock; 5 – de-sublimation device; 6 – control and management system

Preparation of materials that were exposed to sublimation could be defined as their previous freezing. It might be accomplished by procession of raw with liquid nitrogen or other agents until the temperature was lowered up to the indices which were maximally possible in concrete conditions. Although, according to our previous data, this temperature must be sufficient just to turn the main amount of raw’s free water into ice. The temperature was to be set up individually for different objects of research.
2.8. The statistic calculation of research results

All the experiments planned within the framework of our researches were accomplished in threefold sequence. The experimental results were subsequently processed by ‘least squares’ statistic method (See Guter 1990).

Experimental results were calculated by the methods of statistic modeling based on Microsoft Excel 2003 and MathCad 13 problem-oriented software.

3. Results and discussion

3.1. Evaluation of water state in freezing-thawing the plant raw materials

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 tables 1 and 2. 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.

The comparative analysis of the tables showed that the adaptability to overcooling depended on the kind of a material, the grade of its maturity, its chemical composition, and initial humidity. High-molecular compositions and hydrophilic colloids, which are inclined to swelling and water constraining, play the significant role in this process.

There is well-known (See Kaatze, 1984) 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.

Table 1
Experimental data of crystallization / melting of apple water

<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>Freezing water</th>
<th>Non-freezing (constrained) water (percent to the main mass of water)</th>
<th>Starting crystallization temperature, °C</th>
<th>Starting melting temperature, °C</th>
<th>Maximal melting temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.77</td>
<td>76.74</td>
<td>23.26</td>
<td>-23.0</td>
<td>-6.5</td>
<td>-2.5</td>
</tr>
<tr>
<td>80.28</td>
<td>80.28</td>
<td>74.05</td>
<td>-23.0</td>
<td>-11.5</td>
<td>-2.0</td>
</tr>
<tr>
<td>77.32</td>
<td>70.67</td>
<td>29.33</td>
<td>-26.5</td>
<td>-13.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>76.79</td>
<td>65.22</td>
<td>34.78</td>
<td>-24.5</td>
<td>-12.5</td>
<td>-6.5</td>
</tr>
<tr>
<td>68.82</td>
<td>62.12</td>
<td>37.88</td>
<td>-26.5</td>
<td>-9.5</td>
<td>-4.5</td>
</tr>
<tr>
<td>62.28</td>
<td>54.23</td>
<td>44.60</td>
<td>-26.5</td>
<td>-11.5</td>
<td>-7.5</td>
</tr>
<tr>
<td>58.07</td>
<td>46.17</td>
<td>53.83</td>
<td>-26.5</td>
<td>-8.5</td>
<td>-9.5</td>
</tr>
<tr>
<td>57.09</td>
<td>40.99</td>
<td>59.01</td>
<td>-26.5</td>
<td>-11.5</td>
<td>-9.5</td>
</tr>
<tr>
<td>54.58</td>
<td>35.33</td>
<td>64.67</td>
<td>-26.5</td>
<td>-17.5</td>
<td>-11.5</td>
</tr>
<tr>
<td>38.44</td>
<td>-</td>
<td>100.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2
Experimental data of crystallization / melting of currant berry water

<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>Freezing water</th>
<th>Non-freezing (constrained) water (percent to the main mass of water)</th>
<th>Starting crystallization temperature, °C</th>
<th>Starting melting temperature, °C</th>
<th>Maximal melting temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.45</td>
<td>71.15</td>
<td>28.85</td>
<td>-14.0</td>
<td>-21.5</td>
<td>-2.0</td>
</tr>
<tr>
<td>84.03</td>
<td>61.09</td>
<td>38.91</td>
<td>-14.5</td>
<td>-20.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>83.64</td>
<td>75.90</td>
<td>24.10</td>
<td>-16.0</td>
<td>-26.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>62.37</td>
<td>82.96</td>
<td>17.04</td>
<td>-</td>
<td>-22.0</td>
<td>+2.0</td>
</tr>
<tr>
<td>78.61</td>
<td>70.28</td>
<td>29.72</td>
<td>-16.0</td>
<td>-29.0</td>
<td>-3.0</td>
</tr>
<tr>
<td>77.42</td>
<td>77.17</td>
<td>22.83</td>
<td>-13.0</td>
<td>-21.0</td>
<td>+1.0</td>
</tr>
<tr>
<td>71.93</td>
<td>71.56</td>
<td>28.44</td>
<td>-16.0</td>
<td>-31.0</td>
<td>-3.0</td>
</tr>
<tr>
<td>67.83</td>
<td>52.23</td>
<td>47.77</td>
<td>-21.5</td>
<td>-29.0</td>
<td>-6.0</td>
</tr>
<tr>
<td>61.08</td>
<td>48.87</td>
<td>51.13</td>
<td>-21.0</td>
<td>-31.0</td>
<td>-8.0</td>
</tr>
<tr>
<td>50.94</td>
<td>33.86</td>
<td>66.14</td>
<td>-27.0</td>
<td>-29.0</td>
<td>-13.0</td>
</tr>
</tbody>
</table>

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.

3.2. 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 (See Simakhina, 2011).

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 sublimer, 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.

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 lair 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 lair 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 lair.

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.

References


