

Dynamics of Total Content of Antioxidants in Vegetable Products

Eliseeva Svetlana A.

Peter the Great St. Petersburg Polytechnic University
SPbSTU
St. Petersburg, Russia
Eliseeva_sa@spbstu.ru

Smolentceva Alla A.

Peter the Great St. Petersburg Polytechnic University
SPbSTU
St. Petersburg, Russia
smolentseva_aa@spbstu.ru

Irinina Olga I.

Vladimir State University named after Alexander Grigorievich
and Nikolai Grigorievich Stoletov
Vladimir, Russia
irinina.olga2018@yandex.ru

Abstract—In the article the authors give the results of the study of the total antioxidant activity of fresh vegetables, vegetable semi-finished products after heat treatment and in the process of refrigerating storage, dried vegetables, and vegetable cryopowders when designing functional food products. Determination of the total content of antioxidants (TCA) in fresh vegetables and semi-finished vegetable products during refrigerated storage was carried out. As an indicator of the determination of TCA, an ascorbic acid was used.

The value of the TCA measured in fresh vegetables was: beetroot—1.42; carrot—0.81; onion—1.56 mg/g. The loss of TCA during the processing of semi-finished vegetable products, measured while in vacuum-sealed bags at 95°C, was: beetroot—16.9% loss; carrot—35.4% loss; onion—20.6% loss.

The decrease in the TCA for these products was measured again after 7, 14 and 21 days of cold storage, being: beetroot—66.7%; 68.1%; 84.2% loss; carrot—50.2%; 75.3%; 91.1% loss; onion—64.9%; 75.4%; 90.2% loss, respectively. The determination of TCA in dried vegetables and vegetable cryopowders were carried out using the amperometric method, and as an indicator of the determination of TCA, an ascorbic acid was used. The results of the determination of TCA in cryopowders are similar with those of semi-finished vegetable products. The TCA in dried vegetables was 1.1–6.3 times higher than in fresh vegetables.

The minimum quantities of fresh, heat-treated and dried vegetables in a functional food product were determined. The recommendations are given to improve chopped poultry products using dried vegetables as fillers and desserts using cryopowders. The addition, per 100 g of product, of 1.1–3.5% of dried vegetables or of 3.7–8.2% of cryopowders can make the final food product be considered functional.

Keywords—*antioxidants; vegetable products; cryopowders; functional food product*

I. INTRODUCTION

The transition of food production to a new industrial base requires the development of functional and specialized products with increased nutritional value and extended expiring date [1]. The production of processed vegetable products is an inefficient process: additional storage facilities to store and process vegetables are needed; more waste is produced; long-term heat treatments for certain types of vegetables that reduces their nutritional value are used. As a result, the production of processed vegetable products is often limited, despite the steady consumer demand and the nutritional value of these products in a modern diet.

In recent years, there has been an increasing number of domestic developments in food products with functional features due to the introduction of vegetables — a source of antioxidants — into their composition. In addition, vegetable ingredients with reduced humidity (dried vegetables) and fine-dispersed plant cryopowders, obtained by drying and grinding at low temperatures, have been widely used.

Vegetable cryopowders are products obtained from different kinds of edible plant raw material. The constituent parts of these powders are in optimal proportions and can enhance each other's nutritional properties, which makes it possible to use them purposefully for prevention of malnutrition caused diseases.

The cryotechnology helps to prevent oxidation and caramelization of raw materials at the stage of water removal, when the concentration of biologically active substances occurs [2].

Antioxidants are recognized as an integral part of a balanced diet along with proteins, fats, carbohydrates, vitamins and trace minerals. They are included in a variety of nutritional programs as healthy diets or functional nutrition and others.

Such a high interest in antioxidants is due to their ability to block the harmful effects of free radicals, protecting the body from the most dangerous diseases.

Throughout the history of mankind, plants and products made of plants have been used for treatment and prevention of many diseases. Pharmacology offers the public a wide range of medicines based on plants. Scientific studies of nutritional diseases show that nutritional factors have a significant effect on cardiovascular and oncological diseases. Garlic, soybeans, cabbage, ginger, turmeric, brown rice, wheat, flax seeds, tomatoes, celery, parsley, onions, carrots, beets and others plants are referred to as plant products with anti-cancer properties [3].

Latest data in the field of plant biochemistry shows that vegetables are irreplaceable sources of minor biologically active compounds that have an antioxidant effect in the body [4, 5].

The polyphenols are the main and most effective antioxidants. They are water-soluble antioxidants. The most numerous group among them is the flavonoids, present in all plants and synthesized in several plant organs. All flavonoids can be divided into seven main groups: flavones, flavonols, flavanones, flavanols, isoflavones, catechins and anthocyanidins. In plants they can be found in form of substances of varying degrees of polymerization. It is believed that a diet rich in flavonoids helps to protect the body from cardiovascular diseases, certain types of cancer and from neurodegenerative disorders. One of the most common flavonoids is quercetin; it is contained in grapes, wine, tea, apples, leafy green vegetables, onion. It is a powerful antioxidant and has an anti-inflammatory effect [6].

Fat-soluble antioxidants include tocopherols, carotenoids, retinol. Fat-soluble antioxidants protect biomembranes and their lipid structures against free radicals. When some antioxidants are combined with other compounds, both synergistic and inhibitory effects can be observed. [7].

Plant antioxidants from the onion family are included in a separate group — sulphides. Sulfur-containing bioactive compounds of onion-type vegetables inhibit the growth of cancer cells, stimulate the activity of detoxifying enzymes, strengthen the body's immune system and protect it from oxidative damage [3].

The scientific literature provides data on the antioxidant effect of plant pigments. These include betalain pigment of the beetroot [8]. Compared with other countries that cultivate table beet, mainly as a source of natural dye and component of animal feeds [3], in Russia, it firmly holds a place in the daily diet of the population. Now it is known that betalaines are aromatic derivatives of indole, synthesized from tyrosine. Chemically, betalaines are not associated with anthocyanins, which are related to flavonoids [9].

According to the current norms of physiological needs [10], biologically active compounds must enter the human body regardless of the season. Special literature indicates the interest of specialists in the dynamics of antioxidant properties of vegetables. The most frequently studied factors affecting the change in the total content of antioxidants (TCA) include

species, variety, maturity, and chemical composition of vegetables. Data on the influence of the method of cooking is much less common. There is practically no data on the changes in TCA in vegetables and vegetable products during storage. Therefore, the study of the dynamics of TCA in vegetables with varying degrees of processing, including refrigerated storage, is an actual and practical important area.

There is data of the drying effects on the content of total soluble phenolic compounds: ascorbic acid, carotenoids and anthocyanins, and on their ability to absorb free radicals in fresh vegetables (zucchini, white cabbage and red cabbage, celery, carrots, potatoes). The highest content of phenols and antioxidant activity were noted in red cabbage. The drying had an ambiguous effect on all indicators, so, in red cabbage, there was a decrease in TCA, but there was an increase in carrots. This is due to the different nature and solubility of antioxidants (anthocyanins are water-soluble, and beta-carotene is fat-soluble).

The purpose of this work is to study the total antioxidant activity in vegetable semi-finished products and in derived industrially processed products, as well as the possibility of create functional food products using these vegetable derived products. To achieve this goal, the following tasks were accomplished: determination of the total content of antioxidants in vegetable products; determination of the minimum fraction of vegetable component in a functional food product.

II. OBJECTS OF RESEARCH

The objects of research were: tradable parties of fresh vegetables (beetroots, carrots, onions); semi-finished products from vegetables, packed in vacuum sealed bags: beetroots, carrots, onions (after 0, 7, 14, 21 days of cold storage at a temperature from 2 to 6°C); dried vegetables: beetroots, carrots, onions, dried in the laboratory in a drying oven at a temperature of 60°C until the moisture content of the product was not exceeding 14% (GOST 32065); cryopowders from vegetable raw materials (TU 9164-001-97572157-2014): beetroots, carrots, prunes after storage in retail trade for 2 to 6 months.

III. RESEARCH METHODS

It was used in the course of cold storage in accordance with the certified method (MVI.01-44538054-07) using the commercial coulometer "Expert-006". The essence of the method is the determination during the titration of all antioxidants introduced with the analyzed sample and reacting with the electrogenerated radicals of excess bromine numerically equal to the amount of antioxidant substances introduced with the breakdown. The end point of titration is fixed by the device after reaching the initial value of the indicator potential (5 - 50 mA, depending on the total content of antioxidants in the sample from 0 to 100 mg). For one analysis, five parallel samples were taken.

The measurement was carried out as follows. A 20.0 cm³ background solution consisting of an aqueous 0.2 M potassium bromide solution in a 0.1 M sulfuric acid solution was

introduced into a 50 cm³ cell of the coulometre; then the electrodes from the inert material ($\Delta E \leq 1000$ mV) were dipped in it and the generator circuit was turned on. Upon reaching a certain value of the indicator current, an aliquot of the test liquid sample (2.0–4.0 cm³ extract acidified with 2% HCl) was added into the cell. The end point of titration was fixed after reaching the initial value of the indicator potential. In this case, the analyzer showed the time of determination in seconds (s) in the aliquot volume of the test sample introduced into the measuring cell.

The TCA of vegetables was calculated in the amount of electricity (coulombs) consumed per 100 cm³ of a liquid sample (extract) by the formula (1):

$$Q = \frac{100 \cdot J \cdot t}{V} \quad (1)$$

where J stands for the amperage 50 mA;
t - the time to reach the end point of the titration, s;
V is the volume of an aliquot, cm³.

As a standard substance, they used an ascorbic acid in connection with the fact that it has an intermediate position among antioxidant agents such as phenolic and non-phenolic reducing agents.

The total content of antioxidants in terms of mg ascorbic acid per 100 cm³ of liquid sample was calculated by the formula (2):

$$X = K \cdot Q \quad (2)$$

where Q - total antioxidant activity of the analyzed sample in coulombs;
K - the conversion ratio, which was determined by calibrating the electrolytic cell of the coulometer (in mg of ascorbic acid per 1 coulomb).

The volume of aliquot introduced for all samples was 2.0 cm³; the conversion ratio for ascorbic acid was 0.004.

To determine the TCA in dried vegetables and vegetable cryopowders was used an amperometric method based on the measurement of the electric current produced during the electrochemical oxidation of the test substance on the surface of the electrode at a certain potential [7].

Under conditions of amperometric detection, compounds containing a hydroxyl group are well oxidized, the detection limit lies in the range of 10⁻⁹-10⁻¹⁰. A direct quantitative measurement in the samples was carried out on a device Color Yauza-01-AA.

The samples were checked, the experiment was carried out and the results were processed in accordance with GOST R 54037 standard [11]. Using software, the areas (peak heights) of the analyzed and standard substance were calculated. An average of 5 consecutive measurements was used for the analysis. As a standard substance, a solution of quercetin was used. The calibration characteristic of the analyzer is shown in Fig.1 as a linear dependence of the arithmetic values of the

output signal on the mass concentration of quercetin with a correlation of at least 0.98.

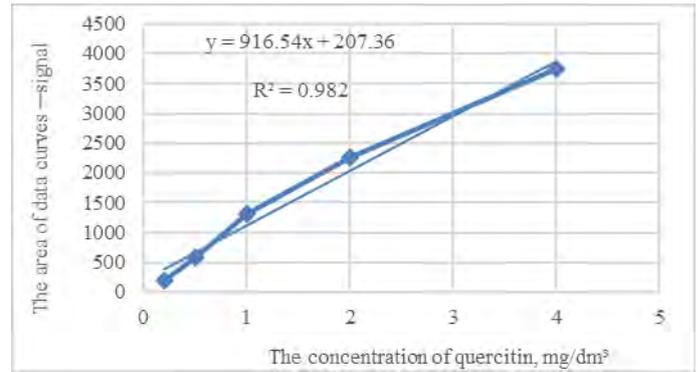


Fig. 1. Graph of the dependence of the signal on the concentration of quercetin in solution

The total content of antioxidants in the CA sample, mg / g, was calculated from formula (3):

$$CA = \frac{CA_k \cdot V_n \cdot N}{m_n \cdot 1000} \quad (3)$$

where CA_k - the total content of antioxidants (recalculated for quercetin), determined using a calibration characteristic, mg/dm³;

V_n - volume of the solution of the analyzed sample, dm³;

N - dilution ration of the analyzed sample;

m_n - the weight of the analyzed sample, g.

The mass fraction of moisture in the investigated objects was determined according to GOST 28561 [12] by drying to constant mass.

IV. RESULTS OF THE STUDY

Thermal treatment of sliced and packed in polymeric sealed bags with the help of vacuumization semi-finished products from vegetables was carried out in a steam convection apparatus at a temperature of 95°C, a moisture content of 90%. TCA in fresh vegetables and vegetable semi-finished products in the process of cold storage is presented in Table 1.

According to the data given in Table 1, it can be seen that the heat treatment of the vegetables packed in vacuum bags leads to a decrease in the TCA in comparison with the initial fresh products: in the heat-treated beetroot, the losses of the TCA were 16.9; in carrots — 35.4; in onions — 20.6%. The better preservation of water-soluble antioxidants in onions and beets can be explained by their higher concentration in the studied products, the absence of its diffusion during the cooking and its contact with oxygen in the air.

TABLE I. TCA IN FRESH VEGETABLES AND VEGETABLE SEMI-FINISHED PRODUCTS IN THE PROCESS OF COLD STORAGE

Object name	TCA, mcg /cm ³ in ascorbic acid				
	Fresh vegetables	Semi-finished vegetable products	In the process of cold storage, day		
			7	14	21
beetroot	284.2±5.7	236.1±5.2	94.6±3.2	44.9±2.1	28.6±1.3
carrot	160.0±8.7	103.4±6.5	79.7±4.9	39.5±1.9	14.3±0.8
onion	300.2±8.2	238.5±7.6	105.5±3.9	73.7±2.0	29.4±0.9

On the 7th, 14th and 21st days of cold storage, the dynamics of the decrease in the TCA amounted to 66.7, 68.1; and 84.2% for semi-finished products from beetroot; 50.2; 75.3; 91.1% — for carrots and 64.9, 75.4; 90.2% for onion respectively. Thus, the storage of heat-treated vegetables is the determining factor in the loss of antioxidants in vegetable semi-finished products. The consumer gets only 10% of the original content. In this regard, it is advisable to investigate the TCA in dried vegetables, which can be considered as an alternative semi-finished product for the preparation of culinary products.

TCA in the studied plant objects recalculated to dry substance, taking into account the coordination of units of measurement and depending on the type of sample analyzed, is presented in Table 2.

The dynamics of the total content of antioxidants in the investigated vegetables is determined by the type of vegetables, the nature of the antioxidants, the degree of processing of vegetable raw materials. A comparative analysis of the data showed the similarity of TCA in heat-treated vegetables in vacuum and cryopowders from vegetables. In both cases, sparing temperature treatment regimes are used that contribute to increase of the safety of TCA.

A higher content of antioxidants was found in dried vegetables, especially in carrots. There are data on the effect of dehydrating vegetables on the content of common soluble phenolic compounds, ascorbic acid, total carotenoid content, anthocyanins, and its ability of absorbing free radicals is known. Dehydrating had an ambiguous effect on all indicators, so while in beetroot there was a decrease in TCA, in carrots there was an increase [13, 14].

The recommended levels of consumption of some flavonoids are a total of 350 mg/day [10]. A food product is considered specialized or functional if the content of the active substance is not less than 15% of the recommended daily intake weight per 100 cm³ or 100 g or a single portion of the final food product [15]. Table 3 shows the minimum amount of input required of an ingredient from vegetables in a single portion of functional food.

TABLE II. VEGETABLES AND VEGETABLE CRYOPOWDERS TCA IN FRESH VEGETABLES, SEMIFINISHED PRODUCTS FROM THEM DURING STORAGE, DRIED

Object name	TCA in sample, mg/g	Mass fraction of dry substance in product, %	TCA in sample recalculated to dry substance, mg/g
fresh beetroot	1.42±0.04	13.0	10.9
fresh carrot	0.81±0.02	9.7	8.4
fresh onion	1.56±0.04	10.3	16.1
semi-finished product from beetroot, 0 days	1.18±0.03	12.5	9.4
semi-finished product from carrot, 0 days	0.53±0.02	9.9	5.4
semi-finished product from onion, 0 days	1.24±0.04	10.3	12.0
semi-finished product from beetroot, 14 days	0.23±0.01	11.9	1.9
semi-finished product from carrot, 14 days	0.20±0.01	9.6	2.1
semi-finished product from onion, 14 days	0.39±0.01	10.2	3.8
dried beetroot	16.0±0.9	88.9	18.0
dried carrot	47.1±1.8	88.2	53.4
dried onion	15.4±0.8	87.5	17.6
cryopowder from beetroot	8.2±0.6	95.9	8.6
cryopowder from carrot	6.1±0.4	96.2	6.3
cryopowder from prunes	13.4±0.9	95.1	14.1

The use of semi-finished vegetable products in vacuum packaging allows the consumer to prepare traditional dishes of Russian cuisine enriched with antioxidants. These dishes include beetroot salads, vinaigrettes, garnishes from carrots and beetroots for a single portion of 100 grams, or a portion of 200 g of borsch. The recommended storage of semi-finished vegetable products in cold conditions leads to significant losses of their antioxidant activity, so the aforementioned dishes lose their definition as functional.

Products enriched with antioxidants of different assortment groups can be created by adding dried vegetables or vegetable cryopowders in small amounts: 1.1–3.5% and 3.7–8.2% per 100 g of product, respectively. Technologies for chopped poultry products with dried vegetables as filler have been developed [16, 17]. Technologies of dessert mousses and creams with cryopowder from prunes are proposed [18, 19].

TABLE III. TCA IN FRESH VEGETABLES, SEMIFINISHED PRODUCTS FROM THEM DURING STORAGE, DRIED VEGETABLES AND VEGETABLE CRYOPOWDERS

Object name	The amount of product that provides a daily rate of antioxidants, g	The minimum quantity of the product in a functional food product, g
fresh beetroot	246.5	37.0
fresh carrot	432.1	64.8
fresh onion	224.3	33.7
semi-finished product from beetroot, 0 days	296.6	44.5
semi-finished product from carrot, 0 days	660.4	99.1
semi-finished product from onion, 0 days	282.3	42.3
semi-finished product from beetroot, 14 days	1521.7	228.3
semi-finished product from carrot, 14 days	1750.0	262.5
semi-finished product from onion, 14 days	897.4	134.6
dried beetroot	19.6	2.9
dried carrot	7.5	1.1
dried onion	22.7	3.4
cryopowder from beetroot	40.9	6.1
cryopowder from carrot	55.2	8.2
cryopowder from prunes	24.8	3.7

V. CONCLUSIONS

In the research carried out, the TCA of vegetable products are taken into account for designing functional food products. The use of innovative technologies for processing vegetable raw materials (heat treatment in vacuum, drying at low temperatures, cryosuffering) allows maximum preservation of the activity of natural antioxidants.

It is established that the adding of plant ingredients as dried vegetables does not disadvantageously effect the organoleptic characteristics of the cooked product. The authors have studied the quality indicators of the developed multicomponent formed products. According to organoleptic and microbiological indicators, the developed products fit in with the requirements of technical documentation, as well as with the technical regulations of Customs Union 021/2011 "On food safety".

References

[1] The strategy of improving the quality of food products in the Russian

- Federation until 2030, approved by the Decree of the Government of the Russian Federation from June 29, 2016 No. 1364-r. (www.pravo.gov.ru) (as of June 29, 2016 Number: 0001201607050014).
- [2] G. Kasyanov, V. Lomachinsky, "Manufacture and use of cryopowder from vegetable and fruits", *Izvestiya Vuzov. Food technology*, 2-3, pp. 64–65, 2010.
- [3] Sh. Damodaran, K. Parkin, O. Fennema, *Chemistry of food products*, 4rd ed., SPb.: Professya, 2012, p.1040.
- [4] N. Golubkina, S. Sirota, V. Pivovarov, A. Yachin, Ya. Yachin, *Biologically active vegetable compounds*, M.: VNISSOK, 2010, p.199.
- [5] I. Skurikhin, V. Tutelyan, *Chemical composition of Russian food products: Handbook*, Ed. M.: DeLi print, 2002, p.236.
- [6] Yu. Bazarnova, O. Ivanchenko, "Investigation of the composition of biologically active substances in extracts of wild plants", *Voprosy Pitaniia*, vol. 85(5), pp.100-107, 2016.
- [7] Ya. Yachin, V. Rijnev, A. Yachin, N. Chernousova, *Natural antioxidants. The content of food products and their effect on human health and aging*, M.: TransLit, 2009, p.212.
- [8] G. Britton, *Biochemistry of Natural Pigments*, M.: Mir, 1986, p.422.
- [9] F. Stintzing, R. Carle, "Betalains: emerging prospects for food scientists", *Trends in Food Science & Technology*, vol.18, 10, pp. 514–525, 2007.
- [10] Norms of physiological needs in energy and nutrients for various groups of the population of the Russian Federation. MR 2.3.1.2432-08, M.: Federal Center for Hygiene and Epidemiology of Rosпотrebnadzor, 2009.
- [11] GOST R 54037-2010 Food products. Determination of the content of water-soluble antioxidants by amperometric method in vegetables, fruits, products of their processing, alcoholic and nonalcoholic beverages. M.: Standartinform, 2011.
- [12] GOST 28561–90 Products for processing fruits and vegetables. Methods for determining dry substances or moisture, M.: Standartinform, 2011.
- [13] F. Reyes, "The increase in antioxidant capacity after wounding depends on the type of fruit or vegetables tissue," *Food Chem.*, V.101, 1, pp.68–74, 2007.
- [14] O. Nistor, L. Seremet (Ceclu), D. Andronoiu, "Influence of different drying methods on the physicochemical properties of red beetroot (*Beta vulgaris* L. var. *Cylindra*)", *Food Chemistry*, vol. 236, pp. 59–67, 2017.
- [15] GOST R 55577– 2013 Specialized and functional food products. Information on the distinctive features and effectiveness (with Amendment No. 1), M.: Standartinform, 2014.
- [16] S. Eliseeva, "Perfection of technology of molded products of functional purpose," *Materials of the V International Baltic Maritime Forum*, vol. 8, Kaliningrad: BGRAF, 2017, pp. 44 – 46.
- [17] S. Eliseeva, A. Dyakova, K. Chuikova, "Investigation of the antioxidant properties of dried vegetables", *Materials of Forum*, pp. 39–41, November 2017 [12th Russian Forum "Healthy Nutrition from the Birth: Medicine, Education, Food Technologies" p. 118, 2017].
- [18] A. Smolentseva, E. Polikarpova, "Development of functional desserts using vegetable cryopowders", *Materials of Forum*, pp. 96–97, November 2017 [12th Russian Forum "Healthy Nutrition from the Birth: Medicine, Education, Food Technologies" p. 118, 2017].
- [19] E. Polikarpova, A. Smolentseva, "Investigation of the antioxidant properties of plant cryopowders", *Materials of scientific conference*, pp. 92–95, November 2017 [Week of Science of SPbPU: with international scientists of the Graduate school of biotechnology and food science, St. Petersburg. Polytechnic University, p.190, 2017].