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EFFECT OF THE PARAMETERS OF RHUBARB AND GOOSEBERRY TREATMENT ON THE FORMATION OF COLOR

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Досліджено вплив різних видів теплової обробки (бланшування, обробка парою, варіння) на ступінь руйнування хлорофілів в аґрусі та ревені. Встановлено вміст хлорофілів у аґрусі та ревені залежно від ступеня подрібнення. Визначено вплив стабілізуючих добавок ($MgSO_4$, $MgCl_2$, $CaCl_2$, KCl) на перетворення хлорофілів і зміну кольору ревеню та аґрусу

Ключові слова: рослинна сировина, технологічна обробка, кольоропараметрічні характеристики, стабілізація пігментів

Исследовано влияние различных видов тепловой обработки (бланширование, обработка паром, варка) на степень разрушения хлорофилла в крыжовнике и ревне. Установлено содержание хлорофиллов в крыжовнике и ревене в зависимости от степени их измельчения. Определено влияние стабилизирующих добавок ($MgSO_4$, $MgCl_2$, $CaCl_2$, KCl) на преобразование хлорофиллов и изменение цвета ревеня и крыжовника

Ключевые слова: технологическая обработка, цветовые характеристики, стабилизация пигментов

1. Introduction

Production of "healthy" food is extremely important and is the focus of constant attention from a broad range of professionals involved in the development of modern technologies for manufacturing food products and determining the criteria of quality. Development and a substantial increase in food production based on plant raw materials, which is rich in natural functional ingredients (carotenoids, vitamin C, bioflavonoids, food fibers, mineral elements), is an important task. Rhubarb and gooseberry are the cheap raw materials grown in Ukraine possessing a valuable set of biologically active substances. These raw materials, however, are hardly used in processing industry. The reason is the lack of industrial technologies for processing rhubarb and gooseberry, which would make it possible to keep the pigment complex of raw materials and to obtain food products with high quality.

Natural color of these raw materials is predetermined, first of all, by the content of such coloring substances as chlorophylls. These compounds are very valuable due to their antioxidant, antimutagenic and antimicrobial properties. Interest in these compounds can be explained by the fact that they ensure necessary activity of the antioxidant system. This universal regulating system of the human organism controls the level of the free-radical oxidation reactions and prevents the accumulation of toxic substances. Nevertheless, chlorophylls are known to be very labial.

It is known that such factors as the type of heat treatment, the degree of shredding, the influence of stabilizing additives on the pigment complex of rhubarb and gooseberry substantially alter the natural color of these raw materials due to the destruction of plant pigments. To prevent the destruction of plant pigments and stabilize the color of raw materials, scientists developed a large number of techniques. Those methods, however, are not of the universal character. There are also objective difficulties related to determining the optimal amount of stabilizing additives because known techniques for preventing destruction of plant pigments and stabilizing the color of raw materials do not take into consideration specific features in the technological processing of raw materials.

Therefore, it is the important and relevant task to study the processes that lead to changing the color-forming substances during processing, as well as to identify techniques to stabilize the color, as these transformations affect the formation of quality and consumer properties of the product.

2. Literature review and problem statement

The results of previous studies [1, 2] allowed us to establish qualitative and quantitative composition of the pigment complex of berries of gooseberry and stalks of rhubarb. Analysis revealed that the basic color-forming components are chlorophylls whose total content for different varieties of rhubarb is $(3.7...4.5)\cdot10^{-3}$ %, for berries of gooseberry, it is $(3.5...4.7)\cdot10^{-3}$ %.

The vast majority of studies that address chlorophyll deal mainly with the problems of photosynthesis.

Paper [3], for example, reports the study into composition and interactions between compounds of two light-harvesting complexes of Amphidinium carterae. It was established that in both complexes the quenching of triplet states of chlorophyll by carotenoids occurs with a very high efficiency (~100 %), with the transfer time estimated to be about 0.1 ns or even less. The presence of two different carotenoid triplets makes it possible to effectively protect a photosynthetic apparatus from photoinjuries.

In paper [4], authors examined changes in the efficiency of photosynthesis, due to salt stress, for two varieties of lawns of perennial Lolium perenne L. After sowing, in 8 weeks, NaCl in aqueous solution (0 M, 0.15 M, and 0.30 M) was added. The measurements were carried out in 0, 24, 48, 96, 144, 192, 240, 288 hours. The results allowed the authors to identify different boundary parameters for the photosynthetic efficiency of perennial varieties of grass grown under conditions of salt stress. This helps select plants with the higher potential efficiency of the photosynthesis (vitality), which can be successfully employed for the roads where salt is used.

The study of plants resistance to the impacts of chemical agents is described in paper [5]. The authors reported results of the effect of different concentrations of the insecticidal preparation dimethoate on the photosynthetic activity and intensity of growth of Cajanus cajan L. over 30 days. It was established that the insecticide is very toxic for the plant Cajanus cajan L. even at a very low concentration, if used over a long time. Thus, the optimal dose of the insecticide for agricultural practice was determined in the study.

Many papers focused on studying new preparatory and technical methods for isolating the pigment and its derivatives. Ultrasonic extraction, for example, was applied to obtain chlorophyll compounds from biomass of the microalgae Phormidium. It is proved that the extract of chlorophyll is a powerful absorber of the peroxyl radical, which is almost 200 times more effective than α-tocopherol [6].

In order to obtain a stable food dye in the form of a zinc complex with chlorophyll derivatives, the cellulose of spinach was treated with 300 mg/l of Zn^{2+}, followed by heating at 110 °C for 15 minutes. The concentration of the zinc complex increased at pH values of 7.0 or higher. Pretreatment with an enzyme and extraction in ethanol resulted in an increase in the yield of Zn-chlorophyll by 39 % [7].

In the scientific literature [8] it was also reported a technique for manufacturing pastes from fresh nettle using a method of mechano-chemical activation, which makes it possible to increase the content of chlorophyll compared with the method of maceration in alcohol paste by 11 %, in oil paste by 31 %, in alcohol-oil paste by 14 %, and to reduce duration of pastes preparation to 12…35 minutes.

Scientists proposed a technique for producing canned food with green peas [9], in which NaCl, $CaCl_2$ or other water-soluble organic edible calcium salt are used as additive, which contributes to obtaining the darker coloring of peas and prevents the loss of biologically active substances.

A study was conducted to investigate the mechanism of degradation of chlorophyll when storing broccoli under microvacuum (MV). Following the thermal treatment, broccoli was stored under MV (70±5 kPa) and under atmospheric pressure, at 3±1 °C, for 49 days. The results revealed that the degradation of chlorophyll can be inhibited under condition of storing under microvacuum (MV). The authors studied the relationship between a chlorophyll content in broccoli and color parameters (values a/b) in order to construct a model for predicting the content of chlorophyll in broccoli. This model is based on a change in the color parameters under conditions of MV. Verification showed that the prediction model can reflect changes in the content of chlorophyll during storage, to provide a theoretical basis for subsequent application of the technology of non-destructive control [10].

In [11], authors examined effect of microwave irradiation (1,000 W over 340 s) and conventional heat treatment at 97 °C, over 30 s (pasteurization) on the content of carotenoids and chlorophylls in mash made from kiwi. The results revealed a noticeable loss of chlorophyll (42–100 %) and carotenoids (62–91 %). The authors also explored influence of storage conditions (4, 10, 22 °C for a period to 63 days) on the reduction of content of natural pigments. It was established that the exposure to microwave irradiation preserves the pigments better.

Therefore, in order to stabilize plant pigments and the coloration of raw materials, there were developed a large number of techniques that make it possible to manufacture products with high organoleptic indicators and nutritional value. For example, to prevent the destruction of chlorophyll and to stabilize coloration of the chlorophyll-containing raw materials, different additives are used: mineral compounds (salts), organic acids, alkaline agents; known antioxidants such as carotenoids, tocopherols. Nevertheless, the universal method is missing as the processes are sufficiently complex and ambiguous in nature and depend both on the chemical composition of a raw material and processing parameters. Hence, practically each particular case requires specific approach.

Technologies of processing rhubarb and gooseberry involve the following operations: cleaning, shredding, pressing, heat treatment (cooking, blanching, treatment with hot steam, boiling).

Shredding the chlorophyll-containing raw materials to a puree-like condition leads to a thorough mixing of the components of chemical composition of plant raw materials. This process results in breaking the bonds in pigment-protein-lipid complexes and in extracting free chlorophyll. The released chlorophyll is rapidly destroyed due to the processes of pheophytinization, which has a negative impact on the coloration of food products.

It should be noted that the use of many substances is very dangerous to human health. Some techniques are challenging technically and require re-equipment of production, while efficiency of many techniques is questionable. Given the above, it is a promising direction to search for new methods for stabilizing plant pigments during processing of fruits and vegetables, which would be more effective and safe. In addition, authors of the abovementioned papers describe effectiveness of stabilization of the pigment complex only by the quantitative content of pigments and by the visual estimation of color. An objective assessment of color is lacking. In this regard, it is impossible to provide a comparative analysis of the proposed methods and to determine the most efficient and universal. It is necessary to consider the possibility to characterize a technique for stabilizing the color of product using objective parameters: wavelength, brightness, saturation, purity of tone, etc.

3. The aim and objectives of the study

The aim of present study was to determine special features of the effect of heat treatment, the degree of shredding and the type of stabilizing additives on the transformation of chlorophylls and change in the coloration of rhubarb and gooseberry. This would make it possible to determine optimal conditions for processing in order to preserve chlorophylls and color of rhubarb and gooseberry.

To accomplish the set aim, the following tasks have been solved:

– to determine the effect of heat processing (blanching, treatment with steam, boiling for 10–60 s, boiling for 30–60 s) on the extent of destruction of chlorophylls in rhubarb and gooseberry;

– to determine the content of chlorophylls in rhubarb and gooseberry depending on the degree of shredding the samples;

– to determine the effect of stabilizing additives ($MgSO_4$, $MgCl_2$, $CaCl_2$, KCl) on the content of chlorophylls in the examined raw materials.

4. Materials and methods of research

The objects of research were berries of gooseberry of the variety Malachite and petioles of rhubarb of the variety Monarch. In order to determine a stabilizing effect of different salts on the chlorophyll and color of rhubarb and gooseberry, we used a 1 % solution of salts of $MgSO_4$, $MgCl_2$, $CaCl_2$, KCl. Rhubarb and gooseberry were shredded to a puree-like condition, then we added salt in ratio 1:1; the mixture was kept at room temperature for 30–60 s and then blanched. Following the blanching, we determined the content of chlorophyll a and b, as well as the degree of destruction of pigments relative to the starting value.

More details on materials and methods of research are given in [12].

5. Results of study of the content of chlorophyll depending on the type of technological treatment

The results of impact of heat treatment on the color of rhubarb and gooseberry are given in Table 1. As the data indicate, 85.8±4.2 % of chlorophyll in rhubarb and 82.0±4.1 % of chlorophyll in gooseberry are destroyed during boiling. Blanching in water results in the loss of 76.2±3.8 % and 66.1±3.1 % of chlorophyll in rhubarb and gooseberry, respectively.

After treatment with steam (boiling in steam-air mixture at a temperature of 80...90 °C), 72.4...78 % of the starting content of chlorophyll are destroyed in rhubarb and gooseberry. We determined by visual observation that the color of samples of rhubarb and gooseberry changes depending on the degree of destruction of chlorophyll: from green to yellow with a dirty tint. The boiling employed in the manufacture of products with high content of dry substances (pastes, jams, jam, etc.) leads to almost total destruction of chlorophyll both in samples of rhubarb and gooseberry.

Shredding (Fig. 1) of petioles of rhubarb into pieces of varying lengths (15, 20, 25, 30 mm) and puree-like crushing of gooseberries reduce the content of chlorophyll. The content of chlorophyll in the berries of gooseberry prior to heat treatment (control) was $3.11 \cdot 10^{-3}$ %, after blanching – $0.1 \cdot 10^{-3}$ %, it decreased in rhubarb from $3.85 \cdot 10^{-3}$ % (control) to $0.55...1.16 \cdot 10^{-3}$ % depending on the degree of shredding.

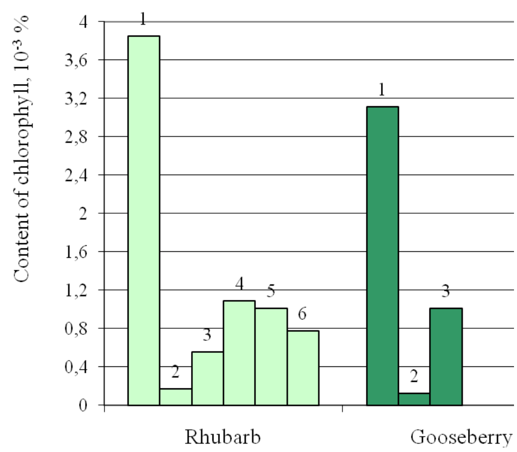

Fig. 1. Chlorophyll content depending on the degree of shredding the samples (after thermal treatment): Rhubarb: 1 — starting raw material, 2 — puree-like shredding, 3 — 15 mm, 4 — 20 mm, 5 — 25 mm, 6 — 30 mm; Gooseberry: 1 — starting raw material, 2 — puree-like shredding, 3 — whole berries

Table 1

Effect of heat treatment on the content of chlorophyll in petioles of rhubarb of the variety Monarch (pH=2.14) and berries of gooseberry of the variety Malachite (pH=2.35), and on color (Sr=0.05, n=5, p=0.95)

Type of heat treatment	Rhubarb			Gooseberry		
	Content of chlorophyll, 10^{-3} %	Destruction in % of the starting value	Visual estimation of color	Content of chlorophyll, 10^{-3} %	Destruction in % of the starting value	Visual estimation of color
Raw material (prior to treatment)	4.51	–	green	3.89	–	green
Blanching, 80...85 °C	1.07	76.0	yellow with a greenish shade	1.32	66.0	yellow with a greenish shade
Steam treatment, 80...90 °C	1.01	78.0	light-yellow	1.07	72.0	yellow
Boiling, 10-60 s	0.64	86.0	yellow	0.70	82.0	yellow
Boiling, 30-60 s	0.12	98.0	yellowish-brown	0.10	97.0	dark yellow-brown

As the data obtained indicate (Fig. 2, 3), from 78.2 to 87.5 % of chlorophyll *a* and 63...65 % of chlorophyll *b* are destroyed in control samples of rhubarb and gooseberry.

Adding a salt of $MgCl_2$ exerts the greatest effect on the stabilization of chlorophyll. In this case, the degree of destruction of chlorophyll *a* in rhubarb and gooseberry is 33.0...44.2 %, of chlorophyll *b* – 22.7...37.4 %.

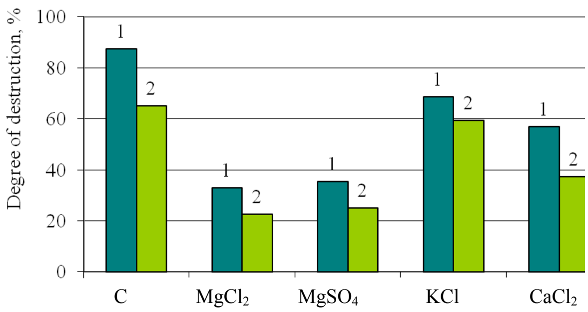

Fig. 2. Effect of additives on the destruction of chlorophyll in rhubarb: C — control (without additives), 1 — chlorophyll *a*, 2 — chlorophyll *b*

Based on the results of conducted research, we selected, for the stabilization of chlorophylls in rhubarb and gooseberry, potassium chloride and magnesium chloride as the substances that have the same anion in order to avoid substitution reaction between salts.

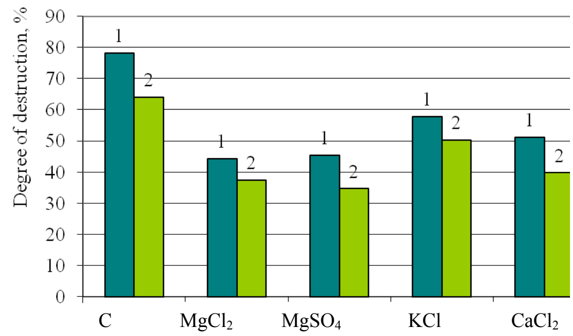

Fig. 3. Effect of additives on the destruction of chlorophyll in gooseberry: C — control (without additives), 1 — chlorophyll *a*, 2 — chlorophyll *b*

To determine the optimal conditions for treating plant raw materials, taking into consideration results of the research conducted, we performed a multi-factor experiment. The concentrations of MgCl and KCl salts, the degree of shredding (rhubarb), duration and temperature of the treatment were chosen as variables. The criterion of treatment efficiency was the color characteristics of samples.

Estimated color characteristics are given in Table 2, 3.

Table 2

Impact of the treatment parameters of rhubarb on its color-parametric characteristics

No. of entry	Samples	Treatment parameters					Color-parametric characteristics			Visual estimate of color
		Concentration of $MgCl_2$ in solution, %	Concentration of KC1 in solution, %	Dimensions of pieces, mm	Treatment duration, τ, min.	Treatment duration, *t*, °C	Dominant wavelength, λ_{nm}	Color purity *P*, %	Brightness *T*, %	
1	Control, rhubarb (raw material)	–	–	–	–	–	574	58.5	42.3	Green
2	Treated rhubarb (aged in solution)	0.25	2	20×20	10	20	575	56.8	41.7	Green
3		0.25	2	20×20	20	20	574	59.9	42.6	Green
4		0.25	2	20×20	30	20	575	63.9	43.2	Green
5		0.25	2	20×20	40	20	574	56.1	41.7	Green
6		0.05	2	20×20	30	20	574	59.8	42.5	Green
7		0.15	2	20×20	30	20	576	58.8	41.9	Green
8		0.25	2	20×20	30	20	575	63.9	43.2	Green
9		0.35	2	20×20	30	20	578	57.7	41.1	green-yellowish
10		0.25	0.5	20×20	30	20	578	47.8	39.4	green-yellowish
11		0.25	1	20×20	30	20	577	56.9	41.3	Green
12		0.25	2	20×20	30	20	575	63.9	43.2	Green
13		0.25	3	20×20	30	20	578	59.1	41.4	green-yellowish
14		0.25	2	10×10	30	20	578	53.2	40.5	Green
15		0.25	2	20×20	30	20	575	63.9	43.2	Green
16		0.25	2	30×30	30	20	576	60.2	42.1	Green
17		0.25	2	40×40	30	20	575	58.3	41.9	Green
18		0.25	2	20×20	30	20	575	63.9	43.2	Green
19		0.25	2	20×20	30	40	585	40.5	45.8	Yellow with a greenish shade
20		0.25	2	20×20	30	60	588	41.9	84.6	Yellow
21		0.25	2	20×20	30	90	613	34.1	56.5	Yellow-brownish

Table 3

Impact of the treatment parameters of gooseberry on its color-parametric characteristics

No. of entry	Samples	Treatment parameters				Color-parametric characteristics			Visual estimate of color
		Concentration of $MgCl_2$ in solution, %	Concentration of KC1 in solution, %	Treatment duration, τ, min.	Treatment temperature, t, °C	Dominant waveguide, λ_{nm}	Color purity P, %	Brightness T, %	
1	Control, gooseberry (raw material)	–	–	–	–	575	42	41.0	Green
2	Treated gooseberry (aged in solution)	0.25	2	10	20	574	53	43.0	Light-Green
3		0.25	2	20	20	574	53	43.0	Light-Green
4		0.25	2	30	20	575	41	40.7	Green
5		0.25	2	40	20	571	46	42.1	Green
6		0.05	2	30	20	578	45	40.7	Green-yellow
7		0.15	2	30	20	575	46	42.1	Green
8		0.25	2	30	20	575	41	40.7	Green
9		0.35	2	30	20	571	32	40.7	Green
10		0.25	0.5	30	20	583	41	39.5	Green-yellow
11		0.25	1	30	20	576	40	40.2	Green
12		0.25	2	30	20	575	41	42.1	Green
13		0.25	3	30	20	574	57	43.0	Light-Green
14		0.25	2	30	40	583	43	56.5	Yellow with a green shade
15		0.25	2	30	60	585	42	73.5	Yellow
16		0.25	2	30	90	620	28	62.0	Yellow-brownish

The obtained results allow us to state the following. Duration of treatment only slightly affects color characteristics of rhubarb and gooseberry. Thus, the wavelength ranges from 571 to 575 nm, color purity of rhubarb is 56.1–63.9 %, of gooseberry – 41–53 %, brightness is 41.7–43.2 % (rhubarb) and 40.7–43.0 (gooseberry). Visually, all samples are of green color.

6. Discussion of results of studying effect of different kinds of technological treatment on preservation of chlorophylls in rhubarb and gooseberry

When manufacturing products from plant raw materials whose pigment complex contains mostly chlorophylls, the color, due to the destruction of natural pigments, typically turns, under the influence of various factors, from green to yellow-brown, which adversely affects consumer choice.

Results of the impact of different types of heat treatment on the color of rhubarb and gooseberry revealed that various types of heat treatment affect destruction of chlorophylls and accumulation of the products of their degradation in different ways, gradual changing the color from bright green to olive green to yellow-brown. The resulting product completely loses its original color after a certain time. Results of the studies conducted allowed us to establish that the application of blanching leads to a minimum degree of destruction of chlorophyll and color in the petioles of rhubarb and berries of gooseberry compared with other types of heat treatment.

Examining the influence of the degree of shredding of raw materials allowed us to establish that the optimal size of rhubarb pieces is 20...25 mm, which makes it possible to decrease chlorophyll destruction by 1.5...2 times in comparison with other samples. Shredding larger than 30 mm requires longer duration of thermal treatment owing to the fibrous structure of rhubarb petioles.

If we compare the stabilizing effect of $MgCl_2$ and $MgSO_4$ salts, it is almost the same for the samples of rhubarb and the samples of gooseberry. Minimum stabilizing effect was demonstrated by salts of calcium chloride and potassium. The degree of destruction of chlorophyll *a* in the samples of rhubarb reaches 57.0 and 68.6 %, in the samples of gooseberry – 51.1 and 57.8 % for salts of calcium chloride and potassium, respectively.

It was also found that the nature of anion does not impact significantly the content of chlorophylls in the samples with the same cation ($MgCl_2$, $MgSO_4$). The concentration of potassium chloride does not considerably affect the change in color-parametric characteristics. However, combined use of $MgCl_2$ and KCl salts in a solution produces synergy. It is most pronounced, first of all, in the samples of rhubarb. This is probably due to the microstructure of petioles whose fibrous structure increases specific surface to enable the intermembrane osmotic diffusion of $MgCl_2$ and KCl salts to the cell, as well as by the larger ion permeability of K^+, Cl^-.

Dense shell of gooseberries prevents active course of the specified processes, which is why effectiveness of the protective effect of these additives is lower not only relative to the chlorophylls, but to the color as well.

Temperature is an important factor in the treatment of both petioles of rhubarb and gooseberries. Temperatures below 20 °C reduce effectiveness of the treatment, because, in this case, the rate of diffusion processes reduces. An increase in the temperature of the solution above +30 °C leads to changes in color characteristics.

The multi-factor experiment performed allowed us to determine a dependence of the color parameters of raw materials on the concentration of $MgCl_2$ and KCl salts, the degree of shredding (rhubarb), duration and temperature of the treatment.

The study we performed also revealed that a certain protective effect of additives is observed not only relative to the chlorophylls, but also to the carotenoid complex and vitamin C.

Results of the conducted experiments allowed us to establish parameters for the treatment of rhubarb and gooseberry in order to preserve chlorophylls (*a*+*b*) in the product. For the petioles of rhubarb, the size of 20 mm, and the whole gooseberries, the optimal parameters are aging in a stabilizing mixture (0.25 % solution of magnesium chloride and 2 % of potassium chloride) over 30 minutes at a temperature of 20 °C.

Determining the parameters makes it possible to ensure improved consumer properties of rhubarb and gooseberry through maximal preservation of physiologically active substances and the original color of raw materials. This renders an increased level of competitiveness to new products.

Present work is part of the comprehensive research into assessment of the quality of chlorophyll-containing plant raw materials. We plan to conduct similar experiments with other varieties and hybrids of gooseberry and rhubarb, as well as other pomological varieties of fruits and vegetables.

7. Conclusions

1. It was established that technological treatment impacts objective color-parametric characteristics of fruits and vegetables, specifically, deviations in values of the dominant wavelength, purity of color, and brightness, from the value for the untreated samples. The determined color characteristics allowed us to establish that the red component of the color of samples increases considerably during heat treatment, while the green component of the raw material decreases. The indicator “purity of color” characterizes green color of the raw materials. Yellow shade in the color of samples appears during blanching and hot steam treatment. Yellow color appears in samples during boiling; brown shade in the yellow color of samples – during prolonged boiling.

2. It was established that the application of blanching leads to a minimum degree of the destruction of chlorophyll and color in the petioles of rhubarb and gooseberries compared with other types of heat treatment. The experimental study allowed us to determine the degree of rhubarb shredding into pieces the size of 20…25 mm; optimal for gooseberry is the processing of whole berries.

3. We determined conditions for processing plant raw materials with a stabilizing mixture that contains a solution of 0.25 % magnesium chloride and 2 % potassium chloride, for 30 minutes at a temperature of 20 °C. The obtained color characteristics of the raw materials treated using a given technique are at the level of color characteristics of control, testifying to the effectiveness of the designed technique.

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