

This paper has substantiated the possibility of using an IR spectroscopy method to study patterns in the chemical composition of wild and cultivated raw materials with the addition of algae as iodine-containing supplements.

It has been found that the IR spectra of sauces based on the mashed blueberry and sea buckthorn or cranberry with or without algae demonstrate a set of absorption bands attributed to the respective types of oscillations. The valence fluctuations in the hydroxyl groups in the molecules of organic acids, carbohydrates, flavonoids are observed at $3,365\text{ cm}^{-1}$ to $3,400\text{ cm}^{-1}$ $\nu(\text{OH})$. The bands of valence and deformation fluctuations of the $-\text{CH}$ double bond of polyunsaturated fatty acids manifest themselves in the range of $3,005\text{ cm}^{-1}$ and 722 cm^{-1} . The bands of $2,925\text{ cm}^{-1}$, $2,855\text{ cm}^{-1}$ belong to the asymmetric and symmetric valence oscillations of the $\nu(\text{C}-\text{H})$ carbon skeleton in $-\text{CH}_2-$. The presence of the carboxylic, amino-, and fatty acids is indicated by the following absorption bands: $1,746\text{ cm}^{-1}$ – $\nu(\text{C}=\text{O})$ valence fluctuations in the protonated carboxyl group – COOH ; $1,545\text{ cm}^{-1}$ – $\nu_{\text{as}}(\text{C}=\text{O})$; $1,415\text{ cm}^{-1}$ – $\nu_{\text{s}}(\text{C}=\text{O})$ – the asymmetric and symmetric valence fluctuations of the COO groups; and $1,240\text{ cm}^{-1}$ – the valence fluctuations of $\nu(\text{C}-\text{O})$. The presence of flavonoids is confirmed by the presence of bands at $1,380\text{ cm}^{-1}$ and $1,050\text{ cm}^{-1}$ – the deformation $\delta(\text{O}-\text{H})$ and symmetrical fluctuations of $\text{O}-\text{H}$ groups. The fluctuations of pyranose cycles of pectins are manifested in the range of $1,163\text{ cm}^{-1}$.

It is noted that the composition of berry raw materials and sauces include polyunsaturated fatty acids, anthocyanins, flavonoids, organic acids, and pectin substances.

An analysis of the IR spectra of berry sauce samples with the addition of algae has shown that the use of these additives in sauce technologies ensures a significant increase in the content of the physiological and functional ingredients and improves the hydrophobic properties of the raw materials

Keywords: wild and cultivated berries, algae raw materials, iodine-containing additives, berry sauces, IR spectroscopy

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DETERMINING THE CONTENT OF MACRONUTRIENTS IN BERRY SAUCES USING A METHOD OF IR-SPECTROSCOPY

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1. Introduction

The variety of fruit and berry raw materials makes it possible to increase the range of functional products. At present, the industry mostly uses traditional European fruits and berries. However, berries that are typical of our region are rarely used in food technology, most of them are frozen and then exported. In particular, according to statistics, in 2015–2019, the volume of exported wild raw materials in the world in-

creased by an average of 6% [1]. For example, the leader in the export of frozen berries is blueberries; over the past three years, about 17–18 thousand tons/year are exported abroad. In total, about 30,000 tons of frozen Ukrainian berries are exported to foreign markets every year. Berries are grown across all the natural and climatic zones of Ukraine. The most common among wild berries are mainly blueberries, viburnum, cranberries, sea buckthorn, dogwood. Berries quickly enter the fruiting stage (at the second, third year after planting); there-

fore, it is possible to increase the resources of their consumption in a short period. In addition, many berry crops begin to bear fruit earlier than other fruit crops [2].

The development of organic food products using wild and cultivated berry raw materials implies the use of modern equipment for their more ergonomic use. However, only about 10 % of entrepreneurs have modern equipment, which is why promising are the proposals for newly developed products with enriched chemical composition but without the use of modernized expensive equipment [2].

Given the limited resources for technical re-equipment, manufacturers address the issue of competitiveness by expanding the range and improving the consumer properties of the product, taking into consideration the rational nutrition of the population using non-traditional plant raw materials [3].

It should be emphasized that in a short time an unusual combination of flavors is becoming more widespread in the food industry. Combining wild and cultivated berries with the addition of algae as an iodine-containing additive is characterized by the difficulty to combine these components, due to the difference in their taste properties.

A significant amount of iodine contained in aquatic organisms allows them to be used as iodine-containing additives. Leaders among them are edible brown seaweed, including kelp, focus, and undaria pinnate, whose iodine content can reach hundreds of milligrams per gram of algae. In addition, it is known that up to 95 % of their iodine is in the form of organic compounds, which is the main advantage. The most important disadvantage of the use of inorganic iodine compounds is that the body does not participate in the regulation of iodine intake of these compounds into the thyroid gland. However, when using organic compounds of iodine, the human body absorbs only the required amount of iodine while the excess is excreted from the body.

The results reported here are of practical importance for substantiating the selection of the combination of raw materials, in particular, wild and cultivated berries in a complex with seaweed raw materials. This would help create a product with enhanced nutritional value and reduce iodine deficiency in the population.

2. Literature review and problem statement

Emulsion and tomato sauces account for most of the innovations in the food and canning industries. The newest advancements in these technologies are mostly considered from the standpoint of improving their nutritional and biological value.

It should also be noted that there is a rather narrow range of technologies in the production of berry sauces, which are represented mainly from the standpoint of improving their mineral and vitamin composition through the use of various flavors and new structuring ingredients.

The main shortcomings of these technologies are the insufficiently pronounced taste characteristics and a low nutritional value, which predetermines the low content of dietary fiber, a lack, or low content of iodine.

Given that the consumption of a few grams of algae can meet the daily human need for a micronutrient such as iodine, they can be used as food additives for the iodization of food [4]. This can be confirmed by a series of existing developments. However, it should be noted that currently most developments that use algae as food additives belong

to the production of raw materials of animal origin. First of all, one can note those studies that report new products involving the brown seaweed fucus, cystosira, kelp in the technology of cheese [5], yeast buns, bread, dumplings, pancakes, fish cakes, salads made from fresh vegetables [6], etc. A series of different technologies have been developed, such as minced vegetables and meat, other meat products, cheesecakes, bars with sour milk filling, as well as others in which the seaweed kelp and focus were used [7]. A series of studies have been performed [8], starting with the development of a formulation and specifying the quality of minced meat with the addition of a kelp extract, and to the development of formulations for their possible consumption, such as pies, cooked sausages, etc. The possibility of stabilizing the system with the addition of oil extracts of algae to the composition of drinking milk and butter has been studied [9].

Currently, there are a series of developments including iodine-containing additives in the sauce technology. Thus, a technique was developed in [10] to receive a fruit and vegetable sauce with an iodine-containing additive, which, as it was proposed, is iodocasein. The base of this sauce was a mixture of apple, tomato, zucchini, pumpkin, carrot, beet puree with the addition of acetic acid, sugar, salt, a mixture of black and red peppers. The development implied the task of reducing the cost of sauces production and providing the resulting product with preventive properties. Thus, in [11], sour cream and vegetable sauces were developed for the prevention of iodine deficiency diseases with the addition of a multifunctional additive from kelp. There are formulations of sauces from brown seaweed, using the technology of lactic acid fermentation [12]. A series of experiments have been performed regarding the possibility of adding seaweed extracts to food [13]. However, our analysis of the scientific literature did not reveal any developed products with the use of seaweed raw materials in berry sauce technology.

The relevance of the combination of algae and berry raw materials is primarily due to the chemical composition of these raw materials.

Among the algae raw materials, in terms of the iodine content, the following algae can be distinguished – *Laminaria Digitata* (kelp), *Undaria pinnatifida* (Undaria pinnate), *Fucus* [14]. In addition to iodine, these raw materials are characterized by a significant content of proteins and amino acids and broad carbohydrate composition, in particular alginic acid, which can act as a structuring agent and emulsifier. Kelp contains mannitol, water, fat, protein, carbohydrates, amino acids, some microelements: calcium, sodium, iron, zinc, vitamin C, carotene [15]. Undaria algae are rich in such vitamins and minerals as beta-carotene, vitamin B₁, B₂, PP, potassium, calcium, magnesium, iodine, manganese. The organic components of Undaria pinnate consist of carbohydrates, nitrogen-containing substances, lipids. In addition to alginic acid, carbohydrates are represented by fucoidan and mannitol. The monosaccharide composition of Undaria pinnate is represented by mannose, fucose, galactose, xylose, and glucose [16]. Fucus contains a complete set of micro- and macronutrients. It includes iron, calcium, potassium, silicon, magnesium, selenium, sulfur, zinc, phosphorus, boron, barium, etc. Fucus is rich with vitamins (A, B₁, B₂, B₃, B₁₂, D₃, E, K, F, H, PP, C), organic acids (alginic, folic and pantothenic, etc.), fiber, polysaccharides (alginates, laminarin, fucoidan), polyphenols.) Fucus contains the largest amount of fucoidan [17].

It can be noted that brown algae include a significant amount of substances with high functional and technological properties, which are characterized by the high-quality compo-

sition of carbohydrates and proteins. Table 1 gives the content of the main macronutrients in algal raw materials [18–20].

Table 1

Aglae chemical composition

Substance	Content, % per dry matter		
	Kelp	Fucus	Undaria pinnate
Proteins	8–15	3–11	11–24
Lipids	1–2	4–11	2–3
Carbohydrates	34–55	12–18	37–53
including fucoidan	2–4	9–11	5–16
Mineral substances	24–56	32–37	22–30
including iodine	<3	<8	<7

Among the berry raw materials are wild blueberries and cranberries, as well as the cultivated sea buckthorn berries. These raw materials are primarily rich in flavonoids, carotenes, tocopherols, pectins, alginates, ascorbic acid. In addition:

- cranberries include the following components: organic acids – citric, quinine, benzoin; water-soluble vitamins, macro- and microelements – calcium, magnesium, sodium, potassium, phosphorus, and iron; flavonoids and tannins, dietary fibers [21, 22];

- blueberries include the following components: organic acids – citric, milk, malic, amber, oxalic; vitamins of the B, PP, K group, fiber; essential oils; tannins, glycosides, anthocyanins [21, 23];

- sea buckthorn fruits contain organic acids – malic, citric, coffee, and tartaric; vitamins – B₁, B₂, B₅, B₆, B₉, H, PP; macro- and microelements – calcium: magnesium, sodium, potassium, phosphorus, and iron; polyunsaturated fatty acids [21, 24].

The listed components that act in a combination yield the expressed positive effects that influence practically all systems of the human body. It is proven that the proposed berries provide pronounced health and preventive effect on humans and can be used in the technology of culinary dishes and by the manufacturers of functional-purpose food. Thus, the issue of improving existing and creating new food technologies based on berry raw materials, typical of our region, in order to obtain products with an enhanced biological value is quite relevant.

Earlier studies developed sauce technologies based on blueberry and cranberry or sea buckthorn puree with the addition of different percentages of kelp, focus, and pinnate algae [5]. A series of analytical and experimental studies were performed to confirm the iodine content in the algae raw materials. Given the formation of organoleptic quality indicators, it was possible to add hydrated algae in quantities of 3–8 % of the original formulation mass [25]. Rheological studies have proven that there are enough natural pectin substances in the berry raw materials to stabilize the system, so the additional introduction of stabilizers does not make sense. Those studies were conducted by comparing the rheological dependences that reveal control samples and samples of sauces, which were prepared on the basis of the developed technology. Control samples were the sauces that had been prepared according to existing technologies based on the most common stabilizers. It was found that the similar dynamics, in comparison with control samples, are demonstrated by the samples of sauces with the addition of up to 8 % of hydrated kelp and 3 % of fucus and Undaria pinnate. By examining the safety indicators of sauces, we proved the inexpediency of adding components that extend the shelf life and microbiological purity of finished products, including pre-

servatives and antibiotics [26]. Thus, the proposed technology, in addition to the expected increased biological and nutritional value, differs from existing analogs by its naturalness.

At this stage of our research, there is an issue related to determining the chemical composition not only of the raw materials but the finished sauces as well by the method of IR spectroscopy. Literature sources were used to assign absorption bands to the corresponding functional groups of the components of the studied samples.

According to data given in [29], the absorption bands in the range of 3,650–3,200 cm⁻¹ characterize the presence of the –OH group in the intermolecular hydrogen bonds. This occurs because during the formation of a hydrogen bond the force of the O–H constant bond decreases; the band shifts to the low-frequency region to 3,500–2,500 cm⁻¹. The stronger this interaction the lower the oscillation frequency is. Thus, the absorption bands of 3,317–3,279 cm⁻¹ in the IR spectra of the experimental samples are due to the valence fluctuations of phenolic hydroxyl in the intermolecular hydrogen bonds.

It should also be noted that the bands of 1,657–1,628 cm⁻¹ are caused by a double bond of the oxygen-containing cycle. Some bands in this range are characteristic of the benzene nucleus. The strong peak at 1,460–1,440 cm⁻¹ is attributed to the deformation oscillations, –CH– in –CH₂–, and a maximum of the peak intensity at 1,420 cm⁻¹ is attributed to the common band of the valence oscillations C–O and the planar deformation fluctuations of OH in –COOH.

It should be noted that the group of weak bands in the range from 1,200 cm⁻¹ to 1,400 cm⁻¹ is characteristic of the fluctuations in the –CH₂– carboxylic acids, whose number provides information about the length of the carbon chain.

The presence of carbohydrates in the samples can be indicated by the absorption bands caused by the valence oscillations of –CH₂ groups at a frequency of 2,925–2,934 cm⁻¹. The fluctuations associated with the C–O–H group are R–O–H (the frequencies of 1,450–1,250 cm⁻¹, 750–650 cm⁻¹), primary alcohols (the frequencies of 1,075–1,000; 1,350–1,260 cm⁻¹), secondary alcohols (the frequencies of 1,350–1,260 cm⁻¹), tertiary alcohols (the frequencies of 1,170–1,100; 1,410–1,310 cm⁻¹), phenols (the frequencies of 1,270–1,140; 1,410–1,310 cm⁻¹). The fluctuations of the carboxylic acid groups are the valence oscillations of COOH groups (1,760; 1,725–1,700 cm⁻¹), OH-group (3,300–2,500 cm⁻¹, 995–890 cm⁻¹), the oscillations of C–O bonds (1,320–1,210 cm⁻¹); the oscillations of C–O–C in the esters of aromatic acids (1,300–1,250 cm⁻¹) [30].

In the range of 1,200–1,030 cm⁻¹, there are complex bands attributed to the valence fluctuations of the ether and hydroxyl groups ν (C–O) (1,024 cm⁻¹ for glucose, 1,059 cm⁻¹ for cellulose, 1,072 cm⁻¹ for sucrose). The presence of the band of 924–922 cm⁻¹ is attributed to the oscillations of –C–O–C– ether bonds [31].

Berries are rich in carotene, so it should be taken into account that the IR spectrum of carotene is characterized by the average intensity band of 1,564 cm⁻¹ that corresponds to the valence fluctuations of the bonds –C=C–. In the range of 1,450 cm⁻¹, in the IR spectrum, there is a wide band of the asymmetric deformation oscillations of CH₃ group (a change in the angle of connection HCH) and CH₂ group (scissor fluctuations). The subsequent bands of the low or medium intensity of 1,396–1,369 cm⁻¹ are formed by the umbrella oscillations of CH₃ and CH₂ groups – ionic rings. The band of 960 cm⁻¹ corresponds to the deformation oscillations of the isomerized ring mixed with the deformation oscillations of the CH₃ groups

located on the same ring. The absorption bands of $1,150\text{ cm}^{-1}$ and $1,312\text{ cm}^{-1}$ are attributed to the deformation oscillations of ionic rings and the ring CH_2 groups [32].

The presence of tocopherol in berry raw materials is evidenced by the following data. For tocopherol, in the IR spectrum, symmetric deformation oscillations of the C-CH_3 and C-CH_2 groups are located in the frequency range of $1,380\text{--}1,300\text{ cm}^{-1}$. The symmetric and asymmetric valence oscillations of the C-O-C group bonds are represented by absorption bands in the frequency range of $1,280\text{--}1,010\text{ cm}^{-1}$. The absorption band of $1,169\text{ cm}^{-1}$ is characteristic of the deformation oscillations of the free OH group of phenol. The valence fluctuations of free phenolic hydroxyl, according to the literature, are in the frequency range of $3,634\text{--}3,439\text{ cm}^{-1}$. The IR spectrum of α -tocopherol is characterized by the absorption bands of $1,097$ and 813 cm^{-1} , associated with the presence of a tetrahydropyran cycle in its structure. The absorption band of $1,169\text{ cm}^{-1}$ is attributed to the oscillation of the tocol fragment. These structural fragments of the α -tocopherol molecule are responsible for the manifestation of the specific E-vitamin pharmacological activity. The specific frequencies detected in the spectrum can be considered characteristic of α -tocopherol, and, therefore, they can be used as the markers of the presence of tocopherols in various complex biological objects [33].

It should be considered that plant raw materials contain a significant amount of pectin. The pectin IR spectrum is characterized by a wide absorption band in the range of $1,100\text{--}1,000\text{ cm}^{-1}$, which is characteristic of the C-O-C bond of the pyranose ring of the pectin macromolecule. The absorption range of $2,900$ and $2,820\text{ cm}^{-1}$ is characteristic of the C-H bonds, and the absorption bands in the region of $1,730\text{ cm}^{-1}$ are characteristic of the valence fluctuations of the C=O group in the -COOH groups of polyuronide. The absorption bands in the region of $1,620\text{ cm}^{-1}$ are characteristic of the ionized carboxyl (-COO-) group and the C=C bonds. Pectin is characterized by a band of valence oscillations of the OH group in the region of $3,600\text{--}3,400\text{ cm}^{-1}$ and the deformation oscillations of the OH group in the region of $1,400\text{--}1,250\text{ cm}^{-1}$; oscillations in the region of $1,200\text{--}1,000$ and $850\text{--}400\text{ cm}^{-1}$ relate to the pulsation fluctuations of the pyranose rings (-C-C- and C-O).

When interpreting the IR spectra, it should be noted that the wide absorption band in the range of $1,420\text{--}1,390\text{ cm}^{-1}$ can be attributed to the oscillations of >C=C and >C=O bonds.

The content of alginate in the raw materials was found along the main absorption lines of alginate – $3,438$, $1,616$, $1,415$, $1,302$, $1,095$, $1,025$, and 815 cm^{-1} [34].

The presence of flavonoids in the IR spectra is indicated by the absorption bands characteristic of the aromatic part: $3,385\text{--}2,850\text{ cm}^{-1}$ (phenolic oxy groups OH), $1,680\text{--}1,615\text{ cm}^{-1}$ (carbonyl group of γ -pyrone), $1,620\text{--}1,470\text{ cm}^{-1}$ (skeletal fluctuations of aromatic rings -C=C-), $1,100\text{--}1,000\text{ cm}^{-1}$ (C-O glycosidic bonds). Maxima at $2,950\text{--}2,880\text{ cm}^{-1}$ correspond to methoxyl groups and may indicate the presence of lignin.

The content of ascorbic acid in plant raw materials is indicated by the presence in the IR spectrum of an intense absorption band of the valence fluctuations in the region of $1,675\text{ cm}^{-1}$, which corresponds to the C=C bond; the absorption band in the region of $1,750\text{ cm}^{-1}$ corresponds to the oscillations of the carbonyl C=O group in the unsaturated ring of γ -lactone. In addition, a series of characteristic absorption bands in the range of $3,500\text{--}3,200\text{ cm}^{-1}$ is observed for ascorbic acid due to the valence oscillations of the alcohol and enediol hydroxyl OH groups. The region of “fingerprints” demonstrates the absorption bands that characterize the single C-C and C-O bonds.

The following data were also considered: the valence oscillations of the $\text{C}\equiv\text{C}$ bond are observed in the form of a weak absorption band in the region of $2,300\text{--}2,100\text{ cm}^{-1}$; the band of $1,640\text{ cm}^{-1}$ corresponds to the valence oscillations C=C- ($\nu(\text{C=C})$) that can indicate the existence of a double band in the carbon skeleton. The bands of $2,860\text{ cm}^{-1}$ and $2,850\text{ cm}^{-1}$ correspond to the valence symmetric oscillations of -C-H ($\nu_s(\text{C-H})$), which indicates the presence of the saturated carbon atoms in the molecule. The band of $1,380\text{ cm}^{-1}$ corresponds to the deformation symmetric oscillations of C-H ($\delta_s(\text{C-H})$), which indicates the presence of saturated carbon atoms in the molecule. Moreover, this band indicates the presence of a methyl (-CH_3) group in the molecule ($\delta_s\text{CH}_3$).

Thus, the increase in the chemical composition of berry sauces is achieved both through the use of stabilizing substances and through the use of non-traditional technological processes. However, such a technique assumes changes in the hardware involved in the technology, which is economically unprofitable. More promising is the use of raw materials of natural origin, which include stabilizing substances and micro- and macronutrients beneficial for the human body.

Our analysis of the scientific literature published in the past 10 years reveals that the possibility of stabilizing emulsion systems for sauces with berry raw materials by using algae has not been investigated. The issue of studying the effect of algae on berry raw materials has remained unresolved. This is a prerequisite for research in this area.

3. The aim and objectives of the study

The research aims to determine features in the qualitative chemical composition of berry sauces, namely sauces based on blueberry puree with the addition of cranberry or sea buckthorn puree, when combining these sauces with hydrated seaweed.

To achieve this goal, the following tasks were set:

- to analyze the IR spectra of sauces;
- to analyze the IR spectra of seaweed raw materials;
- to study changes in the qualitative chemical composition when combining sauces with seaweed raw materials.

4. Materials and methods to study the IR spectra of berries and sauces that contain them

During the research into the technologies of sauces, we used blueberries, cranberries, sea buckthorn under the trademark “Snowman”, gathered in Ukraine, tested for quality indicators; algae raw materials are imported from Asian countries. The objects of our study are berry raw materials, berry sauces, berry sauces with the addition of seaweed raw materials, the seaweed raw materials ground to powder.

New spectroscopy methods were used to identify the food raw materials [27]. The method of IR-Fourier spectroscopy of total internal reflection (TIR) is becoming increasingly common in studying the quality of the chemical composition of raw materials. When using this method, the IR radiation penetrates the sample to a depth of about one micrometer, and the detector registers the absorption spectrum. The method has some advantages over the technique of measurement by transmission [28].

The IR spectra were recorded at a Fourier spectrometer and the Perkin-Elmer SpectrumOne FTIR Spectrometer from potassium bromide tablets. This method is a professional

and reliable technique for functional analysis and control over components in complex systems. The spectra of the test samples were recorded in a thin layer between zinc selenide plates.

5. Results of the IR spectroscopy study of berry sauces and the raw materials they were made of

5.1. Results of studying wild and cultivated berries

The range of basic molecules' oscillations, which is also called "average infrared", lies between the wavenumbers from 4,000 to 400 cm^{-1} .

At the first stage, the IR spectra of berry raw materials were studied (Fig. 1). For the IR spectra of berries samples from wild raw materials are characterized by the presence of the specific absorption bands, the assignment of which is given in Table 2.

The chemical composition of the cranberry, sea buckthorn, and blueberry samples is quite complex and is represented by both general substances and individual ones for each berry. The samples of berry raw materials have individual spectral characteristics, different peak intensities, and areas under the spectral curve. The region of 1,000–1,600 cm^{-1} is individual for each sample, which allows determining the presence of each type of berries in the sauces.

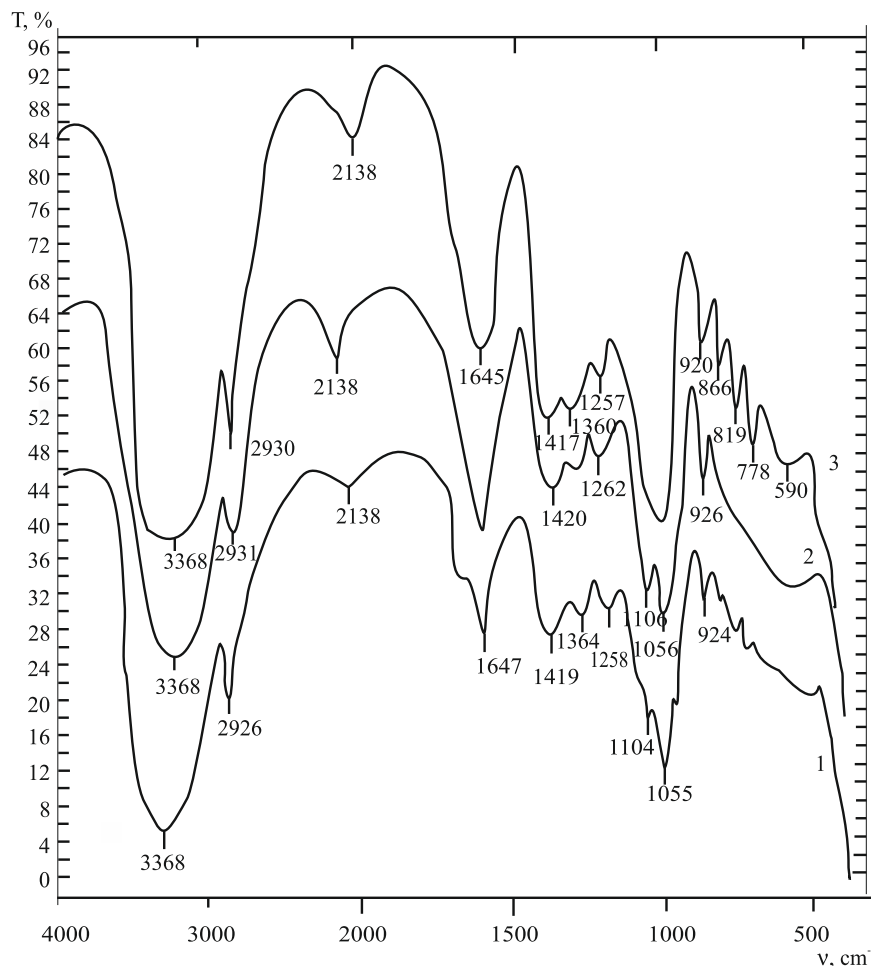


Fig. 1. IR spectra of berry samples from wild raw materials: 1 – cranberry, 2 – sea buckthorn, 3 – blueberry

Table 2

Assigning the characteristic absorption frequencies in the obtained IR spectra for the samples of berry raw materials

v, cm^{-1} (on the spectrum)			Functional group	Oscillation type	Main components
Sea buckthorn	Blueberry	Cranberry			
3,364	3,368	3,369	phenolic hydroxyl	valence oscillations O-H in intermolecular water bonds	flavonoids, water, sugar, cellulose, tocopherols, myrtillin
			C-OH	bound -OH group	
2,931	2,927	2,934	C-CH ₃ C-CH ₂	valence oscillations	sugar, cellulose, pectin, amino acids, carotene, flavonoids, tocopherols, myrtillin
1,420				asymmetric deformation oscillations	
1,360	1,364	1,362		symmetric deformation group oscillations	
1,645	1,647	1,647	-HC=CH- COO-	valence oscillations C=C of aromatic nucleus carbonyl group of γ -pyron deformation oscillations of HOH free and bound water oscillations of the C=C bond in six-membered aromatic rings ionized COO group	flavonoids, carotene, acids, pectin, vitamin C
1,262	1,259	1,261	C-OH	symmetric asymmetric oscillations of valence C-O bonds	flavonoids, fructose, glucose, sucrose, tocopherols,
1,106	1,105	1,105			
1,057	1,056	1,056			
1,645	1,647	1,647	(NH ₃ ⁺)	deformative, amino acid deformative,	amino acids
722			-CH ₂ -	(-CH ₂) ₄ , skeletal, deformative, -C-H	amino acids
1,360	1,364	1,362	-C-O-	valence, symmetric, carboxylate ion	fructose, glucose, cellulose, tocopherol, carotene
926	924	924	-C-O-C-	ester	fructose, glucose, cellulose, tocopherols, pectin, fats
1,106	1,105	1,105			

5. 2. Results of studying seaweed raw materials

At the next stage of the research, the IR spectra of dry samples of kelp, Undaria pinnate, and fucus algae were analyzed (Fig. 2–4). The IR spectra of algae samples are characterized by the presence of the specific absorption bands, the assignment of which is given in Table 3.

Assigning the characteristic absorption frequencies in the obtained IR spectra of seaweed samples

v, cm ⁻¹ (on spectrum)			Functional group	Main components
Kelp	Undaria pinnate	Fucus		
3,401	3,429	3,410	v(OH)	Carbohydrates Polysaccharides Mannitol Carotene
1,424	1,420	1,419	δ(OH)	
1,261	1,259	1,260	δ(CH ₂), v(C–C), v(C–O)	
1,086, 1,024	1,034	1,035	v(C–O)	
932, 889	–	–	δ(CH)	
2,926	2,924	2,925	v _{as} (–CH ₂ –), v _{as} (–CH ₃)	Fats Proteins Amino acids Carotene
1,424	1,420	1,419	v _s (C=O), δ _{as} CH ₂ , δ _s (NH ₃ ⁺)	
–	–	2,854	v _s (–CH ₂ –), v _s (–CH ₃)	
3,401	3,429	3,410	v(NH)	Amino acids Pantothenic acid Folic acid Alginate Ascorbic acid Carotene
1,626	1,633	1,622	v(–HC=CH–) v _{as} (C=O) σ(HOH) δ _d (NH ₃ ⁺)	
–	–	1,521	v _{as} (C=O)	
582	545	579	ρ(COO ⁻)+δ(C–C)	
–	–	820	δ(C–O–S)	
–	–	1,260	v _s (S=O)	Fuoidan

The chemical composition of algae samples is represented by both general substances, carbohydrates, proteins, fats, amino acids, and individual acids. Algae samples have absorption bands characteristic only of a given sample in the range of 800–1,600 cm⁻¹, which allows determining the presence of each type of algae in sauces, as well as different peak intensities and the area under the spectral curve.

5. 3. Results of studying berry sauces with the addition of seaweed raw materials

It is well known that the components of the formulation components, under the influence of technological factors, can interact with the constituent substances of iodine-containing additives.

The proposed sauces technologies imply the use of dry algae as an iodine-containing component, namely kelp, Undaria pinnate, and fucus. Since the hygroscopicity of algae is not the same, the optimal hydro-modules have been established: for kelp – 1: 5...1:6; for Undaria pinnate – 1:8...1:9; for fucus – 1:3...1:4.

Organoleptically, the optimal content of seaweed raw materials has been established, namely the content of hydrated algae can amount to: Undaria pinnate – 3%; fucus – 3 %, 5 %; kelp – 3 %, 5 %, and 8 %.

According to the established indicators of the rheological research, the following samples of dry algae raw materials and sauces with the content of hydrated algae were studied: Undaria pinnate and fucus – 3 %; kelp – 8 %.

Fig. 2 shows the results of the IR spectroscopic studies of berry sauces with the addition of kelp (8 %): sample 1 (based on blueberries and cranberries in a ratio of 1:1 with the addition of kelp), sample 2 (based on blueberries and sea buckthorn in a ratio of 1:1 with the addition of kelp), and a sample of dry kelp.

Table 3

sample 1 (based on blueberries and cranberries in a ratio of 1:1 with the addition of kelp), sample 2 (based on blueberries and sea buckthorn in a ratio of 1:1 with the addition of kelp), and a sample of dry kelp.

The absorption bands of berry sauces samples with the addition of kelp algae confirm the lack of interaction between the functional compounds of berry raw materials and kelp. This conclusion can be drawn by conducting the comparative analysis of samples 1 and 2 in Fig. 1, 2.

Fig. 3 shows the IR spectra of the berry sauce samples with the addition of Undaria pinnate (3 %): sample 3 (a sauce is based on blueberries and sea buckthorn in a ratio of 1:1 with the addition of Undaria pinnate), sample 4 (a sauce is based on blueberries and cranberries in a ratio of 1:1 with the addition of Undaria pinnate), and a sample of dry Undaria pinnate.

The belonging of the absorption bands of berry sauces with the addition of Undaria pinnate in Fig. 3 to certain types of compounds (groups of atoms) was determined based on comparing the IR spectra of a sample of berry raw materials and a sample of algae.

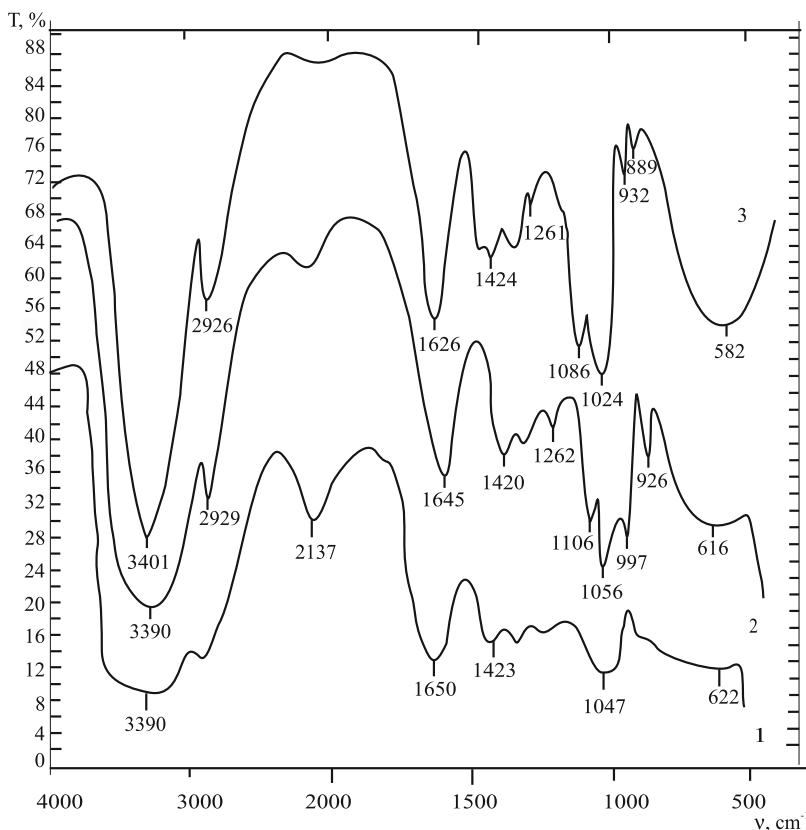


Fig. 2. IR spectra of the samples of kelp and berry sauces with the addition: 1 – sample 1; 2 – sample 2; 3 – kelp

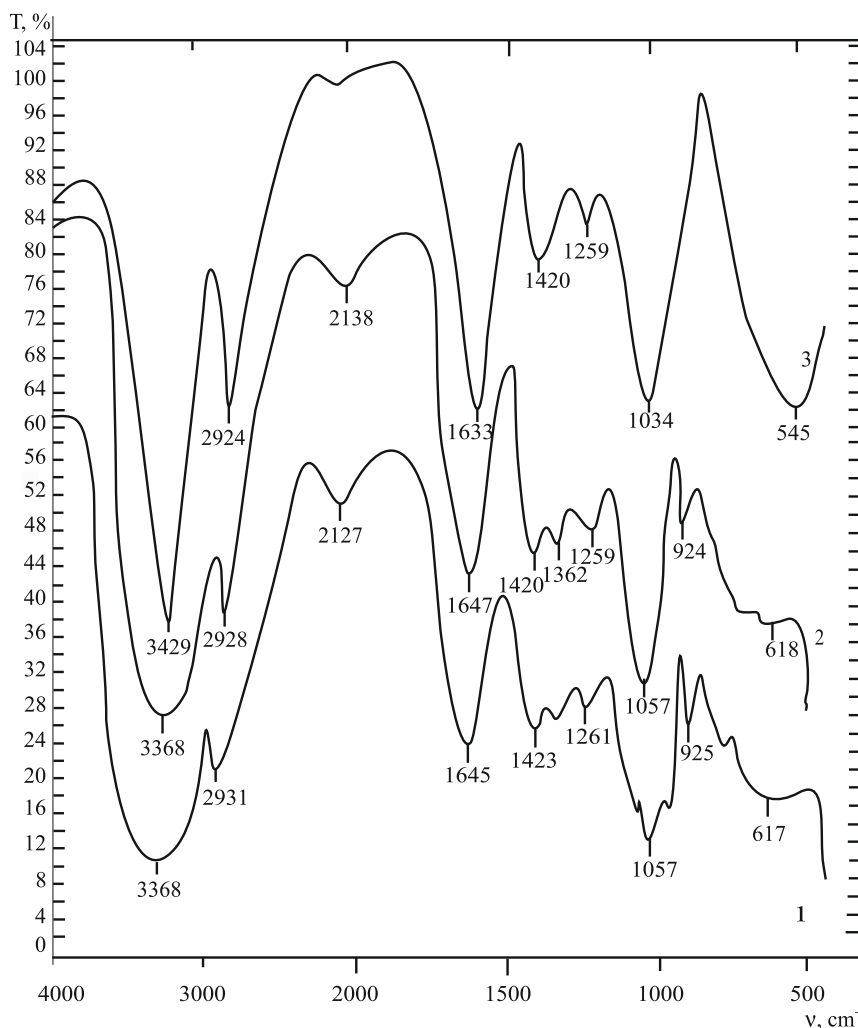


Fig. 3. IR spectra of *Undaria pinnate* and berry sauce samples with the addition: 1 – sample 3; 2 – sample 4; 3 – *Undaria pinnate*

Fig. 4 shows the IR spectra of berry sauce samples with the addition of fucus (3 %): sample 5 was prepared from blueberries and cranberries in a ratio of 1:1 with the addition of fucus; sample 6 was prepared from blueberries and sea buckthorn in a ratio of 1:1 with the addition of fucus.

The study of the obtained IR spectra of the components for sauces has shown that each type has differences in the degree of the intensity of the absorption bands and the size of the area under the spectral absorption curve, which is determined by the chemical composition of the raw materials. The IR spectra of sauces prepared from a combination of berries and algae contain the components of raw materials (Table 4, Fig. 4).

Table 4

Assigning the absorption bands of sauce samples that contain seaweed

Absorption intensity, cm ⁻¹						Functional group
Sample						
1	2	3	4	5	6	
3,390	3,390	3,368	3,368	3,366	3,368	$\nu(\text{OH})+\nu(\text{NH})$
2,929	2,929	2,931	2,928	2,933	2,926	$\nu_{as}(-\text{CH}_2-)+\nu_{as}(-\text{CH}_3)$
–	–	–	–	–	2,854	$\nu_s(-\text{CH}_2-)+\nu_s(-\text{CH}_3)$
1,650	1,645	1,645	1,645	1,644	1,634	$\nu(-\text{HC}=\text{CH})+\nu_{as}(\text{C}=\text{O})+\sigma(\text{HOH})+\delta_d(\text{NH}_3^+)$
1,423	1,420	1,423	1,420	–	1,524	$\nu_s(\text{C}-\text{O})+\delta(\text{OH})+\delta_{as}\text{CH}_2+\delta_s(\text{NH}_3^+)$
–	–	–	–	1,417	1,419	$\nu_{as}(\text{C}=\text{O})+\delta_d(\text{NH}_3^+)$
1,360	1,360	1,360	1,362	1,360	–	$\delta(\text{OH})+\delta_s(\text{CH}_2)$
1,262	1,262	1,261	1,259	1,259	1,258	$\delta(\text{CH}_2)+\nu(\text{C}-\text{C})+\nu(\text{C}-\text{O})$
–	1,106	1,106	–	1,106	1,104	$\nu(\text{C}-\text{C})+\omega(\text{CH}_2)$
1,047	1,056	1,057	1,057	1,057	1,038	$\nu(\text{C}-\text{O})$
–	997	925	924	924	924	$\delta(\text{CH})+\delta(\text{OH})+\delta_s(\text{NH}_3^+)$
–	–	–	–	820	826	$\delta(\text{C}-\text{O}-\text{S})$
622	616	617	618	580	570	$\rho(\text{COO}^-)+\delta(\text{C}-\text{C})$

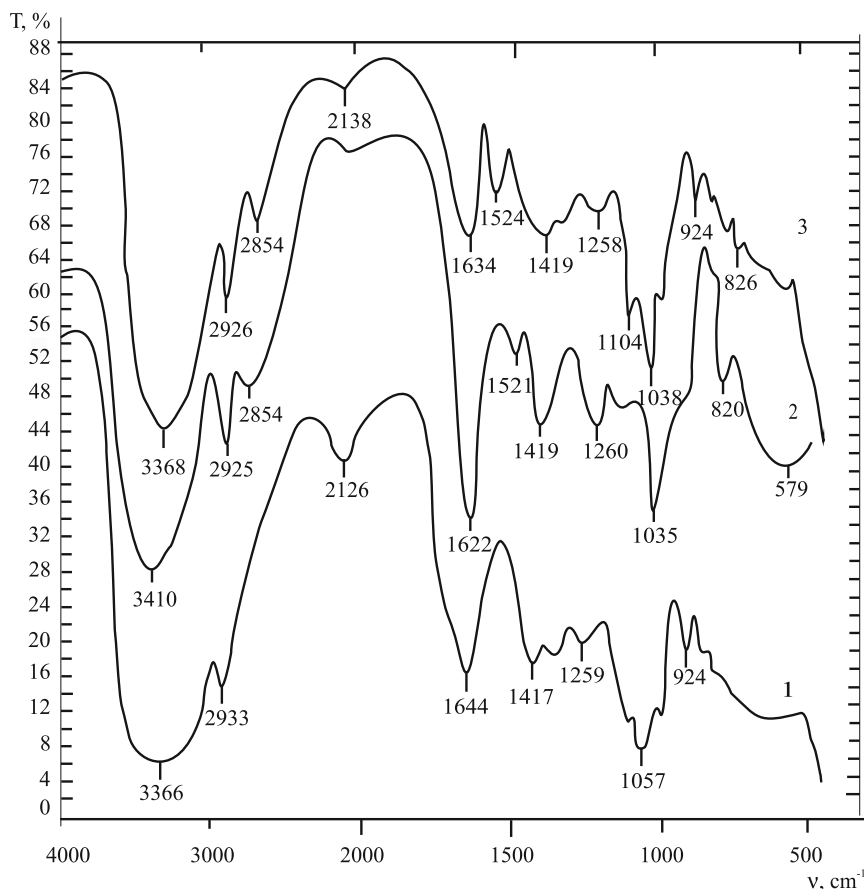


Fig. 4. IR spectra of focus and berry sauce samples with the addition: 1 – sample 5; 2 – focus; 3 – sample 6

6. Discussion of results obtained via the IR spectroscopy method

The acquired IR spectra and spectral characteristics such as the intensity of the absorption bands, the area under the spectral curve are specific to each type of algae and berry raw materials. This is due to the peculiarities of the chemical composition and components structure.

The possibility of using the method of IR spectroscopy to identify complex food mixtures makes it possible to argue that this method allows determining the presence, in the sauces from berry raw materials and algae, their inherent unique components, as well as establish whether the main components of the raw materials participated in the interaction, and to find out which losses occur in the nutrients under the effect of technological factors when the sauces are made.

In the IR spectra of the samples of berry raw materials, the following absorption bands, characteristic of the aromatic part of flavonoids and myrtillin, can be distinguished: $3,368\text{ cm}^{-1}$, $1,645\text{ cm}^{-1}$, $1,417\text{ cm}^{-1}$, and 866 cm^{-1} of the deformation oscillations = C-H.

The presence of carbohydrates is evidenced by the absorption bands characterized by the valence oscillations of $-\text{CH}_2-$ groups in the region of $2,931\text{ cm}^{-1}$, oscillations for C-O-H: $1,420$, $1,262$, $1,057$, cm^{-1}) and OH-groups ($3,364$, $1,420\text{ cm}^{-1}$).

The absorption bands of 990 and 924 cm^{-1} may be associated with the deformation non-planar oscillation of $\delta(\text{CH})$ in $\text{HRC}=\text{CR}'\text{H}$ fatty unsaturated acids and the extraplanar deformation oscillation $\delta(\text{OH})$.

The presence of sucrose, glucose, and myrtillin is confirmed by the presence of the band of $1,360\text{ cm}^{-1}$ associated with the deformation oscillations of C-H bonds in the saturated six-member rings, and the band of 920 cm^{-1} for ether bonds $-\text{C}-\text{O}-\text{C}-$. The spectra show the bands predetermined by the valence fluctuations of the carbonyl group of $1,645\text{ cm}^{-1}$ $\nu_{\text{as}}(\text{C}=\text{O})$, $1,417\text{ cm}^{-1}$ $\nu_{\text{s}}(\text{C}=\text{O})$ of organic acids.

A maximum at $1,417\text{ cm}^{-1}$ corresponds to the deformation oscillations $-\text{CH}-$ in $-\text{CH}_2-$. The presence of carbohydrates is evidenced by the absorption bands due to the valence fluctuations of CH_2 groups at $2,931\text{ cm}^{-1}$. The oscillations associated with the C-OH group are $1,417$; $1,258$; 729 ; and 590 cm^{-1} ; OH-group: $3,368$ and $2,931\text{ cm}^{-1}$ of glucose, myrtillin. All the carboxyl, amino, and hydroxyl groups form a single system of hydrogen bonds [35].

Our results agree well with the literature data on the macronutrients of berry raw materials, which indicate a significant content of carbohydrates (which is about $6\text{ g}/100\text{ g}$ for sea buckthorn; $3\text{ g}/100\text{ g}$ for cranberries), flavonoids ($210\text{ mg}/100\text{ g}$ for sea buckthorn, 422 mg for cranberries/ 100 g), unsaturated fatty acids (for sea buckthorn – $1.8\text{ g}/100\text{ g}$ of omega-3 and $1.8\text{ g}/100\text{ g}$ of omega 6) [21–24, 36–37]. Thus, it can be assumed that the results of the IR spectroscopy of berry sauces can serve as confirmation of analytical calculations regarding the chemical composition of the finished sauces.

The presence of tocopherols, carotene, and carbohydrates in the sea buckthorn and cranberry samples is confirmed by the presence of a band at $1,360\text{ cm}^{-1}$, which is attributed to the deformation oscillations of the C-H bonds of the saturated six-member rings.

According to calculations conducted in previous studies, the content of tocopherols for sea buckthorn sauce is 3,091 $\mu\text{g/g}$, for cranberry sauce – 1,273 $\mu\text{g/g}$, the carotene content for sea buckthorn sauce – 712 $\mu\text{g/g}$, for cranberry sauce – 48 $\mu\text{g/g}$ [38].

Besides, the IR spectroscopy of berry samples has revealed that the band of 1,261 cm^{-1} is associated with the valence oscillations of $-\text{C}-\text{O}-$ ether bonds of higher carboxylic acids in acyl glycerides. The bands of 1,056 cm^{-1} and 1,258 cm^{-1} can also be associated with the symmetrical and asymmetric valence fluctuations of C-O bonds in the hydroxyl groups in glucose and myrtillin.

An analysis of the results from the algae IR spectra demonstrated the following most important results, which are consistent with the data of the literature analysis regarding their chemical composition:

– for kelp: the presence of protein in kelp is indicated by the band of 3,401 cm^{-1} associated with the valence fluctuations of the amide group. In the spectrum of kelp, there is an intense band with a maximum of 1,626 cm^{-1} , which is associated with the oscillations of the amide group I for $\text{R}'\text{-CONH-R}$; there is a shift of the amide I band towards the lower frequency region, and the amide II band – towards the higher frequency region; the bands merge into one. This is due to the formation of hydrogen bonds between the hydroxyl and amide groups. The band of 2,926 cm^{-1} is associated with the asymmetric valence oscillations of C-H bonds on carbohydrate rings and the asymmetric valence oscillations of C-H bonds in $-\text{CH}_2-$ and $-\text{CH}_3$ groups of fats and proteins. The presence of carbohydrates and mannitol in kelp is indicated by the bands of the valence fluctuations of OH group at 3,400 cm^{-1} and the deformation oscillations of the OH group at 1,424 cm^{-1} , the valence oscillations of CO bonds in the end groups of CH_2OH carbohydrates at 1,086 cm^{-1} , the deformation oscillations of OH and CH bonds in the six-member rings and the end groups of CH_2OH at 1,261 cm^{-1} . The appearance of frequencies in the region of 932 and 889 cm^{-1} is associated with certain combinations of CH groups, in the structure of carbohydrates, these frequencies are due to the deformation oscillations of CH groups of the pyranose ring of carbohydrates. The bands of 1,626 cm^{-1} that are characteristic of the $-\text{C}=\text{C}-$ polyene chain of the carotenoid molecule, as well as methyl groups ($\sim 2,926 \text{ cm}^{-1}$) and aromatic C-H -plane deformation oscillations (the bands of 932, 1,024 cm^{-1}), are observed in the algae IR spectrum) in carotenoid molecules;

– for *Undaria pinnate*: the band at 2,924 cm^{-1} is associated with the asymmetric valence oscillations of C-H bonds in the carbohydrate rings and the asymmetric valence oscillations of C-H bonds in the $-\text{CH}_2-$ and $-\text{CH}_3$ lipid groups. It can be noted that a wide strong absorption band appeared in the frequency range of 3,500–3,200 cm^{-1} under the conditions of undaria addition, which can be explained by the formation of an intermolecular hydrogen bond between polar groups (amine and hydroxyl). The presence of carbohydrates in the sample of dry algae *Undaria pinnate* is indicated by the bands of the valence fluctuations of the OH group at 3,429 cm^{-1} and the deformation oscillations of the OH group at 1,420 cm^{-1} , the valence oscillations of CO bonds in the end groups of CH_2OH carbohydrates at 1,034 cm^{-1} , the deformation oscillations of OH and CH bonds in the saturated six-member rings and in the end groups of CH_2OH at 1,259 cm^{-1} . The bands of 3,429 and 1,633 cm^{-1} correspond to the valence and deformation oscillations of the amide group of nitrogen-containing substances;

– for fucus: the NH group of nitrogen-containing compounds such as pantothenic, folic acid, amino acids, is indicated in the sample of dry fucus algae by the bands at 3,410 cm^{-1} , which belong to the valence oscillations $\nu(\text{NH})$, 1,622 cm^{-1} , which are due to the deformation oscillations. The presence of alginate in the composition of fucus is indicated by the absorption bands of 3,410, 16,22, 1,419, 1,035, and 820 cm^{-1} because they can be attributed to the structural features of alginate: this indicates a high content of this polysaccharide in fucus. The presence of ascorbic acid is confirmed by the intense band of absorption of valence fluctuations in the range of 1,622 cm^{-1} , which corresponds to a double $\text{C}=\text{C}$ bond. In addition, a series of characteristic absorption bands in the region of 3,500–3,200 cm^{-1} is observed due to the valence fluctuations of alcohol and endiol hydroxyl OH groups. The presence of fucoic acid is confirmed by the following absorption bands: 1,260 ($\text{S}=\text{O}$) and 820 ($\text{C}-\text{O}-\text{S}$) cm^{-1} . The bands at 2,925 and 2,855 cm^{-1} are associated with the asymmetric and symmetric valence oscillations of C-H bonds in the carbohydrate rings and the asymmetric and symmetric valence oscillations of C-H bonds in the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of lipids and organic acids; the presence of chelate-bound acids is confirmed by the presence of the symmetric and asymmetric valence fluctuations of the carboxyl group (COO) $\nu_{as}(\text{C}=\text{O})$ and $\nu_s(\text{C}=\text{O})$ ($\Delta=1,521-1,419=102 \text{ cm}^{-1}$).

In the IR spectra of sauces, it is possible to note the characteristic absorption bands of the starting components, due to changes in the intensity of the absorption bands, the planes under the spectral curve, the appearance of new bands, or a shift. The match between the spectral curve of the sauces and the pattern of the spectrum of the starting components indicates the identity of their composition.

This study has some limitations as regards the results obtained. Due to the multicomponent nature of the samples, it is possible to detect only macro components by an IR spectroscopic examination while the most significant micro components remain unnoticed on the spectra.

The main shortcoming of this study is the complexity of data processing. This is due to the need for in-depth analytical analysis and the establishment of similarities between the absorption bands and their corresponding chemical compounds.

At this stage of our research, there is an issue related to determining the micronutrients that are part of the sauces as they exert a significant physiological impact on the human body. It should be noted that the data acquired from the IR spectroscopic examination are consistent with the literature-based and estimation data regarding the chemical composition of raw materials and sauces. It follows that there is a high probability that the estimation data reported in previous studies are reliable. This greatly facilitates further experimental chemical analysis of sauces. This is due to the fact that not only probable micronutrients are known but also their approximate amount, which allows for the correct choice of procedures with the required sensitivity for quantifying the components.

7. Conclusions

1. When analyzing our IR spectroscopic study of sauces made from wild and cultivated berries, it should be noted that all the IR spectra of the examined samples have revealed

those absorption bands that reflect the overall chemical composition, which have approximately the same set of absorption bands. The absorption bands that are specific for a given type of raw material have been identified, confirming the presence of such macro components as flavonoids, sucrose, glucose, and organic acids. In addition, all carboxyl, amino, and hydroxyl groups have been found to form a single system of hydrogen bonds.

2. The IR spectroscopic study of seaweed raw materials has shown that the samples are characterized by a multicomponent nature and the high content of fucoidan, especially for fucus. In addition, it is noted that kelp and *Undaria pinnate* contain protein compounds and can be recommended as a vitally-important concentrate for humans.

3. It was found that the samples of sauces with the addition of algae are as close as possible to sauces without additives. The absorption bands of the samples of berry sauces with the addition of algae confirm the lack of interaction between the functional compounds of berry raw materials and algae. This is due to the similarity of the IR spectra of sauces with and without additives and the absence of new peaks when adding seaweed. This fact confirms that the ingredients of formulation components did not react, under the impact of technological factors, with the constituent substances of iodine-containing additives. This finding is extremely relevant from the standpoint of iodine preservation during processing. The latter is supported by some separate studies into the iodine content in seaweed raw materials and ready-made sauces.

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