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APPLICATION OF SMOKING PREPARATIONSIN MODERN TECHNOLOGIES OF SMOKED FISHERY PRODUCTION

ЗАСТОСУВАННЯ КОПТИЛЬНІХ ПРЕПАРАТІВ У СУЧАСНИХ ТЕХНОЛОГІЯХ ВИРОБНИЦТВА КОПЧЕНОЇ РИБОПРОДУКЦІЇ

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Abstract.*The article is devoted to the actual problem of creating of new types of smoked fish products. The article discusses the modern technologies of production of smoked fish products, shows that the development of smoked sausages from ocean fish is a promising trend in the fishing industry. The analysis of sausage casings used for sausage production is carried out. Polyamide shells have been shown to have several advantages over both natural (from intestinal raw materials of slaughtered animals) and artificial (from collagen skins of slaughtered animals or cellulose). These advantages are high barrier, elasticity, mechanical strength, biological inertia, gas- and moisture-proof, heat resistance. As a result, the shelf life of the finished product is significantly extended (for some products more than 60 days). Skimmed fillet of Atlantic mackerel Scomber scombrus was selected as the main raw material for the production of sausages. The choice of this type of fish based on good organoleptic properties, high biological value, large industrial reserves, relatively low price and a long tradition of using in smoked products. Information on the chemical composition and basic properties of a wide range of smoke preparations available on the market has been collected. It is shown that, notwithstanding the availability of a wide range of preparations on the market, which are manufactured in different countries of the world, none of them has the properties inherent to the traditional smoke. Smoke EZ PN 9, manufactured by Red Arrow, USA, is very close to them. For this reason, it was used in our work. The dose of the preparation was 2 g per 1 kg of minced fish.*

The technology of production of smoked sausages was developed, which includes the following operations: obtaining of frozen blocks of skimmed mackerel fillet, inspection of blocks, defrosting of blocks, grinding of fillet, salting the minced fish, aging in salting, stirring with smoking preparation, forming of sausages, thermal processing of sausages in water, cooling of sausages in water, subsequent cooling with air, storage of sausages.

The obtained products are characterized by high organoleptic characteristics, microbiological indicators are within the normal limits for 14 days of storage, which allows us to recommend the developed technology.

Анотація.*Стаття присвячена актуальній проблемі створення нових видів копченої рибопродукції. В матеріалах статті розглянуті сучасні технології виробництва продукції з копченої риби, показано, що розробка копчених ковбас з океанічної риби є перспективним напрямком у рибній промисловості. Виконано ааналіз ковбасних оболонок, які на сьогодняшний день використовуються при виробництві ковбас. Показано, що поліамідні оболонки мають ряд переваг як перед натуральними (з кишкової сировини забійних тварин), так і штучними (з колагену шкур забійних тварин або целюлози). Цими перевагами є висока бар'єрність, еластичність, механічна міцність, біологічна інертність, газо-, вологонепроникненість, термостійкість.Внаслідок цього терміни зберігання готової продукції значно подовжені (для деяких видів продукції більш, ніж 60 діб). Підібрано основнусировину для виробництва ковбас - знешкурене філе скумбрії атлантичної Scomber scombrus. Вибір цього виду риби обумовлений добрими органолептичними властивостями, високою біологічною цінністю, великими промисловими запасами, відносно невисокою ціною і тривалої традицією вживання в їжу в копченому вигляді. Зібрано інформацію щодо хімічного складу та основних властивостей широкого спектру коптильних препаратів, наявних на рин-*

ку. Показано, що, незважаючи на наявність на ринку широкого асортименту коптильних препаратів, які виробляються у різних країнах світу, жоден з них не має властивостей, притаманних диму традиційного копчення. Максимально наближається до них препарат «Smoke EZ PN 9» виробництва корпорації Red Arrow, США. З огляду на це, саме його було використано в нашій роботі. Доза препарата становила 2 г на 1 кг рибного фаршу.

Розроблено технологію виробництва копчених ковбас, яка включає такі операції: приймання заморожених блоків знешкуреного філе скумбрії, інспекція блоків, розморожування блоків, подрібнення філе на вовчку, посол фаршу, витримка в посолі, перемішування з коптильною рідиною, шприцювання фаршу в оболонку, кліпсування батонів, осаджування фаршу, теплова обробка батонів у воді, охолодження батонів у воді, подальше охолодження батонів повітрям, зберігання батонів.

Отримана продукція характеризується високими органолептичними показниками, мікробіологічні показники знаходяться у межах норми на протязі 14 діб зберігання, що дозволяє рекомендувати розроблену технологію до впровадження у виробництво.

Ключові слова: *риба, ковбаси, копчення, коптильні препарати, ковбасні оболонки, технологія,технологічна схема*

Key words: *fish, sausages, smoked products, smoke preparations, sausage casings, technology, technological scheme*

The modern range of smoked fish production in Ukraine is quite wide and includes cold smoked fish (processing temperature not higher than 40 ° C), hot smoked (temperature above 80 ° C) and semi-hot smoked fish (in the range 40...80 ° C). In some countries, for example, in Japan, Germany and some others, fish sausages are made, with smoked sausages being the most in demand [1, 9]. At the Ukrainian market, these products are currently not presented. At the same time, the production of smoked fish sausages will allow to expand the range of products and increase the consumption of fish by the population, which is a source of animal protein, essential polyunsaturated fatty acids, minerals. This causes the urgency of the development of smoked fish sausages technology [7].

To solve this problem, it is necessary to develop a recipe for sausages, make a choice of the shell, select modes of heat treatment of products, evaluate the possibility of storage of the obtained products. The main raw material used was the skinless fillet of atlantic mackerel Scomber Scombrus. The choice of this type of fish is due to good organoleptic properties, high biological value, large industrial stocks, relatively low price and a long tradition of eating in smoked form.

The shelf life of the sausage depends largely on the choice of shell. Currently, natural intestinal casings which are produced from the intestinal raw materials of slaughtered animals are widely used and artificial casings based on protein (collagen of slaughtered animals skins) or cellulose, as well as synthetic casings based on polymers, in particular polyamide [8].

The choice of the polyamide shell is due to its high barrier properties, which do not allow microflora to penetrate into the sausage loaf after heat treatment and in the process of storage and transportation of finished products. In this regard, we used a barrier polyamide shell "Pentaflex Universal" caliber 40 mm made by "Pento Pak", Ukraine.

This shell is a five-layer and is intended for packing of all kinds of sausages, ham, pates, as well as for packing of butter, processed cheeses and other similar products.

Compared to viscose-reinforced, natural and collagen casings, Pentaflex Universal has several advantages:

1) high barrier (provides long shelf life);

2) elasticity (high stuffing capacity);

3) mechanical strength;

4) biological inertness (does not affect the taste and smell of packaged products);

5) gas- and moisture-tightness (ensuring stable outputs of finished products, absence of losses during heat treatment);

6) heat resistance (wide temperature range (- 18 ° C to + 121 ° C), which allows to process sausages at high temperatures, as well as to apply freezing);

7) extended shelf life of finished products: for some types of products more than 60 days (at a temperature of + 2 ° C...+ 4 ° C).

Sausages in the casing of Pentaflex Universal look like straight straight loaves with a smooth stretched surface. The shell is very convenient for transportation and does not change its properties during storage.

Despite the obvious advantages of using this shell, it has significant features that necessitate a thorough revision of a number of traditional technological processes. In particular, the high barrier properties do not allow smoke components to penetrate the product through the shell. Traditional smoking can not be used in the case of

shells of this type, although the components of smoke not only affect the organoleptic properties of products, but also inhibit the development of microflora [2, 16], including pathogenic [11, 15], as well as increase the production shelf life due to the presence of antioxidant properties [10], especially in combination with subsequent cooling [17]. An alternative to traditional smoking is the use of smoking preparations [4, 6, 12]. Their advantages include a much lower content of substances harmful to the humans, first of all - polycyclic hydrocarbons having carcinogenic properties [13].

The following smoking preparations are promising for use:

- smoke preparation "VNIRO" TU 15-0872-92;
- smoke preparation "Liquid smoke" TU 9299-001-11824738-94;
- smoke preparation "Scansmoke PB 1145" manufactured by P. Broste A / S, Denmark;
- smoke preparation “Scansmoke PB 2110” manufactured by P.Broste A / S, Denmark;
- smoke preparation Smoke EZ SupremePoly C manufactured by Red Arrow, USA;
- smoke preparation Smoke EZ PN 9 manufactured by Red Arrow, USA.

All abovementioned smoke preparations from Red Arrow and P.Broste A / S are certified in Ukraine and meet the requirements of Ukrainian law. Their chemical composition and properties have been well studied [5, 14].

The analysis of the physical and chemical properties of smoke preparations was carried out according to the following nomenclature of indicators [3, 5]: appearance, smell, density, dry residue, total acid content (in terms of acetic acid), phenol content (in terms of guaiacol), the total content of carbonyl compounds (in terms of furfural). The results of the studies are presented in table 1.

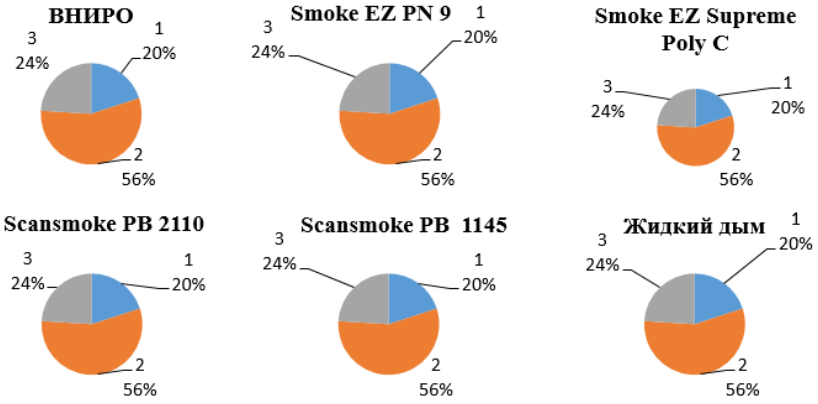
Table 1 - Physico-chemical composition of smoke preparations

№	Indicator	The characteristic of the indicator
«Smoke EZ PN 9»		
1	Appearance	Transparent dark brown liquid
2	Smell	Specific smell of hard wood smoke
3	Density, g / cm	1,0…1,2 / 1,4
4	Dry residue, %	42,2…42,48 / 42,34
5	Phenol content, %	5,46…6,46 / 5,96
6	Content of acid compounds, %	5,70…7,42 / 6,56
7	Content of carbonyl compounds, %	6,37…11,19 / 8,78
«Smoke EZ SupremePoly C»		
1	Appearance	Dark brown viscous liquid
2	Smell	Specific smell of hard wood smoke
3	Density, g / cm	1,12…1,14/1,13
4	Dry residue, %	49,54…50,18/49,86
5	Phenol content, %	12,8…13,7/13,25
6	Content of acid compounds, %	15,68…19,22/17,45
7	Content of carbonyl compounds, %	21,22…28,4/24,81
«Scansmoke PB2110»		
1	Appearance	Transparent dark brown liquid
2	Smell	A distinct smell of smoke
3	Density, g / cm	1,03…1,04/1,02
4	Dry residue, %	6,02…6,16/6,09
5	Phenol content, %	1,6…1,9/1,75
6	Content of acid compounds, %	6,6…8,4/7,5
7	Content of carbonyl compounds, %	9,47…15,23/12,35
«ScansmokePB 1145»		
1	Appearance	Light brown viscous liquid
2	Smell	Specific with smoke scent
3	Density, g / cm	1,015…1,025/1,02
4	Dry residue, %	6,52…7,32/6,92
5	Phenol content, %	2,1…2,3/2,2

Table 1 - Physico-chemical composition of smoke preparations

№	Indicator	The characteristic of the indicator
6	Content of acid compounds, %	9,03…13,97/11,5
7	Content of carbonyl compounds, %	11,87…19,03/15,45
«VNIRO»		
1	Appearance	Dark colored liquid with burgundy
2	Smell	Specific with smoke scent
3	Density, g / cm	1,015…1,02/1,02
4	Dry residue, %	1,9…2,1/2,0
5	Phenol content, %	0.78…1,48/0,8
6	Content of acid compounds, %	2,0…2,5/2,3
7	Content of carbonyl compounds, %	0,53…1,01/1,0
«Liquid smoke»		
1	Appearance	Transparent light brown liquid
2	Smell	Specific with smoke scent
3	Density, g / cm	1,002…1,003/1,001
4	Dry residue, %	0,2…0,22/0,2
5	Phenol content, %	0,6…0,9/0,78
6	Content of acid compounds, %	2,8…3,1/2,92
7	Content of carbonyl compounds, %	5,86…7,9/7,5

The ratio of the main smoking components in the studied smoking preparations can be represented in the following form:



1 - the content of phenols, %; 2 - the content of acid compounds, %;
3 - the content of carbonyl compounds, %

Fig. 1 - The ratio of the main groups of organic compounds of smoking preparations

Data on the ratio of the main chemical components (phenols, acids and carbonyl compounds) in smoking preparations (Fig. 1) shows their heterogeneity, which complicates the prediction of the quality of finished products.

To clarify the role of smoking components in the formation of specific properties of smoked products, by the method of gas-liquid chromatography, the individual substances of the ether-soluble fractions of the studied smoking preparations were identified. The identification results are presented in table 2.

Table 2 - Identification of the phenolic fraction of smoking preparations

Phenolic component	«Smoke ZP N9»	«Smoke Z SupremePoly C»	«Scansmoke PB 2110»	«Scansmoke PB 1145»	«VNIRO»	«Liquid smoke»
1. Phenol	7,0061	2,5638	1,1788	0,3807	1,8707	3,6418
2. Cyclothymes	6,9036	2,3874	-	-	0,818	0,6182
3. O-cresol	2,0523	11,6208	13,2855	14,969	1,9964	1,6305
4. P-cresol	0,2062	0,653	1,8911	-	4,6528	-

Table 2 - Identification of the phenolic fraction of smoking preparations

Phenolic component	«Smoke ZP N9»	«Smoke Z SupremePoly C»	«Scansmoke PB 2110»	«Scansmoke PB 1145»	«VNIRO»	«Liquid smoke»
5. M-cresol	3,0613	1,1312	2,1559	1,0227	2,776	2,9606
6. Guaiacol	6,4836	2,1384	2,6369	1,3201	8,2146	4,8343
7. 2,6-dimethyl phenol		0,7414	0,9206	2,7799	1,2564	0,9635
8. O-Ethylphenol	0,314	0,4686	-	-	-	-
9. Verotrol	0,1231	1,4585	2,4254	3,2498	2,7913	0,1711
10. 2,5-xylene	0,3807	0,1956	-	-	0,8565	0,1157
11. 2,6-xylene	0,6271	1,0949	2,511	0,2064	1,2915	0,6089
12.Dimethyl ether-hydroquinone		1,096	0,3268	0,5772	0,7895	0,2171
13.2,4-dimethylphenol		0,1136			0,4568	0,3082
14. 2,4-xylene	0,1154	0,4149	-	-	0,8457	0,4015
15. 3,5-xylene	3,0167	1,1111	0,8104	0,5143	4,2568	5,2206
16. Furan	4,8285	20,82	9,4208	18,9477	6,7116	7,0771
17. 3,4-xylene	0,1426	0,0959	0,1468	-	0,7790	0,1336
18. 3-ethyl 5-methylphenol	2	3	4	5	6	7
19. 3-Methylpiro-catechin	0,1862	0,2894	0,5058		0,9871	0,8838
20. Hydroquinone	1,1038	0,5052	0,9158	3,8956	5,2132	2,2014
21. 2,3,5-Tirmen-tilphenol	0,789	0,84	1,8222	-	-	-
22. 3-methoxy 2-methylphenol	0,3957	0,9971	1,2382	2,8752	2,0801	0,4995
23. Timol	0,6922	0,4049			1,8839	0,957
24. 2,3,4-trimethylphenol	0,262	0,96	-	-	0,5499	0,6585
25.4-methylpyracate-quin	0,2152	0,4829			0,5942	0,384
26. Siringon	0,0851	0,1404			0,3896	0,14
27. Cis-, trans-isoengol	28,889	3,6837	8,5944	5,0264	2,1839	25,0097
28. Eugenol	0,2966	0,5787			0,8849	0,5912
29. Vanillin	0,1319	0,1644	0,6345	0,3546	0,3312	0,1552
30.3-isopyrocatechin	1,0621	4,1213	1,7371	1,7831	4,8915	2,4331
31. Isoethylovengol	1,0215	0,2699	0,7279		0,7658	0,1503
32.4-Ethylresortin	0,1602	0,2648	1,4662	0,5694	0,3998	0,3773
33. Acetovanilon	9,0783	0,7489	-	-	2,3794	19,7251
34. 2,4-Butylphenol	0,2196	1,8992	1,667	2,0365	0,8231	0,2839
35. Lilac aldehyde	2,3177	0,5295	1,3882	5,8954	2,3794	5,0428
36. Benzaldehyde	0,2162	0,272	-	-	1,8778	-
37. P-naphthol	0,8653	0,9616	1,0406	0,7899	2,1357	-
38. Acetosiringone	2,4103	5,0325	5,7306	3,5485	1,6927	1,0738
39. Pyrogallol	0,3104	5,1425	6,9861	5,4887	7,4807	0,6794
40. 2-acetylfuran	0,7558	-	1,1788	0,5132	0,7584	0,5432
Total,%:	87,100	78,1315	76,1554	76,7728	81,0459	90,6919

Analyzing the data in table 2, it should be noted that the phenolic fractions of smoking preparations are represented by a large number of individual substances.

Based on the study of the literature, data were collected on the sensory characteristics of the pure substances of the components of the phenolic fraction. This allows us to determine the role of individual substances in the formation of the aroma of smoking. The sensory characteristics of the identified individual substances are given in table 3.

Table 3 - Sensory characteristics of the individual components of the ether-soluble fraction of smoking preparations

Name of the substance	The recognition threshold	Odor characteristic
1. Cyclothymes	0,05	Complex with a touch of smoked meat products, sweet, caramelized.
2. O-cresol	0,014	Cresol with a slight tinge of spicy
3. M.-cresol	0,004	Cresol

Table 3 - Sensory characteristics of the individual components of the ether-soluble fraction of smoking preparations

Name of the substance	The recognition threshold	Odor characteristic
4. P-cresol	0,001	Cresol with a spicy tinge
5. Guaiacol	0,03	Phenolic with a nice spicy tinge
6. 2,4-xylene	20,0	Chemical with a touch of fresh bread and beer wort
7. Pyrocatechin	28,0	Mixed, spicy, cloves with weak carbol-cresol
8. 3-methylpyrocatechin	3,2	Complex, spicy-smoky, with a floral hue
9. 4-methylpyrocatechin	1,2	Complex, spicy-smoky, with a floral hue
10. C-methoxy-2-methylphenol	0,2	It is reminiscent of guaiacol with a smoky hue
11. Veratrol		Flower-herbaceous
12. Dimethyl etherhydroquinone	0,14	Spicy with floral hue
13. O-Ethylphenol	0,06	Cresol
14. Hydroquinone		Chemical with floral hue
15. 3-isopropyl-pyrocatechin	0,07	Complex spicy with floral hue
16. 2,3,4-trimethylphenol	8,0	Floral with a spicy chemical tinge
17. Vanillin	6,0	Specific vanilla
18. Acetosiringone		Sweet, vanilla
19. Acetovanilone	1,0	Sweet, vanilla
20. Benzaldehyde	-	Almonds
21. Lilac aldehyde	2000	Sweet vanilla
22. Phenol	5,5	Specific cresol
23. 2,5-xylene	3,2	Chemical with a phenolic tint
24. 2,6-xylene	0,6	Mixed chemical, floral, musty
25. 3,4-xylene	0,6	Chemical, weak with a floral tinge
26. Furan	40	The smell of petroleum ether
27. 3-ethyl 5-methylphenol	40	Phenolic, spicy medium efficiency
28. 2,3,5-trimethylphenol	1,0	Mixed, floral, chemical, weak
29. Pyrogallol	18,0	Weak chemical
30. 2-acetylfuran	14,0	Reminds of furfural with shades of benzene and furan
31. Evengol	2,4	Complex spicy, cloves, floral
32. 2,6-dimethylphenol	-	not identified
33. 2,4-dimethylphenol	-	not identified
34. Timol	-	not identified
35. Siringon	2,0	Sophisticated, spicy, reminiscent of allylsiringon, with a floral tinge
36. Cis-, trans-isoengol	-	not identified
37. Isoethylovengol		not identified
38. 4-Ethylresortin	-	Spicy, floral, not pronounced.
39. 2,4-Butylphenol	1,2	not identified
40. 3-Naphthol	-	not identified

Summarizing all of the above, it should be noted that the components of the ether-soluble part of the smoking preparations, as can be seen from table. 3, have quite a variety of shades characteristic for smoked meat or fish products.

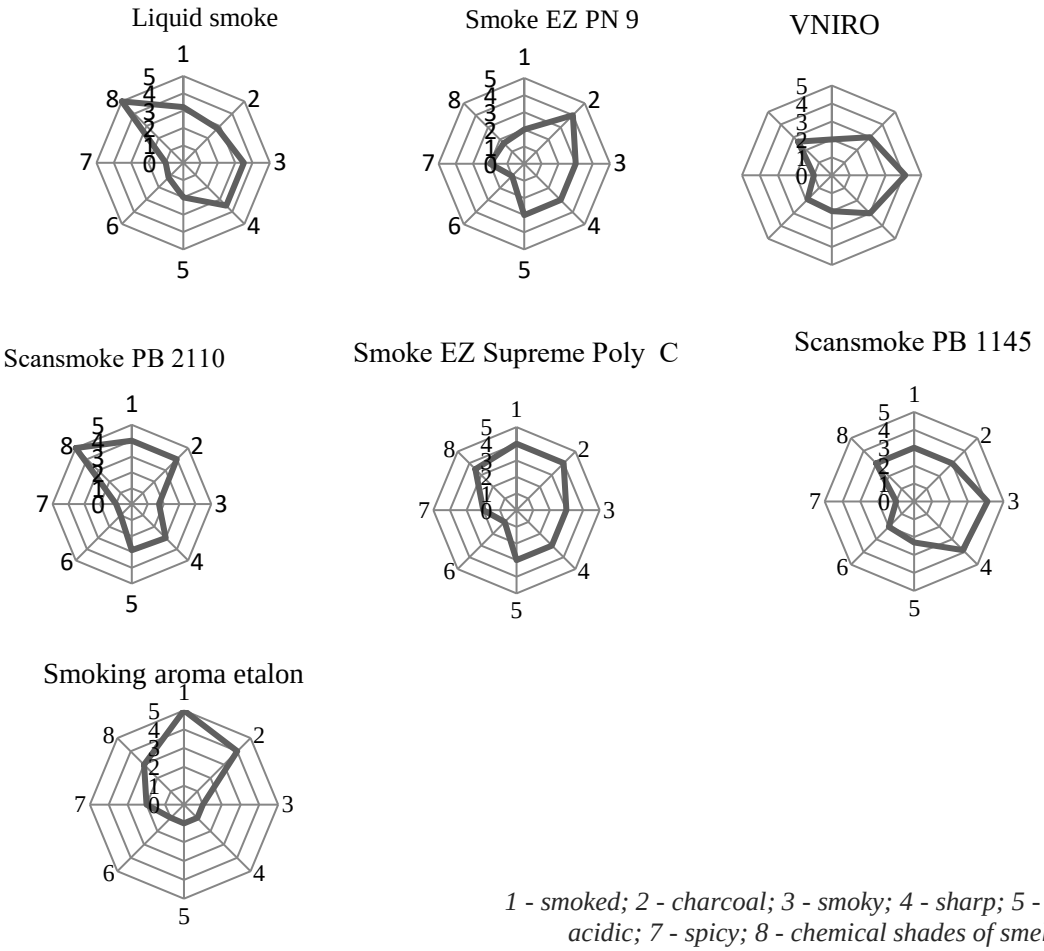
The aromatic index shows how many times the concentration of a substance exceeds its threshold concentration. If the aroma index is less than one, the aroma of the substance will not be perceived.

Aromaticity indices of individual substances were calculated for each smoking preparation (table 3). Substances whose aromaticity indices exceed the value of one, and therefore significantly affect the ability of the investigated smoking preparation to give the processed product the flavor of smoking, are presented in table 4.

To determine the sensory characteristics of smokers, model mixtures of smoking preparations were created. "Scansmoke PB 2110", "Smoke EZ SupremePoly C", "Smoke EZ PN 9" were used in a 1: 4 dilution based on the concentration of phenols in the working environment, "Scansmoke PB 1145", "VNIRO", "Liquid smoke" was evaluated without dilution. Impressions from the study of sensory characteristics of smoking preparations are presented in Fig. 2.

Table 4 - Aromaticity indices of smoking components of smoking preparations

Name of the substance	Aroma index					
	«Smoke EZ PN 9»	«Smoke EZ SupremePolyC»	«Scansmoke PB2110»	«Scansmoke PB 1145»	«VNIRO»	«Liquid smoke»
m-cresol	765,3	2828	1891,1	1069,2	4652,8	740,2
guaiacol	216,1	830,0	948	255,7	694	161,4
p-cresol	206,2	653	583,9	89,5	273,6	121,6
o-cresol	146,6	206,6	87,9	44,0	244,6	116,4
cyclotime	138,1	156,2	86,8	23,2	142,6	12,5
o-ethylphenol	104,6	71,3	17,3	13,9	19,9	12,4
vanillin	53,1	47,8	5,5	9,6	16,4	10,2
siringola	14,4	18,3	4,6	2,9	4,4	4,8
3-methoxy 2-methylphenol	3,6	11,3	4,3	2,5	2,2	4,8
phenol	1,3	1,8	3,2	1,2	1,7	1,3
2,6-xylene	1,0	1,3	1,3	0,3	1,6	1,2
Total aroma index:	1545,7	4832,6	3638,1	1512,2	6086,4	1545,7



1 - smoked; 2 - charcoal; 3 - smoky; 4 - sharp; 5 - burned; 6 - acidic; 7 - spicy; 8 - chemical shades of smell

Fig. 2 - Profiles of the standard of aroma of smoking (points)

The analysis of the data presented on the profiles indicates that the studied preparations are significantly different in the intensity of the smell and aromatic composition. Differences in sensory characteristics, chemical composition, and physico-technological properties cause differences in the functional properties of preparations.

Despite the wide assortment of tested preparations, none of them has the properties of the standard of traditional smoking. The closest to them is the Smoke EZ PN 9. This preparation was used by us at a dose of 2 g per 1 kg of minced fish.

Our technology of production of smoked sausage products includes the following operations:

receiving frozen blocks of mackerel fillet, inspection of blocks, defrosting the blocks at + 2 ° C…+ 4 ° C, grinding the fillet on the meat grinder with a diameter of the holes 6..8 mm, minced meat salting, aging in the process of salting at a temperature of + 2 ° C… + 4 ° C for 72 hours, mixing with Smoke EZ PN 9 smoking liquid, vacuum filling of minced fish into the Pentaflex Universal shell, clipping of loaves, precipitation of minced meat at + 8 ° C… + 12 ° C for 2…3 hours, heat treatment of loaves in water at + 90 ° C…+ 95 ° C until reaching temperature in the center + 75 ° C…+ 77 ° C, cooling the loaves in water at + 2 ° C… + 4 ° C until reaching temperature in the center of the loaf + 12 ° C… + 14 ° C, then cooling the loaves with air at a temperature + 1 ° C… + 4 ° C until reaching temperature in the center + 4 ° C… + 6 ° C, storing the loaf at + 2 ° C… + 4 ° C.

The obtained products are characterized by high organoleptic characteristics, microbiological indicators are within the normal limits for 14 days of storage, which allows us to recommend the developed technology for implementation into production.

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