Electronic taster applied for identification of a rainbow trout spoilage specifics

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Abstract. The research is aimed at the study of control possibilities of freshness degree and storage technology violation of frozen fish (Rainbow trout) using chemical piezo sensors array in the «e-nose» system. There have been demonstrated the opportunities of qualitative and quantitative determination of priority highly volatile compounds-markers of native and modified state of fish and gills after a 2-minute measuring by sensors array with minimal sample preparation and without additional preparation or odour components concentration. We can fixate early signs of changes in the fish fillet of a trout after three days of storage mode non-compliance and subsequent freezing, using chemical sensors. We can evaluate the storage time of fresh fish in any conditions with an error of measurement of no more than 10 %. We have developed the method of fish odour simple analysis and of obtaining diagnostic information about fish freshness according to fillet and gills state. The application mode of chemical sensors and e-nose «MAG-8» allows acquiring objective information, and is highly sensitive, expressive and economically acceptable for laboratories and mobile monitoring stations of any level.

1. Introduction
In the world fisheries, aquaculture is recognized as one of the main factors contributing to the increase in the production of fish products and to meeting the needs of the population. Fish and fish products are related to so-called "health food products." Their value is primarily due to the presence of a large number of high-grade proteins – which include all the vital amino acids – in their composition.

At the same time, fish products being the source of proteins, vitamins, fatty acids, trace elements necessary for the organism can carry a potential hazard. This fact is because imported frozen fish products dominate the market. At the same time, often, there is a non-compliance with the requirements for transportation and storage, which leads to the loss of consumer properties and makes it unsafe. The circumstances as mentioned above set a task to carry out a more profound research on the safety of fish products using modern methods and analytical equipment, which is also necessary for the development of new competitive technologies in the international market of fish products.

An objective quantitative and qualitative assessment of the leading organoleptic indicators and the establishment of early signs of ageing and deterioration play an important role in the development of new technologies and optimization of storage conditions, transportation of perishable products, in...
particular, fresh fish. Therefore, it is a topical task to organize an integrated control system over the quality of raw materials and finished products at different stages of technological processing, not only by physical and chemical indicators but also by organoleptic ones [1]. For chilled and frozen fish, mainly when transported to points of sale and processing, as well as when implemented in trading networks, storage regime violations and, accordingly, a significant decrease in quality and safety are typical. Meat and fats are among the fastest objects of spoilage. The establishment of the peculiarities of changes and spoilage to different types of fish meat with the possibility of a rapid and straightforward determination of deviations at the place of purchase requires an analytical solution.

The existing evaluation methods of fish meat freshness are multifarious, and they vary greatly in terms of accessibility (organoleptic sensor analysis, pyrolysis) and complexity of the equipment and accompanying technique (chromatographic and titrimetric). Withal, a variety of physical and chemical methods of research are the least evaluating the most informative consumer indicator - the odour of a product. The peculiarities of the structure of the olfactory organ and the perception of signals determine the peculiarities of the odour impact on a man. Insignificant changes in the odour of a product, to a greater extent than for any other feature, alter the consumers' evaluation of a product and influence the demand. Sensor organoleptic analysis – the most popular in odour study – has restrictions of objective nature: regulated loading and productivity, special conditions for testing, an overestimation of both pleasant and unpleasant odours. It can be claimed that at present, the most informative indicator of food remains undervalued.

The research trend into the development of integral analytics methods, and their application has recently been actively cultivated. By integral analytics, we understand methodological approaches and evaluation means of total generalized properties of an analyzed object. «E-noses» based on chemical (or other) sensors arrays of various nature with elaborate and straightforward algorithms of registered information processing and solution-taking can be attributed to integral analytics systems. Laboratory «electronic noses» have been known for more than 30 years. They are capable of solving a significant number of tasks [2, 3]. Application of chemical sensor-based analyzers for the study of multicomponent systems of variable composition (highly volatile odour fraction) allows evaluating several quantitative and qualitative indicators of studied samples in one measurement. In the USA, Canada, Germany and other countries there are being developed and widely used gas analyzers with «electronic nose» (e-Nose) methodology, of such brands as FOX, BEMINI, HERACLES, 4300 zNose GS/SAW, MOSES II, KAMINA, for express analysis of animal and vegetable protein systems (dairy, meat, seafood, starch, vegetables, fruit, spices) [4].

2. The purpose of the study
The scrutiny of the changes, the establishment of early stages and peculiarities of spoilage of fresh fish, Rainbow Trout (Oncorhynchus mykiss), through chemical «electronic nose» piezo sensors while stored in various modes. Evaluation of the impact of different storage regimes (cooling, freezing) on the change in the odour of carcass and other parts of fish (raw fillet, gills) to develop a method and a portable device capable of determination of a fish freshness degree was also included into the research tasks.

3. The object of the study

| Fresh Sample (initial control point): | Gills (sample 1) | Fillet (circumlex area, sample 4) | Preliminary Spoilage Initiation |
|--------------------------------------|-----------------|----------------------------------|--------------------------------|
| Fridge Storage, 4°C                  | 3 days (sample 2) | 4 days (sample 5) | 3 days (sample 9) |
|                                      | 14 days (sample 3) | 14 days (sample 6) | 12 days(sample 10) |
| Freezing Chamber Storage, -18°C      | Notstored | 34 days (sample 7) | Subsequent Freezing |
|                                      |                  | 47 days (sample 8) |                                      |
Spoilage features and trout fillet and gill state control were studied in 2 storage regimes with two sampling modes in 3 control points for gills and six control points for fillet (Table 1).

4. Materials and methods

4.1 Samples preparation for analysis

Average samples of gills and raw trout flesh of a constant weight (10-30 gr.) were placed into glass samplers, then were tightly covered by a soft neutral membrane, and were kept at room temperature (20±1 °C) for at least 20min for saturation of EGP above the sample. After fridge storage at the temperature of 4 °C and in the freezer at the temperature of -18 °C, samples firstly were defrosted within 60-120 min, and then were thermostated, as described above. The samples were extracted through a membrane with 3sm³ syringes in Equal Gas Phase (EGP) – without affecting the sample – and injected into a detection cell (Figure 1a).

Sensors array background was from 15 to 30Hz·s with natural sensor noise no more than ± 1-2 Hz (Table 1b). The odour study was conducted on the laboratory odour analyzer «MAG-8» (the Russian Federation) based on «electronic nose» methodology (Figure 1).

Eight sensors based on BAW-type piezo quartz resonators with basic frequency of 10,0 MHz with various film sorbents on electrodes [1-3] were applied as a measuring array. Coatings were chosen according to the test task, which was to fixate emission from samples of various organic compounds: polar, moisture-sensitive – polyvinyl pyrrolidone (PVP), (sensor 1); nonpolar, sensitive to ketones and amines – propolis (sensor 2), to acids, alcohols, esters – crown-ethers of dicycHexane-18-crown-5, 18C6 (sensor 3); to acids, amines – Bromo cresol green, BCG (sensor 4); to amines – polyethylene glycol succinate, PEGsk (sensor 5); to amines, alcohols, aldehydes, ethers – polyethylene glycol PEG-2000, PEG-2000 (sensor 6): Tween 40, Tween (sensor 7); to phenolic and other aromatic compounds – trioctylphosphine, TOPhO (sensor 8). All modifiers were mass optimized and stabilized.

4.2. Measuring mode

Measurement time was 120s., sensor feedback mode was steady with 1-s step, an optimal algorithm for representing sensor responses was based on the maximum response of individual sensors. Measurement error constituted 5-7 %.

The initial primary analytical information of the «e-nose» system is chrono-frequency – output curve of the piezo sensor during the measurement time – of the dependence of each sensor’s oscillation frequency on time. Then selective information from chrono-frequency patterns of all eight sensors is used for processing and decision-making.
The total analytical signal is formed by one of the methods for visualization of multidimensional data in the form of radial diagrams («visual print») with the help of integral algorithm for processing the signals coming from eight sensors. To establish the overall composition of the samples' odour, full «visual prints» of maxima – the greatest responses of 8 sensors – are applied. «Visual prints» of maxima are built on maximum sensors responses in EGP of samples within measurement time (120s.). They allow establishing similarities and differences in the composition of the smell's volatile fraction above the analyzed samples [2]. The figure areas are calculated automatically in the device software. As the criteria for assessing the difference in the odour of the analyzed samples, the following characteristics were chosen:

**Qualitative characteristics of gas samples composition:** 1) «Visual print» shape with characteristic distribution along response axes was defined by a set of compounds in the equal gas phase (EGP) above studied samples. 2) A\textsubscript{i/j} identification parameters – calculated according to sensor signals in the analyzed samples – were applied for the recognition of individual classes of compounds in a mixture [5, 7]. As the parameters reflecting the qualitative composition of the odor, there were used parameters listed below: 1 (i/j) – Propolis/PVP, 2 (i/j) – Tween/PVP, 3 (i/j) – TOPhO/PVP, 4 (i/j) – TOPhO/PVP, 5 (i/j) – BCG/Tween, 6 (i/j) – BCG/18C6, 7 (i/j) – 18C6/PEG-2000, 8 (i/j) – BCG/PEGsk, 9 (i/j) – PEGsk/TOPhO.

**Quantitative characteristics:** 1) \( S \), Hz\textsubscript{s} – 1) SS, Hz\textsubscript{s} – the total area of the «visual print» – evaluates total aroma intensity, is proportional to the concentration of highly volatile substances, including water, and is built on all the signals of all the sensors during all the measurement time; 2) maximum sensor signals with the most active and specific sorbent films DFI, Hz is used for content evaluation of individual classes of organic compounds in EPG by normalization method [3, 5]. The sensors responses were fixated, processed and compared in the software of «MAG Soft» analyzer. The laboratory air after long ventilation was used as samples to verify the correctness of the measurement, completeness of system regeneration, and sensors reaction. The general methodology for obtaining and processing the results was as follows:

1. For the selected control points (the scheme is in Table 1), we fixated sensors response in EGP selected above the samples with twofold repetition for each sample.
2. From the obtained primary data (chrono-frequency), there were chosen quantitative array indices: maximum sensors responses and «visual print» area.
3. «Visual prints» of maximum sensors responses in the array for all samples were fixated in the software of the device. The overall difference or similarity of the figures of these integral responses of the sensors array reflects the identity or divergence in the composition of EGP above the samples and their change in time or under the impact on the samples.
4. There were calculated additional parameters for comparison of samples: A\textsubscript{i/j} and mass fraction (\( \omega, \% \) mass) of individual groups of compounds by the signal proportion of a certain sensor in the total quantitative index using the normalization method (various quantitative signals can be used for the calculation) using formula (1):

\[
\omega = \frac{\Delta F_{\text{max}}}{\sum_{k=1}^{n} \Delta F_{\text{max}}} \cdot 100 \%
\] (1)

In case of the identity of the qualitative and quantitative composition of the samples, these indices are close within the limits of the permissible variation. At the same time, the most reliable reflection of the change in the composition of the odor is the deflection of several indices or even a set of them, for example, the change of the qualitative composition spectrum for individual samples (a set of A\textsubscript{i/j} identification parameters).

5. Calculation of similarity parameters of A\textsubscript{i/j} indicators sets was carried out according to the formula (2):

\[
\partial = \sqrt{\frac{\sum_{k=1}^{n}(A_{ij}(s,k)-A_{ij}(c,k))^2}{\sum_{k=1}^{n}(A_{ij}(c,k))^2}}}
\] (2)
Where $S_t$ is indicators of the Standard (initial points), $x$ is indicators for a compared sample, $k$ (index) is a serial number of an $A_{ij}$ indicator (from 1 to 9).

5. Determination (at the reliable detection) of the nature of volatile organic compounds causing changes in the EGP composition above the sample during storage time. All the results applied for processing are statistically reliable, gross blunders and heterogeneities are excluded.

6. Discussion of the results

Absolute signals of «electronic nose» are both individual analytical signals of each sensor and qualitative characteristics of the integral (generalized) signal of sensors array – «visual print» area. This signal is formed as a pie chart and represents n-sided figure (where $n$ is the number of sensors which responses are considered as informative) [2, 5, 6]. This minimal set of data allows evaluating the presence of changes and their severity in the chemical composition of the highly volatile fraction of sample odour at the first stage. «MAG-8» software quantifies these differences in absolute and relative terms. When the measurement conditions are constant, the sensors and the algorithm for processing primary data are stable, the differences are determined only by the odour of the samples. The obtaining and processing of such information do not exceed more than 5-7 minutes. Table 2 presents data for the extreme points of the state control for all analyzed samples (gills, fillet) stored in various modes.

**Table 2.** Comparison of initial information from «electronic nose» for trout samples in the first and the critical control points. On the circular axis are the numbers of sensors in the array. On the vertical axis are the responses of the maximum sensors during measurement time ($\Delta F_{max}, Hz$).

|                  | Chilled Samples                        | Frozen Fillet Samples                    |
|------------------|----------------------------------------|------------------------------------------|
| **Gills**        |                                        |                                          |
| 1st control point (blue), 3rd control point (pink), total area (purple) | «Visual print» area: first point - 300Hz·s; final point - 748Hz·s. Absolute difference: 448Hz·s; relative difference: 150 %. | «Visual print» area: first point - 420Hz·s; final point - 325Hz·s. Absolute difference: 95Hz·s; relative difference: 23 %. |
| **Gills**        |                                        |                                          |
| 1st control point (blue), 3rd control point (pink), total area (purple) | «visual print» area: first point - 420Hz·s; final point - 405Hz·s. Absolute difference: 15Hz·s; relative difference: 3.8 %. | «Visual print» area: first point – 420Hz·s; final point – 540Hz·s. Absolute difference: 120Hz·s; relative difference: 29 %. |

The odour intensity of the samples numerically reflects the area of the figure ($S_k \pm 30, Hz·s$). This characteristic alters for all samples stored in various conditions, yet it changes differently. Thus, EGP for the gills samples modifies almost uniformly from the zero to the 14th storage day.
There was established a reliable linear dependence of highly volatile compounds content, registered by «e-nose» above the surface of trout gills, on storage time at the temperature of 4 °C.

The equation, connecting the value («visual print» area) registered by the device with storage time (t, days), confirms the stable dependence of changes in the registered parameter on the storage time:

\[ S_e = 31.2 \cdot t + 309 \quad (R^2 = 0.999). \]

The acquired dependence proves that variations in the chemical composition of gills start with the moment of their first contact with air. Based on the acquired dependence, it is possible to determine the duration of fish storage at the indicated temperature from the first day of the catch.

Table 3. Relative content of components in EGP above trout gills and fillet samples, calculated using the normalization method by cross-selective sensors signals, \( \omega \) (± 2.0) % mass.

| Samples / Control points of their state | S1 PVP | S2 propolis | S3 18C6 | S4 BCG | S5 PEGsk | S6 PEG2000 | S7 Tween | S8 TOPhO |
|----------------------------------------|--------|-------------|--------|--------|---------|------------|---------|---------|
|                                        | free moisture | ketones, alcoh | acids, alcohols, ketones | amines, other | alcohols acids aroma |
| Gills 1st point                         | 24.7   | 4.5         | 13.5   | 5.6    | 12.4    | 9.0        | 18.0    | 12.4    |
| Gills 2nd point                         | 24.3   | 4.9         | 12.6   | 4.9    | 15.5    | 9.7        | 18.4    | 9.7     |
| Gills 3rd point                         | 19.2*  | 4.6         | 12.3   | 6.9    | 11.5    | 11.5       | 16.9    | 16.9    |
| Fillet 1st point                        | 19.6   | 6.9         | 14.7   | 6.9    | 12.7    | 9.8        | 18.6    | 10.8    |
| Fillet 2nd point                        | 22.5*  | 5.6         | 13.5   | 5.6    | 15.7    | 10.1       | 20.2    | 6.7     |
| Fillet 3rd point                        | 17.0   | 7.0         | 15.0   | 6.0    | 14.0    | 10.0       | 20.0    | 11.0    |

|                | 1st point | 2nd point | 3rd point | 4th point |
|----------------|-----------|-----------|-----------|-----------|
| Cooling Chamber (gills, fillet)         |           |           |           |           |
| Gills 1st point                           | 25.0      | 28.2      | 34.6*     | 31.4      |
| Gills 2nd point                           | 25.0      | 28.2      | 34.6*     | 31.4      |
| Gills 3rd point                           | 25.0      | 28.2      | 34.6*     | 31.4      |
| Fillet 1st point                          | 25.0      | 28.2      | 34.6*     | 31.4      |
| Fillet 2nd point                          | 25.0      | 28.2      | 34.6*     | 31.4      |
| Fillet 3rd point                          | 25.0      | 28.2      | 34.6*     | 31.4      |

|                | 1st point | 2nd point | 3rd point | 4th point |
|----------------|-----------|-----------|-----------|-----------|
| Freezing Chamber (fillet)                 |           |           |           |           |
| 1st point                                   | 25.0      | 28.2      | 34.6*     | 31.4      |
| 2nd point                                   | 25.0      | 28.2      | 34.6*     | 31.4      |
| 3rd point                                   | 25.0      | 28.2      | 34.6*     | 31.4      |
| 4th point                                   | 25.0      | 28.2      | 34.6*     | 31.4      |

* marks indicators different from the initial control point.

It was found that with the stable operation of the sensors array, gills spoilage is reliably registered by «e-nose» on the second day. During the storage process from the 0 days to the 14th day and 47th day, respectively, the intensity of the odour changes in fish meat samples with the various speed in the cooling and freezing chambers (Table 3). Throughout the storage, odour intensity of the frozen trout is much lower after defrosting than at the starting point (fresh). This fact is explained by natural processes of water freezing, by loss of highly volatile compounds while defrosting. On the 47th storage day, an insignificant increase of «visual print» area of sensors response is fixated, yet this increment is negligible (at the level of an error). Thus changes in the qualitative and quantitative composition can be traced by other characteristics and parameters. More detailed information on the chemical composition change of samples odour of different trout parts can be obtained by juxtaposing quantitative and qualitative characteristics (Tables 3 and 4). Let us monitor the changes – evaluated by the normalization method (formula 1) – in a qualitative composition of sample odour by a relative content of major classes of highly volatile compounds (Table 3). Strictly speaking, represented shares are the portion of sensors signals in a common set in pairs above various samples. If they change substantially, the content of those compounds that are predominantly sorbed on certain coatings of sensors modifies, too.
At the same time, only components registered by the same set of sensors are normalized among themselves only in the equilibrium gas phase above samples.

In different control points for samples, there are different degrees of deviation from the initial state. On the third day of storage, the composition changes quantitatively by 30% from the initial one, on the 14th day the change is more than 80%. The third-day alterations are not yet critical. There is an accumulation of volatile amines and a decrease in the content of other specific compounds of fresh odour due to weathering during storage. The content of the free moisture changes too - it decreases, it affects not only the short-chain amines but also the cyclic ones, S-containing compounds. These substances are the markers of the deep spoilage process.

A degree of deviation from the initial condition is different in various control points during storage for fillet samples in a cooling chamber. On the 4th storage day, the composition changed quantitatively by 70% of the initial, and by the 14th day – by 50%. Nevertheless, these modifications are qualitatively different. In particular, on the 4th day, we see the decrease in ketones and alcohols content, and the increase in free moisture, acids and amines. The growth of the first ones is less than the decline of the latter. Therefore the reduction of volatile compounds fraction is fixated according to the general indicator of a microbalance. On the 14th storage day, free moisture drop is much greater than changes of other compound classes and much more than it was for the gills (desiccation); the content of ketones and sulphurous compounds grows, whereas the dose of acids stays stable. That is, on the 4th day, we can see the first signs of percolation, and by the 14th day, protein destruction and fat oxidation are added to this process. While the criticality of these processes is small.

The content of the main groups of compounds changes insignificantly during the freezing process and long-term storage (1st and second points in a freezer). Mainly, it is their content decrease that is established. If trout fillet is kept for three days in a fridge at the temperature of 4°C with the subsequent freezing, after defrosting we are shown the change of the main classes of highly volatile compounds in EGP. In essence, the contents of many compound groups noticeably reduce, while amines and water contents increase. After defrosting of trout fillet samples that were kept in a fridge for 12 days, we found out the more noticeable alterations: the increase of the contents of acids, various amines and sulfur-containing compounds. These signs reflect the deep destructive processes in fish meat.

Table 4. The set of calculated $A_i/j$ identification parameters for the tested samples of trout gills and fillet in various control points and storage conditions, (n=3)

| Sample type/control point | $A_i/j$, sensors with i/j coatings: | Sensor # in array | 2/1 | 7/1 | 8/1 | 7/6 | 4/7 | 3/6 | 4/3 | 4/5 | 5/8 |
|-------------------------|------------------------------------|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                         | propolis/PVP/Tween/PVP/TOPhO/PVP/Tween/PEG-2000/BCG/Tween/18C6/PEG-2000/BCG/PEGsk/PEGsk/TOPhO |                | 2/1 (± 0,02) | 7/1 (± 0,02) | 8/1 (± 0,02) | 7/6 (± 0,2) | 4/7 (± 0,2) | 3/6 (± 0,2) | 4/3 (± 0,02) | 4/5 (± 0,2) | 5/8 (± 0,02) |
| Gills 1st | | | 0,18 | 0,73 | 0,5 | 2,00 | 0,31 | 1,50 | 0,42 | 0,46 | 1,0 |
| Gills 2nd | | | 0,20 | 0,76 | 0,40 | 1,90 | 0,37 | 1,30 | 0,39 | 0,31 | 1,6 |
| Gills 3rd | | | 0,24* | 0,88 | 0,88 | 1,47 | 0,41 | 1,07 | 0,56 | 0,60 | 0,70 |
| Fillet 1st | | | 0,35 | 0,95 | 0,55 | 1,90 | 0,37 | 1,50 | 0,47 | 0,54 | 1,18 |
| Fillet 2nd | | | 0,25* | 0,90 | 0,30 | 2,00 | 0,28 | 1,33 | 0,42 | 0,36 | 2,33 |
| Fillet 3rd | | | 0,41 | 1,18 | 0,65 | 2,00 | 0,30 | 1,50 | 0,40 | 0,43 | 1,27 |
| Cooling Chamber (gills, fillet) | | | | | | | | | | |
| Freezing Chamber (fillet) | | | | | | | | | | |
| 1st point | | | 0,19 | 0,71 | 0,38 | 1,67 | 0,33 | 1,33 | 0,42 | 0,50 | 1,25 |
| 2nd point | | | 0,12 | 0,58 | 0,42 | 1,50 | 0,33 | 1,30 | 0,38 | 0,56 | 0,82 |
| 3rd point | | | 0,11 | 0,44 | 0,25 | 1,45 | 0,50 | 1,18 | 0,62 | 1,14 | 0,78 |
| 4th point | | | 0,13 | 0,51 | 0,28 | 1,67 | 0,45 | 1,42 | 0,53 | 0,82 | 1,0 |

* marks indicators significantly different from the initial control point.
 parameter demonstrates the ratio stability of concentration of individual classes of highly volatile compounds in EGP and its qualitative composition. \( A_{ij} \) parameter allows tracing the changes in EGP qualitative composition above samples and appearance/disappearance of the highly volatile fraction (Table 4). \( A_{ij} \) identification parameters (minimax values of parameters for individual substances) reflect the qualitative composition of an equilibrium mixture of vapours above samples.

If \( A_{ij} \) indices for samples are similar or coincide for such indicators of EGP above samples by the ratio of the sensors signals, we can assume that the ratio of the content of these compounds is the same in samples. If \( A_{ij} \) parameters differ for samples and the Standard, it ultimately means that either qualitative composition differs as well, or that the quantitative one is altered greatly (Table 4). The greater the number of \( A_{ij} \) parameters differs for samples and the Standard, the greater the shift in the odour of samples is, which with a high degree of probability is fixated with an organoleptic evaluation by consumers and tasters.

According to qualitative indicators for gill samples, there has been established the beginning of the composition change on the second day of storage and a significant variation in the chemical composition of the odour on the third day of storage. The different pattern of accumulation of separate groups of compounds at different control points has been ascertained. The acids content decreases, while the content of amines and sulfur-containing compounds increases, at the same time, sulfur-containing compounds accumulate substantially between the 3rd and 14th days of storage. In contrast, amines start accumulation from the first point.

Alterations in the qualitative composition of equilibrium gas phases above fillet samples are established both on the 4th and 14th days of storage in a cooling chamber.

Let us face more detailed changes in qualitative and quantitative composition of highly volatile odour fraction, as well as its modifications during the storage period, and the impact of the preliminary storage duration on the odour composition of frozen samples of trout fillet. There have been found changes in the qualitative composition in all the storage points in a freezing chamber. These changes are especially critical and noticeable for trout samples that were frozen after 3-day and 12-day storage.

After 3-day fridge storage and subsequent freezing of the fillet, qualitative composition of odour – respectively, the sample state – alters in comparison with the initial condition more than by 70 %. In comparison with the first point of defrosting of the fresh and not kept in the fridge sample, the difference is about 50 %. The samples kept for 12 days in the fridge and subsequently frozen differ from the fresh fillet sample by 65 %, while in comparison with the first defrost point of fresh fillet sample (sample 7) the difference constitutes at least 45 %. The differences decrease in odour and thus in the condition of fillet samples after 12-day storage in the fridge and the ones after 3-day storage with subsequent freezing in comparison with the sample of freshly frozen fish meat with subsequent defrosting 35 days later is explained by elaborate processes of changes: freezing-out, odour ageing, sagging processes and proteins destruction. It has been established that the qualitative content of thawed fish after improper storage is different from the Standard. The similarity parameter \( \hat{\partial} \) calculated by the formula (2) – of «visual print» of sensors responses for sample 9 (after three days of storage in the cooling chamber with the subsequent freezing) constitutes 0,342 towards the Standard (sample 7, freshly-frozen fish fillet stored in the freezer for at least 30 days); in case of sample 10 (after 12 days of storage in a cooling chamber with subsequent freezing) similarity parameter is 0,17.

6. Conclusion

We have developed express-method of fish freshness evaluation using «piezo electronic nose» device allowing objectively and continuously identifying and evaluating the freshness and quality of fish and fish products. Chemical sensors make it possible to fixate early signs of changes in trout fish fillet after 3-day storage and subsequent freezing. It is possible to estimate the storage time of fresh fish in any conditions with an error of measurement of no more than 10 %. There has been elaborated the method of the simple analysis of a fish odour and of obtaining diagnostic information about fish freshness by the fillet and gills state. The
mode of chemical sensors and «electronic nose» «MAG-8» application is highly sensitive and express and allows gaining objective information; it is also economically acceptable for laboratories and mobile monitoring stations of any level.

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