

Conference paper

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Electronic nose based on nanoweights, expectation and reality

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Abstract: One of the topical approaches in analysis – outside the framework of traditional ones – is the formation of an integral “image” of the object. There are several approaches to solving the issue of obtaining as much information about the sample by a certain portion of its properties or its composition as possible. The first approach is forming a visual image (diagram) of several different properties of the analyzed sample, for example, the content of certain metals, acids, volatile components and some other indicators of wine quality. The consolidated image of a sample enables us to distinguish samples identical or similar in the selected properties from crucially different ones, even in case of an acceptable change of each indicator. Or else, using the consolidated image one can evaluate the direction of an image shift of a certain sample compared to the set of standard samples. The analysis of the geometry of the sample image by diverse indicators affords ground for assumption of the reasons for this deviation, as well as identification of falsification, or even solution of a more complicated task: detecting the area of growth of raw materials. The second approach is close to the first one in terms of methodology, but it digitizes properties using detectors and presents this as an image (“visual print” of response) of signals of these detectors on some components of the sample (presence, content). The feature of this approach is the use of a detector system that is non-selective and cross-sensitive to certain sample components. These sample images are produced using a system of “electronic nose”. “Visual prints” of array signals of different character sensors contain qualitative and quantitative information about the part of the analyzed sample which is sorbed by sensors. Despite the uncertainty of this information, “electronic noses” of piezoelectric type are widely used in the analysis of samples with complex varying composition.

Keywords: dignity; “electronic noses”; integrated “images”; Mendeleev XX; opportunities; piezoelectric sensors; the new analytics.

Introduction

Modern living conditions, new manufactures and information technologies necessitate the development of analysis methods for prompt obtaining of accurate, correct, objective and the most complete analytical information on the state of the objects and processes. At the same time, further commercial appeal of the measurement tools and methods is very much welcomed, and they should be also easily available with minor costs of training or re-training of staff by laboratories of all levels. Currently there are two directions of development concerning methods and analysis tools. On the one hand, it is the development of high-tech sophisticated

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instruments and techniques; on the other hand, it is the creation of the most simple and informative ones to analyze “*in situ*” (in the field, outside the laboratory).

There is no single method or measuring instrument which would provide full information about the sample itself, its minor and target components. Individual indicators do not provide the detailed answers about the origin of the sample or its production technology. Yet, it is still a commonplace to rely on individual indicators in analysis of sample qualities and safety. As a rule, these indicators are one-dimensional selective, nonselective (pH, specific content of some analytes) or two-dimensional (the electrophoretogram, chromatogram current-voltage curve). Decisions are made on each individual indicator. The insufficiency of such an approach has led to the development of new algorithms for data representation (integrated analytics). The direction which is topical nowadays is to form the consolidated “image” of an object. In this case, several approaches are possible in solving the problem of obtaining as much information about the sample on some part of its properties or its composition as possible.

The first approach is the formation of indicators of several properties of the sample into a visual “image” (pie chart), for example, the content of certain analytes or descriptor (for the sensory test). Even with an acceptable change for each indicator the consolidated “image” allows us to quickly and intuitively differentiate identical or similar in selected properties samples from very different ones, or else to estimate the direction of their ‘image’ deviation compared to the sample group. The analysis of sample “image” geometry, constructed from heterogeneous indicators, allows us to establish the reasons for the deviation from the norm. In case with the food analysis, this will make it possible to identify food adulteration or even to solve a more complicated issue that is to establish the area of raw-stuff growth.

The second approach, which is increasingly used in the analysis of complex objects, is the use of an analytical data multitude of a sample – a compilation of generalized (integrated) “image” on the set of a variety of standard quantitative parameters. Parameters can be divided into one-dimensional selective (specific analytes content) and one-dimensional non-selective (total content of analytes, such as surfactants, APAV, pH, chemical oxygen consumption, COD). The set of standard parameters generalized into a single ‘image’ makes it easier to compare multiple samples and to identify deviations from the norm or properties’ displacement of the object during the monitoring. Limitations of this approach are associated with the certainty of parameters and their low correlation, which does not allow setting hidden undefined connections between the parameters and getting more information about the properties of the object. However, this approach is more informative than the analysis of individual parameters [1].

The third approach, in my opinion, is the most informative and is a key idea of information processing in an integrated analytics. Integral “images”, obtained from a set of individual multi-dimensional indefinite parameters (digitization of smell, taste, color) in numerical form and from one-dimensional selective and nonselective parameters, will greatly enlarge our knowledge about properties of an analyzed object. The presence of parameters correlated with each other in a common data matrix will allow us to establish the latent links between them and to expand the information on the sample to be analyzed significantly. For successful implementation of this processing of data approach, it is necessary to improve the processing of matrix data of intellectual analytical systems, including “electronic noses and tongues”.

Despite the development of analysis fundamentals, the discovery of the mechanisms of smell and taste genesis and their deciphering, despite the discovery of new methods of quality and safety control, including the high-tech, the issues of organoleptic tests, which are the first stage for an analysis of any object, are still topical. Until now, human senses have not been replaced in routine laboratory analysis with the physical devices that can be used to measure (digitize) organoleptic properties, but not just characterize them with descriptors and their evaluation in points.

Rules of tasting, mathematical methods of processing the results, the uncertainty in the interpretation and description of the organoleptic properties as “inherent to this type of product” make these quality indicators vulnerable and unspecific. The absence of solution to the issue of instrumental evaluation of these properties retains the possibility of falsification. It is partially possible to solve the problem of replacing the tasters for routine analysis in case of dangerous and unpleasant samples by using arrays of sensors and software for registration and processing of incoming multi-dimensional signals. It is necessary to develop methods

and measurement tools for translation of undetermined organoleptic properties of the samples, for example smell into digital information. These systems should be deprived of the olfactory fatigue, limitations on the number of measurements and on testing conditions. Their analytical information should be stored, recorded and processed, should be objective, similarly to other physical and chemical properties of the samples.

Such issues are successfully solved by intellectual analytical systems based on arrays of diverse measuring elements (sensor) – so-called electronic “noses and tongues”. These devices make it possible to obtain a multi-dimensional analytic signal (data matrix) in the digital code for a part of the most undetermined object properties (smell, taste). The feature of this approach is the use of a set of non-selective, cross-sensitive to some components of the probe sensors. Yet, it is difficult to establish a detailed qualitative and quantitative composition of the sample, as in chromatography. But it is the undetermined response of the array of diverse sensors that allows us to record the peculiarities of the complex composition of either the sample or its individual properties (taste and odor). Whereupon only some part of the components of the mixture is detected.

These systems have been known for more than 20–40 years and extensive experimental data on their application has been accumulated, but the recognition of it as a new means of measurement of the new (integral) analytics is still complicated. It limits their widespread use in laboratories and its commercialization. Let us examine the reasons for this phenomenon on the example of “electronic noses”-gas analyzers with intellect.

“Electronic nose” based on piezoelectric sensors

“Electronic noses” are devices based on an array of chemical (or other) gas sensors with a fundamentally different approach to the processing of the measurement results and output compared to the classical methods of analysis. They are characterized by the absence of the traditional results of qualitative and quantitative analysis. These systems are widely known, and the market for such devices is noticeable, they are used in more than 60 countries and produced in Germany, the USA, Canada and other countries. However, the certification of these systems as a means of measurement is complicated. First of all, it is connected with a fundamentally different analytical information provided by these devices, as compared to conventional methods: as a rule, they demonstrate the absence of data on the identification of the individual components and their content.

Sensor transducers, which are used in the arrays of “electronic noses” as converters, are sensitive both to the change in electrical conductivity, resistivity and to the changes of electrochemical, optical, oscillatory properties, including mass-sensitive piezoresonator generating bulk acoustic wave (BAW-type), cantilevers. Piezoquartz resonators of BAW-type allow weighing the mass of up to 10^{-15} g, as a result of sorption or adhesion on the surface of electrodes deposited on a quartz crystal platinum. Basic oscillation frequency of the quartz plate is 8–30 MHz. Piezoelectric resonators sensitive to mass are called microbalance, while the method based on their use is called quartz crystal microbalance (QCM) [2]. This terminology has been well-established since the 80-ies of the last century, but the emergence of new oscillatory systems with high mass resolution allows us to talk about nanobalance and nano-weighing.

The most sensitive sensors of the sorption type in “electronic nose” systems are QCM with a sensitivity of up to 10^{-15} g. The advantages of these piezo-balances are the following: easy control of selectivity, fast response time and fast flow of the interaction at the interface due to the application of nano- and micro-sorbative phases.

Piezoelectric resonators, both as individual measuring elements and as arrays, are widely used to solve the issues of the analysis of food products and polymers; they are also used in environmental monitoring, medical diagnostics, manufacturing and in process control in bioreactors [2–4].

There are many theories that describe the relationship between the change of the oscillatory properties of the piezoelectric resonator and the mass attached to the electrodes [2]. Piezosensor response link with the attached mass is roughly described in Sauerbrey [5], eq. (1):

$$F_i - F = -\Delta F = -2.26 \cdot F_o^2 \cdot \Delta m / S \quad (1)$$

where F_i is the oscillation frequency of a quartz plate in the i -time, Hz;

F is the initial oscillation frequency of a quartz plate with a film before loading by vapors, Hz;

ΔF is the change in the frequency of sensor oscillations as a result of vapor sorption, Hz;

-2.26 is the constant associated with the peculiarities of acoustic wave propagation through a quartz plate;

F_o is the oscillation basic frequency of quartz without coatings, MHz;

Δm is the mass attached to the sorbent on the sensor electrodes, g;

S is the surface area on which the mass of the adsorbed substance is distributed (roughly equal to the area of the electrodes), cm^2 .

The equation is used for maintaining the linear dependence of the sensor response under load.

The approach to processing and visualization of the sensor array response matrix by means of the creation and recognition of graphic images is becoming increasingly popular. Algorithms of signal visualization in the processing of multi-dimensional information have long been used, for example, for conversion and display of ultrasonic signals [6] and the acoustic fields [7].

If we interpret the chromatographic retention time in the form of a detector signal or a derivative of the detector signal pie chart, we will get a graphic image (“a visual print”) of a particular odor, or a mixture of volatile components. “Visual prints VaporPrint™” are formed as a pie chart by transforming a variable time from the maximum radial-angle value at the beginning of the analysis to zero (vertical) at the end. They are suitable for the “electronic nose” signal recognition algorithms and also allow us to distinguish the complex surrounding background from standards, and to single out the previously studied (standardized) sets of odor “visual prints” [8–11].

“Visual prints” of array signals of diverse sensors contain qualitative and quantitative information about the detectable portion of the sample. Despite the ambiguity of signals due to cross-selectivity, piezoelectric type “electronic noses” are widely used in the analysis of complex, variable composition samples [3].

To determine the place of piezosensor-based “electronic noses” among traditional instruments, methods, it is necessary to compare them. If to start from the nature of the substances, which register arrays of sensors (analytes – volatile pairs), there are two analogs: the closest analog of nano-weighing is a gas chromatography, next to it in terms of the tasks and purpose is organoleptic (traditional touch tasting analysis). It is necessary to note that the existing regulations require the use of precisely these methods for the determination of volatile compounds in food and non-food materials, and environmental objects.

Piezosensor-based “electronic noses” have a lot in common with gas chromatographs. For example, one of the similarities is the mechanisms of interaction between analytes and sorption coatings, which are analogous to stationary phases. Sorbent films which are used on piezosensors can be solid, liquid and nano-structured. Moreover, the measuring in the “noses” can be made both in dynamic (when combined with chromatographic gas-carriers) and in static conditions.

Identity and conceptual combination of these two methods are shown in the Z-nose systems where sensor array based “electronic noses” are aligned with columns and perform multi-dimensional detector function. This approach allows us to increase the resolution, sensitivity and selectivity of chromatographs.

Analytical information obtained from chromatographs and from “noses” is recorded differently. In case of chromatography, it is a two-dimensional chromatogram as a function of the detector signal from the reading time. The distinctive feature of analytical information provided by “noses” is an integrated (multi-dimensional) response, “a visual print” of piezosensor signals. At the same time, primary output curves – the dependence of frequency changes of oscillation of piezosensors on the time, so-called chrono-frequency graphs [2], $\Delta F = f(\tau)$, (Fig. 1) – are recorded and processed. Such a presentation of results allows us to make initial test evaluations of the object condition, as well as to interrupt the process in case of blunders and instability in the sensors during the measurement.

Reading analytical sensor signals can be carried out via integral and differential methods [12]. Integral method is accomplished by forming the total array response with step-by-step interrogation of sensors from 1

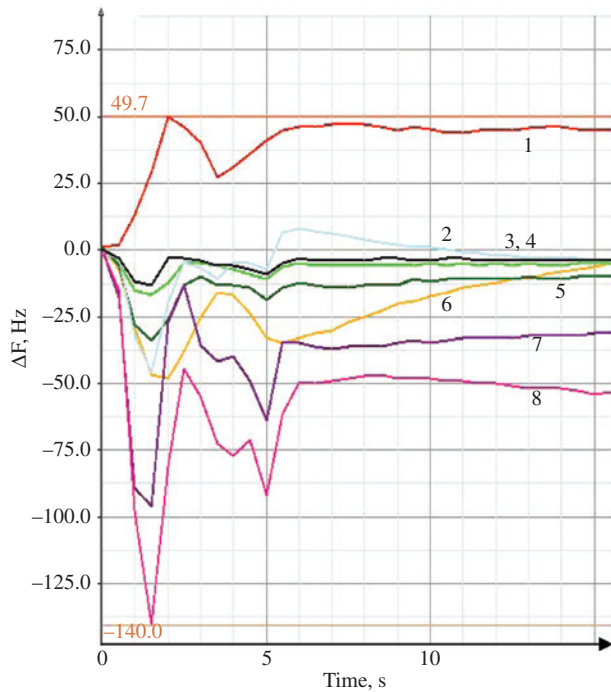


Fig. 1: Output curves of the gas analyzer “MAG-8” detected in the software. The number of lines corresponds to the number of sensors in an array [3]. The lines 1–8 represent responses of individual sensors.

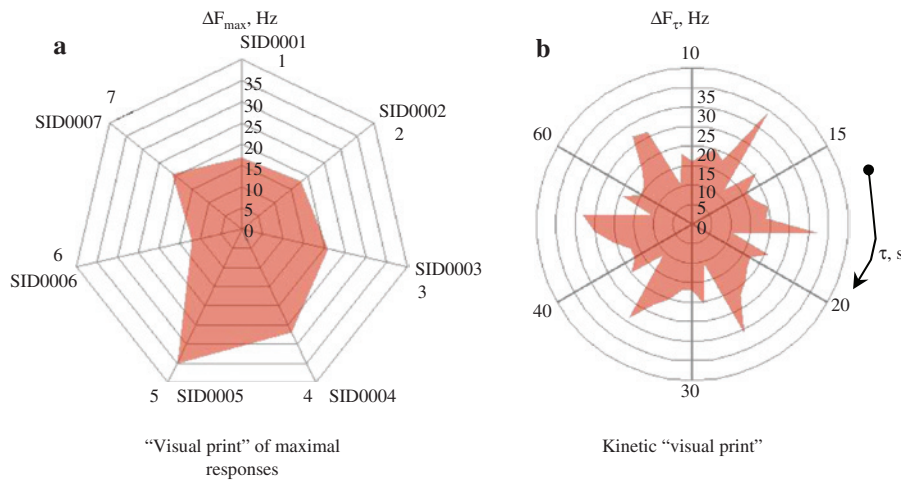


Fig. 2: Multi-dimensional response of a seven sensor matrix in the form of “visual print” [3].

to n . In differential mode, the response of the sensor array is formed at some set period of time by simultaneously fixing the signals on all the sensors – so-called time slice of “visual print” of sensor signals (Fig. 2a,b).

Integral method of “visual print” acquisition involves detecting device functioning during some measuring time τ_{Σ} , c, in the first approximation, and it is estimated according to eq. (2) [12]:

$$\tau_{\Sigma} = \tau_0 + n \cdot \Delta\tau + \tau^{\pm} \quad (2)$$

where τ_0 is time covering the period from sample introduction to the start of sensor signals pick-up; n is a number of elements in the array; $\Delta\tau$ is the time interval at which the sensors are sampled, s; $\tau^{\pm}$ is the drift of time interval of signal fixation, s.

The differential method of producing “visual print” is more expressive. Upon injecting (puffing) vapor (τ_{dif} , c), the response time of the array is determined only by the inertia of the sensors (3):

$$\tau_{\text{dif}} = \tau_0 + \tau^{\pm} \quad (3)$$

The time from the moment the sample is introduced to the start of signal reading (τ_0 , c) is determined by the kinetic parameters of sorption of odor components on the receptor films of piezosensors, and varies between times of half and maximum sorption ($\tau_{1/2}$ and τ_{max} , s). The time interval, which the sensors are sampled at, and its drift ($\Delta\tau$, $\tau^{\pm}$) are determined by the parameters of the electronic circuit in the response registration unit.

If the analyzed sample of complex composition is chemically stable within 1–5 min, the recommended method for forming a “visual print” of its equilibrium gas phase in a static detector is the integral method of cumulative response within 60–100 s (Fig. 2b) whereas differential time method of signal acquisition is preferable for testing volatile samples (Fig. 2a), as this algorithm allows us to observe the change in the composition of the sample in the “on-line” mode within 10–20 s [13].

At present, in case of the analysis of complex or unstable objects, it is common to apply the integral (cumulative) algorithm of simultaneous signal fixation of all sensors in the array, followed by their special placement on a pie chart – so-called kinetic “visual print” (Fig. 2b); it is also common to apply the differential algorithm of sensor response representation, which takes into account the interfering matrix effect coming from samples of complex composition [14, 15].

Basically, these multi-dimensional signals of “nose” are identical to the profiles obtained during sensory evaluation of smell (Fig. 3a), and contain information about the qualitative and quantitative composition of a mixture of components which are detected by a set of sensors (Fig. 3b).

In “electronic nose” systems, only a portion of the vapor from space around the sensors – a certain slice of the chemical composition – is detected, the fullness of which is determined by the number and characteristics of the sensors in the array. In addition, the main ideology of “electronic noses” is cross-selectivity of sensors, the response function of each of them in relation to the concentration of a particular component is not known.

It is because of this uncertainty of the response and cross-selectivity of sensor sorbent films that we cannot solve the traditional chromatography issues. As for processing of “electronic nose” multi-dimensional data, here the methods of chemometrics are applied: without training and with preliminary training, with the opportunity to predict and without it (cluster analysis, projection on latent structures, the principal component analysis, discriminatory analysis, artificial neural networks, etc.) (Table 1).

Currently, the most popular methods are principal component analysis, projection on latent structures, artificial neural networks, and odor comparison of visualized in various ways “visual prints” of sensor signals.

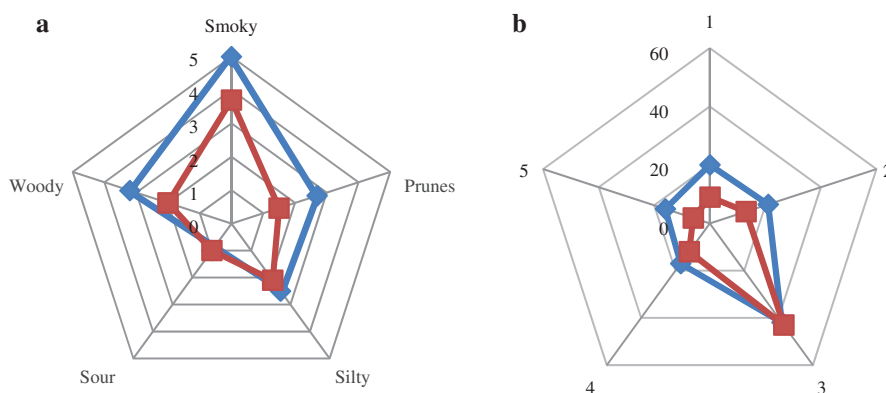


Fig. 3: Profile diagram of the smell for two samples of the smoked fish (a) and “visual print” of maximal responses of piezoelectric sensors 1–5 (ΔF_{max} , Hz) in equilibrium gas phase above samples of the frozen salmon (b).

Table 1: Mathematic methods for signal processing from multisensory system [3].

Main idea of chemo-metric methods	Ref.
Chaotic neural networks	[16]
“Kinetic autograph” of odorants (a time-dependable combination of matrix responses of piezoelectric crystals)	[17, 18]
Translation of digital information into a comfortable visual image on a personal computer by vtk method, which reveals a hidden structure and composition of the analyzed samples and their subtle characteristics	[19]
“Neural networks” algorithm for approximation of any continuous function, defined in a homogeneous field, and for a preliminary determination of the degree of accuracy. This method is more efficient in comparison with other classic methods (partial least squares technique, principal component analysis) in both linear and nonlinear models	[20]
Powell algorithm (regression by the method of nonlinear least squares), Kalman linear and extended filter and partial least squares technique	[21]
Intellectual neural network for simultaneous determination of two or more components by the response of a single sensor	[22]
The combination of partial least squares technique with the method of neural network with feedback for computerized material manufacture	[11]
Multi-kinetic analysis through the use of artificial neural networks	[23, 24]
Neural networks with a robust learning algorithm with feedback. The robustness of neural networks is improved by applying the function of standard training algorithm with feedback without error suppression instead of methods of least squares. The algorithm is suitable for work with data series containing up to 49 % of the outliers	[25]
Robust multivariate calibration algorithm based on the least mean squares (LMS) and the optimization method using the theory of consecutive numbers (TCN). The complexity of the LMS calculations is dramatically reduced by the use of constrains in the concepts and TFC. The algorithm is suitable for the analysis of a large number of sharply distinguished experimental values	[26]

Table 2: Comparison of analytical information of methods.

Chromatography	Organoleptics	System with intellect
Qualitative analysis: identification of separated components of the mixture	Qualitative analysis: the description of an odor (e.g. sweet, phenol, acid, etc.)	A multi-dimensional array response matrix of sensors, which can be visualized as “visual prints” diagrams of various types [3]
Quantitative analysis: determining the concentration of each or major/minor components (determined by the task)	Quantitative analysis: quantitative assessment of the severity of each descriptor and the overall intensity of the odor sample Profiling odor is the final analytical information about the sample	Sample clustering based on proximity of sensor matrix signals

The results obtained via chromatographic techniques, tasting analysis and via the use of “electronic nose” are quite different (Table 2). The identification of the components and their quantification are the results of gas chromatography; as for methods of artificial intelligence systems, such solutions have been made possible only in recent time. The solutions typical of “noses” are clustering and discriminating of samples on a set of output signals. The ones that are not carried out in the gas chromatography analysis or in tasting analysis.

How can the “electronic nose” based on QCN sensors solve complex analytical issues? Why are the “electronic noses” better than chromatographs and tasters?

Answers to the questions above will help:

- To evaluate the capabilities of a new analytics and devices used for it;
- To determine the place and purpose of “electronic nose” among the existing measurement tools;
- To solve the problems with the certification of devices as measuring instruments, their application methods, their inclusion in the state registers, and their implementation in the laboratory.

Here are a few examples of “electronic nose” based on eight piezosensors of various selectivity – “MAG-8” (Russia, OOO “Sensorika-New Technologies”, Fig. 1) for solving complex analytical tasks [27]. For the last 20 years of research the working group has accumulated the rich experimental material to analyze samples of various nature. Search of simple algorithms for processing allowed us to offer innovative solutions for the identification of individual or group components in complex mixtures. This has almost bridged the gap between “electronic noses” and chromatographers.

Combination of piezosensors with different sorption coatings can solve the problems of the analysis of volatile vapor mixture: quality markers, security, the status change of various systems (food, non-food, natural, biological). Application of universal sorbents allows the detection of various nature vapors, comprising the volatile fraction of odor samples (gross weighing). Selective sorbents evaluate the content of individual groups of compounds (e.g. acids, alcohols, phenols). Sensors with highly selective sorbents detect individual compounds (e.g. ammonia, 2-butanol, acetone). However, it is difficult to create such sensors with a long “lifespan” and the reversibility of the analytical signal. The combination of all types of sensors can solve all kinds of tasks. The success depends not only on an array of sensors, but also on the maximally complete processing of the recorded data.

Initial information of “MAG-8” is the matrix of sensor responses generated using integral algorithm of signal processing of eight sensors in the form of “visual print”. The full “visual prints” of highs – the greatest responses of eight sensors during the measurement time, $\Delta F_{\max}$, Hz – are used to establish the total composition of the odor samples. They allow us to establish both similarities and/or gross differences in the composition of the volatile fraction of smell above samples to be analyzed [3]. Subtle differences in the qualitative and quantitative composition of the gas mixture are established by comparing the kinetic “visual prints” built on the responses of all eight sensors within measurement time (Fig. 3). The nature of the mixture components shows itself better in such an analytical signal. Both types of signals and areas of the figures are automatically calculated in the software.

The following criteria are selected for assessing the difference in the smell of the analyzed samples:

- 1) The shape of “visual print” with the characteristic distribution along the axes of responses.
- 2) Quantitative characteristics:
 - The total areas of “visual prints”, S_{Σ} , Hz·s (kinetic) and $S_{\text{v.p.}}$, Hz² (maximum) evaluate the odor intensity from the recorded changes in the frequency of sensor oscillations, and are proportional to the total weight of the components adsorbed on the surfaces of sensors (4)

$$S_{\text{v.p.}} = f(\Sigma m_{\text{sorbate}}) \quad (4)$$

In its turn, the mass of sorbed components is proportional to their concentration in the gas equilibrium phase above the sample and in the sample.

- Areas under chromatograms of sensors, S_i , Hz·s or the greatest sensor responses during the measurement time, $\Delta F_{\max}$, Hz are used for evaluation of certain classes of organic compounds in the mixture by normalization method [28].
- 3) Qualitative characteristic:

Parameter identification A_{ij} used for recognition in a mixture of individual classes of compounds [29] is calculated by the signals of sensors in the analyzed samples for standard compounds (test substance) and standard samples. The set of these parameters corresponds to the individual quality characteristics of mixture compounds similarly to the sets of peaks on chromatograms or absorption spectra. The set of these parameters is an important quality characteristics reflecting the individuality of the sample odor at most.

The general algorithm of task solving consists of the following steps:

1. choice of substances-standards for the compiling and training of optimal array of selective sensors;
2. control of the stability and reproducibility of the sorption properties and analytical signals of sensors, evaluation of permissible variability of responses and noises;
3. establishment of identification parameters for solving the issues of qualitative analysis;

- 4. sample standard test;
- 5. sample analysis;
- 6. result processing.

To justify the correct interpretation of “electronic nose” information there were simultaneously used standard testing methods (according to GOST), other “electronic noses” (Vocmeter, Germany), sensory analysis performed by trained tasters and modern methods (high performance gas chromatography with different detectors, spectroscopy, biological testing).

Application of “electronic nose” based on piezoelectric sensors

“Electronic nose” “MAG-8” has successfully been applied to solve the following issues:

- 1. analysis of raw materials and food products with such purposes as: the construction of new types of products by the smell and production control at critical points (see Fig. 4) [28];
- 2. analysis of polymer materials for the safety assessment by the level of toxicity and by release of organic compounds of vapors [30];
- 3. analysis of human and animal bioassay [31];
- 4. monitoring of the environmental objects (indoor air, wastewater, natural water) [32].

Below we will demonstrate some examples of analytical solutions with the use of “MAG-8” and algorithms for acquisition of specific information about the smell and other properties of the samples.

1. The impact assessment of raw-stuff processing technology on the properties of finished products

The smell is the most valuable consumer property for drinks based on fruit. The samples of various cranberry water odor were compared with the help of “MAG-8” gas analyzer. To determine the impurity content of volatile compounds in the equilibrium gas phase above the samples of cranberry water, the magnitude of responses of all the selected sensors in the array and the area of “visual print” peaks were compared (Fig. 5).

The difference in the qualitative and quantitative composition of the equilibrium gas phase above the sample cranberry water is 20 %. However, this overall figure does not reflect the individual differences of the sample.

The changes in the quantitative composition of the odor above samples reflect the relative content of the main classes of volatile compounds on which the array of sensors is set, which is evaluated by the normalization method (see Table 3).

According to the content of the main classes of organic compounds, composition of odor samples of cranberry water is significantly different, for the selected array the difference is 75 %. At the same time in the sample 2 (improved material-handling technology), the content of volatile gasses, ketones and heavy

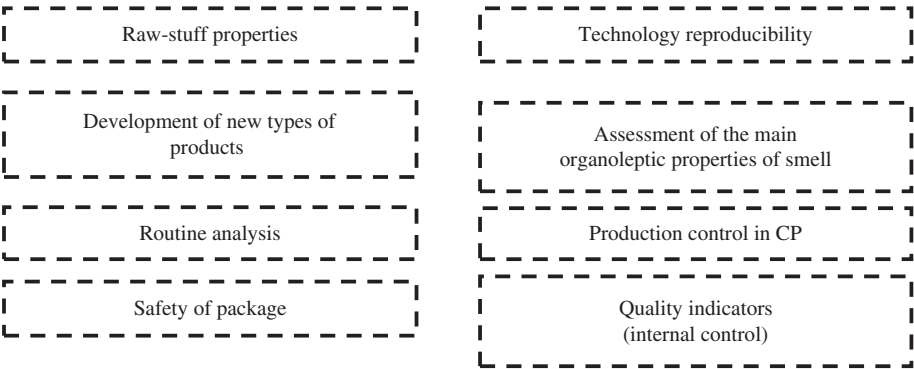


Fig. 4: Main directions of “electronic nose” application in food analysis.

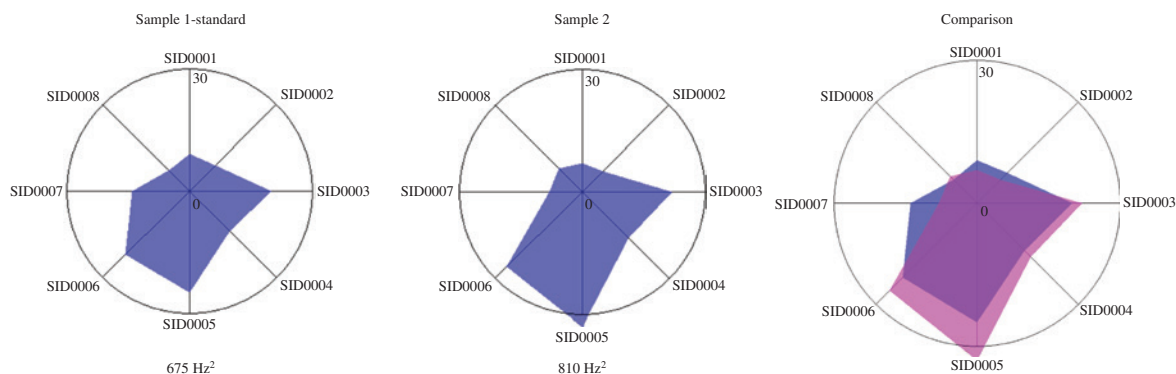


Fig. 5: “Visual prints” of sensor maximal responses in equilibrium gas phase (EGP) above samples of drinks. The axes are specified: a circular axis is the number of sensors in the array, the vertical axis is the maximum response sensors ($\Delta F_{\max}$, Hz).

Table 3: Relative content of components in samples, $\omega\%$ mass.

Group of detectable analytes	Designation of sensors in an array							
	S1 High volatile gas, acetone	S2 Acetone	S3 Alcohols, esters	S4 Amines, esters	S5 Complex esters, ester oil	S6 Complex esters	S7 Aromatic hydrocarbons	S8 Sulfur-containing hydrocarbons, terpenes
Sample 1	7.5	7.5	16.6	11.7	20.8	18.3	11.7	5.8
Sample 2	5.5^a	5.5	17.3	12.6	26.0	20.5	6.3	6.3

^aParameters with maximum deviation from standard (sample 1). Bold values are the components of sample 2 that have changed significantly in comparison with the analogous components of sample 1.

aromatic hydrocarbons reduces, while the content of ethers, esters and essential oil components considerably increases (by 35 %). Under such a high degree of prediction changes, redistribution of organic compounds in the equilibrium gas phase above sample 2 is perceived differently in a sensory evaluation.

The set of identification parameters $A_{i/j}$ allows tracking the changes in the qualitative composition of the mixture of substances above the samples. This indicator shows the constancy of the concentration ratio of individual classes of volatile compounds. If indicators $A_{i/j}$ in samples are close or identical, it can be assumed that the ratio of the content of these compounds in the samples is equal. The more $A_{i/j}$ parameters are discriminated, the more essential the differences in the smell of the samples are. These differences are fixed with a high degree of probability in sensory evaluation by consumers.

It was established that the qualitative composition of the odors above samples 1 and 2 are identical by 60 %. The differences in the composition can be clearly compared with the help of circular spectra of eight identification parameters $A_{i/j}$ (Fig. 6).

Such a visualization of quality information about samples is selected because of its proximity to the shape of sensory charts of tasting analysis.

In spite of the same original fragrance-defining materials (cranberry puree), it is impossible to talk about the identity of smell samples of cranberry water. Judging by the nature of changes in the qualitative and quantitative composition of the vapor mixture of samples 1 and 2, there is a high probability that the tasting evaluation of sample 2 will change compared to sample 1. The “spicy, cranberry” descriptor rating and the overall intensity of the odor of the sample 2 will increase.

Predicted changes in organoleptic properties according to the array of sensors are in good agreement with the tasting evaluation of odor samples, and exceed it according to the information about individual groups of compounds, the analysis time (no more than 20 min) and objectivity of measurement.

By the signals of highly selective sensors in the array, it is possible to estimate, within one measurement, the standard indicators of product quality. For example, on a signal from the sensor with the film

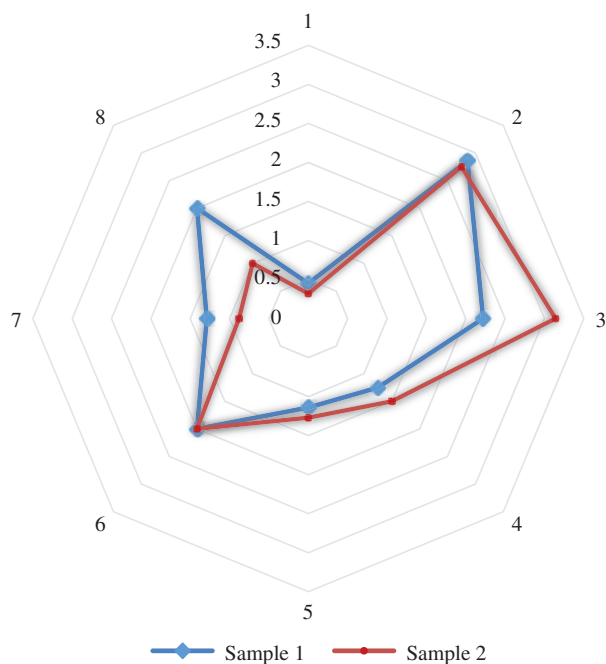


Fig. 6: Spectra of identification parameters for the highly volatile fraction of the odor above cranberry water samples. The conditional parameter numbers for the eight-sensor array are marked along the circular axis, while their numerical values are marked on the vertical axis.

Tween-40 in the equilibrium gas phase above the bun crumb “Moskovskaya” it is possible to estimate titrated acidity (Fig. 7).

The correlation with the free moisture content in many products (bakery, confectionery, cereals, etc.) is established by the polyvinyl pyrrolidone sensor responses.

The detailed information about the qualitative and quantitative composition of a smell is not required in majority of food analysis tasks. For instance, to monitor the state of the grain during storage time, it is only necessary to evaluate change or consistency of “visual print” area as quickly and easily as possible. Grain deterioration or shrinkage is differentiated by the dynamics of displacement of smell integral index.

The parameters $A_{i/j}$ for identification of individual components of the mixtures (acetone, ammonia, acetic acid, butyl alcohols, pentyl alcohols, esters, alkyl amines) have been proposed, established and justified [33]. These components belong to the group of substances-markers of living systems state. For example, the components of fusel oil in strong alcohol drinks are identified by highly selective parameters

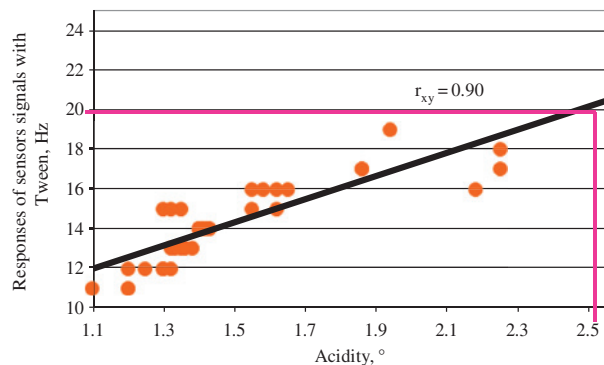


Fig. 7: The correlation of the sensor response with the film Tween-40 ($-\Delta F_{\max}$, Hz) with a titrated acidity of the crumb.

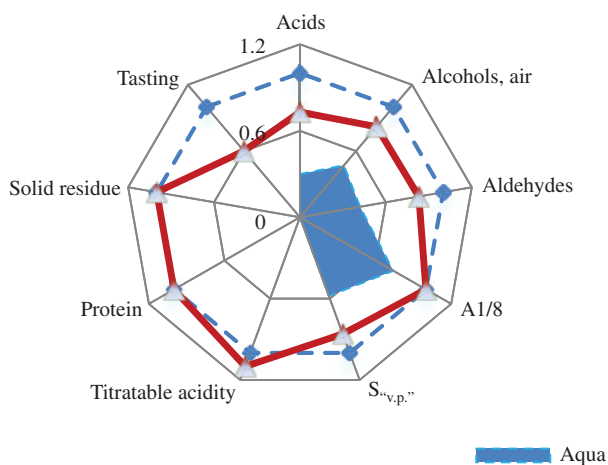
Table 4: Comparison of the results of vodka samples by gas chromatography, degustation and “electronic nose” with piezoelectric sensors.

Sample	Prediction of impurities by A_{ij}	Gas chromatography	Similarity	$S_{v,p,n} \pm 50, \text{Hz}^2$	Ranking by minimal content of volatile substances	Position in tasters ranking
“Russian standard”	No manifest impurities	Not found	Reliable	915	1	1
“Classical”	Insignificant impurities	Methanol	Not reliable	1113	2	2
“Baycal”	Some acetone, butyl alcohols	Methanol, isobutyl alcohols	Not reliable	1202	3–4	3–4
“Russian glory”	Acetone, butyl alcohols	Acetone, ethyl acetate, butyl alcohols	Reliable	1263	3–4	3–4
“Dovgan”	Butyl-amyl alcohols	n-Butyl, n-amyl alcohols	Reliable	1524	5	5

A_{ij} , during the measurement time of 60 s. “Electronic nose” based on eight piezoelectric sensors showed good informativeness in comparison with standard methods (gas chromatography, HPLC and organoleptic evaluation) (Table 4). Heavy alcohols, acetone and ethyl acetate in the samples are reliably detected by piezoelectric sensor signals. Poor agreement of the obtained results with results of HLPC for some samples happened because methanol was not included in the sample of test compounds to train the array of sensors. The set of identification parameters allows us – without complex mathematical algorithms and programs – to select the probes that differ from the sampling and standards, which is analogous to the method of projection on latent structures (PCA – model).

According to the analysis of eight samples of drinking milk with equal fat content, it was found that all of the recommended quality indicators (tasting score, titrated acidity, protein mass fraction, the density, the dry fat-free dairy rest, etc.) correspond to the norm. While, the indicators of the “electronic nose” for them differ. The integration of standard indicators and response of the sensor array into the consolidated “image” of milk samples allows us to establish a latent falsification of samples with dried milk or low-quality raw materials (Fig. 8).

All parameters of water samples (figure with a filling), of standard (marked with a dashed line) and of the analyzed sample (solid border of the figure) are normalized and compared in the same coordinate system. The four indicators for milk marked on the left of the pie chart are standard, whereas five indicators on the right are derived by piezoelectric sensors array.

**Fig. 8:** The integrated image of milk.

The proportion of compliance indicators for the analyzed sample and standard is 40 % for milk, and 0 % for water. The share of compliance with the standard for sample is 40 %. This example demonstrates the complexity of intentional violations of production technology through artificial support of standard indicators when measuring difficult to falsify odor of a sample. So, integral “image” of the properties is more informative than separate one-dimensional or multi-dimensional parameters of the sample.

2. Analysis of non-food materials

On an example of the analysis of products from PVC-plastisol, phenol-formaldehyde polymers and building materials it is shown that the spectra of the identification parameters with high level of reliability allow us to identify toxic compounds and evaluate safety of the products [34].

3. Clinical diagnosis

The analysis of equilibrium gas phase was performed on:

- 1) blood products (surgical, gynecological department) [31, 35];
- 2) smears of cervical mucus “*in situ*” to identify the causative agents of sexually transmitted infections (STIs) [36];
- 3) exhaled breath condensates of calves [37];
- 4) exhaled air of 180 patients from both children and adult divisions of the regional clinical hospital with a view to assess the level of activity of *Helicobacter Pylori* [38];
- 5) samples of bird biomaterial (chickens and hens) during periods of dysbiosis and enzyme preparations treatment;
- 6) samples of cervical mucus of cows in order to predict the development of endometriosis.

The gas-markers of microorganisms and bioassay conditions have been used for preliminary training of the piezosensor based “e-nose” [39–41].

Initial responses from the “electronic nose” – “visual prints” – allow us to split the samples and label them as either “not healthy” or “conditionally healthy”. With the application of chemometric methods, it is possible to further a deeper ranging of samples by the nature of the pathogens [36].

4. Environmental objects monitoring

Environmental monitoring of wastewater treatment degree using an piezosensors array (Research within SC 4.2186/2014–2016 Ministry of Education) is many times faster and commercially more advantageous than using a set of standard procedures and instruments. With the help of integral “image” of the wastewater samples it is possible to assess the efficiency of sewage treatment works, and to set hidden correlation parameters in the data matrix (Fig. 9). For example, area of “visual print” and oil content, metal ions and surface active agents in water are correlated for the wastewater samples before treatment.

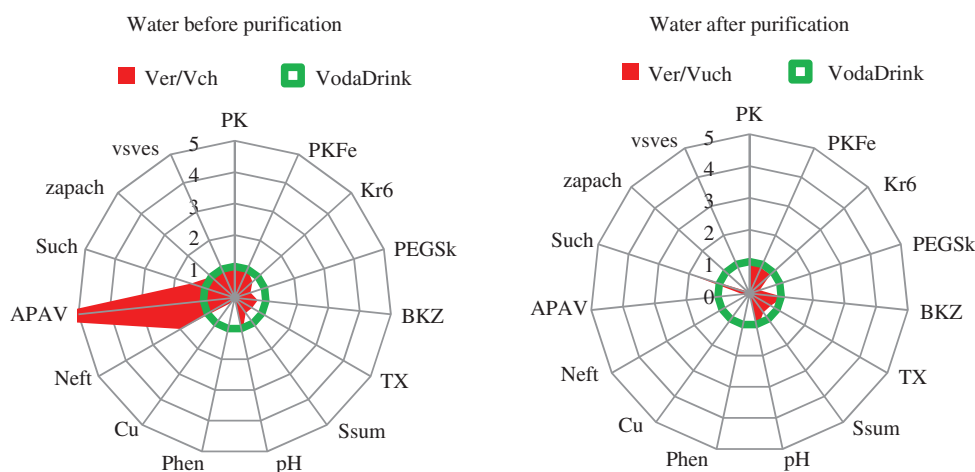


Fig. 9: Integral “images” of waste water samples before and after the purification.

Table 5: Advantages and disadvantages of “electronic nose”.

Advantages	Disadvantages
1. Measuring time is 60–120 s, system recovery time is 120–240 s	1. Modifier-films aging, the necessity of replacement
2. Productivity is up to 36 samples/tests. Sensor array durability is 1–2 years	2. Necessity of sample standards
3. Automatic data processing, data storage, print	3. Number of sample replications, $n=2$
4. The friendly software, low-cost operation	4. Formation of databases of standards and data on selectivity and sensitivity (training in mixes)
5. The minimum sample volume is 1 mL, the minimum weight is 50 μg	5. Measurement error is within 10–20 %
6. The possibility of application “ <i>in-situ</i> ”	6. The difficulty of the quantitative analysis of individual components or groups of compounds
7. No need of a multistage sample preparation	7. Temperature dependency
8. The issues of chromatography regarding preservation of sample ranking are partially solved	

Additional features allow acquisition of the combination of mass-sensitive “electronic noses” with other methods, such as: mass spectrometry [42], microbiological analysis [43], standard physical and chemical indicators of the quality [44], gas chromatography coupled with mass spectrometry (GC/MS) when classifying rice wine and vinegar [43, 45], and for other issues. “Electronic nose” along with the NIR spectrometry, ultrasound and computer colorimetry is attributed to non-destructive testing methods for rapid screening of large numbers of samples in animal husbandry in order to assess their quality [46].

It should be noted that there are research trends to combine several intelligence systems – hybrid methods of multisensory analysis – an electronic ‘tongue/nose/eye’. Such systems are able with high rate of sensitivity and specificity of identification to detect oil varieties, the geographical origin of the raw material [47], to predict palatability [48, 49] and to define the share of sunflower and waste oil in counterfeit products [50, 51].

Conclusion

Examples of the use of “electronic nose” based on eight piezosensors allow us to evaluate the advantages and disadvantages of the device (Table 5). Integral “images” of samples that are built on standard indicators (monomeric selective and non-selective) and multi-dimensional signals of “electronic nose” show perspectives of a widespread use of such systems and approaches in the processing of analytical data.

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