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Multisensor systems of the electronic tongue type as novel opportunities in design and application of chemical sensors

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Abstract. The main types of modern multisensor systems of the electronic tongue type as well as the sensitive materials and sensors (transducers) employed in such systems are considered. The most commonly used analytical applications of the electronic tongue including recognition and classification of various liquid media, quantitative analysis, process monitoring and taste assessment of foodstuffs are discussed. The bibliography includes 84 references.

I. Introduction

A challenge for the development of new analytical methods and instruments consists of the quest for the highest possible selectivity with respect to a given component or components. To meet this goal, a great number of electrochemical (particularly, potentiometric) sensors such as ion-selective electrodes (ISE), ion-selective field transistors (ISFT), *etc*. were developed. The first multisensor systems, as well as many systems of the electronic tongue type proposed to date, are based on the use of ISE or sensors of a similar nature.[1,2] This is why the way from individual sensors to the electronic tongue is traced in the present review by the example of ISE, although many arguments are equally valid for other types of chemical sensors.[3]

The first potentiometric chemical sensor, *viz*., the ion-selective electrode with an oxide glass membrane, was proposed for the determination of the activity of hydrogen ions in aqueous solutions.[4] Later, a great number of various membrane materials for ISE were developed, *viz*., oxide glass, single crystals, pressed polycrystalline blends of inorganic active components, liquid and plasticised organic polymeric compositions containing ion-exchange resins or neutral carriers, chalcogenide glass (for the determination of heavy metal ions). The membrane materials were used in both bulk sensors and various thin-film electrodes and microsensors. For the comprehensive description of the existing ISE and sensors of other types, see books and reviews.[4–9]

Short time of analysis, the possibility of miniaturisation of instruments and automation of the procedure as well as the simplicity and rather low cost of sensors make them an attractive tool for the analysis of solutions. The use of ISE for these purposes is limited, as a rule, to the cases where the concentrations of interfering ions are low and the electrode response is described by the Nernst equation. In addition, the use of ISE for the analysis of real objects is often hampered due to the insufficient selectivity with respect to the detected ion in the presence of other substances.

The most impressive progress in the field of sensor materials is associated with the synthesis of new organic substances employed as ionophores in polymeric plasticised membranes. However, it is the glass pH-electrode that still possesses the highest selectivity and is most popular, because the use of other sensors based on other detection principles often faces the same problem of insufficient selectivity in multicomponent media, which hinders their analytical application. The development and application of multisensor systems of the electronic tongue type offers a possible way towards the solution of this problem.

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II. Multisensor systems

1. The role of biology and chemometrics in the development of multisensor systems

Two fields of knowledge had the greatest effect on the development of multisensor systems. These are, on the one hand, the new achievements in biology, namely, understanding of the structure and operation of the human sensory system, and, on the other hand, the new possibilities and approaches to the processing of multidimensional data that were proposed within the framework of chemometrics.

The development of chemical multisensor systems was largely an attempt to mimic the structure and properties of biological sensory systems, namely, the mammalian olfaction and taste systems.[10] Initially, such an approach was realised in gas analysing systems, *i.e*., electronic noses; later, similar principles were used for the development of liquid analysers — electronic tongues. In the course of evolution, olfaction became the most efficient sensory system due to the high sensitivity of the human nose with respect to certain substances (one can identify up to 10 thousands of substances in the amount of down to 40 molecules).[11] The detection limit of the human nose with respect to certain substances is several ppb, while that of animals' noses may be even lower. Such possibilities of olfaction are attributed to the large number of different types of poorly selective receptors in combination with the specific way the signals from the set of receptors are processed in the peripheral and central nervous systems. The sense of taste is organised in the same way as the olfaction, although the number of taste receptors in humans is smaller.[11] Traditionally, the following four basic taste sensations are distinguished: sweet, salty, sour and bitter. Recently, an

additional (fifth) taste characteristic, *viz*., umami, was introduced, which is determined in particular by sodium glutamate and isocyanate.[12] Five major taste characteristics and their combinations are used to describe and quantitatively assess the taste of foodstuffs by additionally invoking such characteristics as taste sharpness, food texture, mouthfeel, taste duration, *etc*.

At present, the relationship between the structure (and chemical properties) of many substances and their taste is insufficiently studied, as well as many other interesting effects, *e.g*., the interaction of substances with different taste kinds or the increase in the sensitivity limit (desensitising) due to the synergistic effect of substances with different taste kinds.[11] The detection limit is usually higher for tastes as compared with scents, with one exception of alkaloids (for instance, quinine). However, the differential sensitivity of biological sensory systems of tasting and smelling is comparable. Thus, the mechanisms of operation of the taste and olfaction sensory systems are similar, although olfaction is a more sophisticated sense in animate nature (for example, for mammals and people).

The potentials of biological sensory systems based on a great number of nonspecific receptors led to the idea of using their structural principles in the development of artificial sensory systems. The latter were initially intended for the analysis of gases and identification of scents.

The development of electronic noses, *i.e*., multisensor systems for the gas analysis, was initiated by the studies by Moncrieff[13] and Persaud and Dodd;[14] later, different research teams all over the world made their contribution to the solution of this problem.[10] A typical electronic nose consists of a set (array) of nonselective sensors (most often, semiconducting sensors based on tin dioxide with different additives) and a system for processing multivariate data (for instance, on the basis of artificial neural networks). Electronic noses are applied for the identification of various gas mixtures and/or individual gases (for example, in leakage of chemicals).

The same organisational principles (arrays of low-selective sensors and multidimensional methods of data processing) were used in the development of multisensor systems for the analysis of liquids, the so-called electronic tongues. Like its biological prototype, the electronic tongue operates in various liquid media. However, the sensitivity and detection limits of artificial 'tongues' may substantially surpass the parameters of biological prototypes, because the materials of these sensors are capable of far extending the analytical potential of the system.

A common typical feature of electronic noses and tongues consists of combining the arrays of low-selective sensors with the data processing that employs pattern recognition methods. However, the sensor materials used in noses and tongues have virtually nothing in common, the sensors used in tongues being more plentiful both in the number and type. This offers certain advantages, for example, the electronic tongues are used not only for recognition and identification but also for the multicomponent quantitative analysis. In contrast to its biological prototype, the electronic tongue can be employed in the measurements in any media including hazardous and even lethal for living organisms.

What is important is that despite the similar organisational principles one cannot draw parallels between the potentials of artificial and biological systems and must take into account the significant differences between the sensors used for electronic tongues and noses, which leads to different approaches to the development of new sensors and the methods of their application. In the present review, we consider the studies devoted to multisensor systems for the analysis of liquids, *viz*., electronic tongues. The majority of such systems were developed on the basis of potentiometric sensors.

As was mentioned above, most ISE (and also most of sensors based on different principles) exhibit low selectivities in multicomponent solutions. In the case of ISE, the effect of interfering ions on the electrode response is conventionally described by the Nikolsky equation (or similar equations)

$$E = E^\circ + \frac{RT}{z_i F}\ln\left(a_i + \sum_j K_{ij}(a_j)^{z_i/z_j}\right), \quad (1)$$

where E is the potential difference (emf) of the electrochemical cell that consists of a reference electrode and ISE; E° is the standard potential; R is the gas constant; T is the absolute temperature; F is the Faraday constant; z_i and z_j are the charges of the primary and interfering ions, respectively, a_i and a_j are the activities of the primary and interfering ions, respectively; K_{ij} is the coefficient of selectivity of ISE with respect to the primary ion i in the presence of an interfering ion j.

Thus, the response of a low-selective electrode is determined by the concentrations of the primary ion and the interfering ion (or ions). If two terms in parentheses in Eqn (1) are comparable, the electrode response becomes non-linear. A non-linear calibration curve, as long as it is reproducible, can also be used for analytical purposes; however, more than one electrode should be used for the determination of parameters in Eqn (1). Apparently, the number of electrodes should not be smaller than the number of ions to be determined. Within the framework of such an approach, it was proposed to use ISE arrays rather than separate sensors to overcome the insufficient selectivity of ISE in the presence of interfering ions. It was assumed that the response of each electrode in multicomponent solutions is described by the Nikolsky equation. Solving the system of such equations allows certain parameters of the electrode response in multicomponent solutions to be determined, namely, the standard potential, the selectivity coefficients and(or) the slope. The mentioned parameters can further be used for the determination of concentrations of ions in solutions of unknown composition. It is well known that many parameters of the ISE response (for instance, the detection limit or the selectivity coefficient) depend on the conditions and methods of their determination. Numerous attempts to develop standard methods for their determination failed. Thus, the fact that all parameters of sensors are determined directly in multicomponent solutions with compositions close to those of analysed solutions pertains to advantages of the approach described above, in addition to the possibility of taking into account the effect of interfering ions. The calculated parameters of the response are more adequate than the theoretical parameters and make it possible to enhance the accuracy of the analysis, even being far from versatile. Various mathematical methods were proposed for solving the system of the Nikolsky equations, including different versions of regressions (Multi Linear Regression, Non-linear Regression, Partial Least Squares) and artificial neural networks.[15–23]

The next step involved abandoning the Nikolsky equation in favour of the methods that do not require any *a priory* information on the functional dependences between the potentials of sensors and the activities (concentrations) of determined substances. Thus, a new direction in the application of chemical sensors, which substantially differs from the use of conventional ion-selective electrodes and is known as the 'electronic tongue', was developed.

The electronic tongue is an analytical instrument that comprises a set (array) of chemical sensors of relatively low selectivity, being simultaneously sensitive to several components in the analysed solution (cross-sensitivity), and employs a suitable method for the processing of multidimensional data from the array of sensors (*e.g*., the methods of pattern recognition and multivariate calibration). A system that uses sensors with reproducible analytic response and employs, if necessary, an adequate calibration procedure (calibration as such, training) is capable of the recognition (identification, classification) of various liquid media and the multicomponent quantitative analysis of inorganic and organic constituents.

2. Requirements to sensors for electronic tongue-type systems

It is evident that the array of sensors forms the key part of the electronic tongue. Sensors with relatively low selectivity or cross-sensitivity rather than highly selective sensors are most promising candidates for these systems.[18–20] Reproducibility of their characteristics is the necessary condition. Thus, an electronic tongue requires sensors with reproducible analytical characteristics and high cross-sensitivity. Although the term 'cross-sensitivity' is generally accepted for describing the properties of sensors in the literature devoted to multisensor systems, to date we have no its unambiguous definition. Quite a number of terms to describe the same phenomenon are used as synonyms (*e.g.*, non-selectivity, cross-reactivity, low selectivity, partial selectivity and even global selectivity). Hereinafter, we will use the term 'cross-sensitivity'.

At present, there is no generally accepted method for the assessment of cross-sensitivity. The use of the selectivity coefficient [Eqn (1)] or its reciprocal value seems to be a poor choice, because it contains no information on the sensitivity itself and its value strongly depends on the determination procedure (there is no standard method). When determining the selectivity coefficient, it is assumed that the response of a sensor to both primary and interfering ions corresponds to the theoretically calculated value, which is rarely the case. Moreover, the selectivity coefficient is by definition a value that characterises a binary system (which consists of one primary and one interfering ion), whereas for the case of a complex solution that contains several interfering ions, the question of the primary ion remains open and the selectivity coefficient value is far from real.

The authors of this review have put forward [24] an empirical method for assessing the cross-sensitivity. For this purpose, the following three parameters were used: the average slope, the reproducibility factor and the non-selectivity factor, which describe the sensitivity and reproducibility of a sensor's response and also its selectivity with respect to the studied ions. These parameters were originally determined for sensors with chalcogenide glass membranes with respect to a group of transition metal cations.[24] Later, the proposed approach was applied for assessing the cross-sensitivity of other sensor materials (*e.g.*, polymeric) with respect to other groups of ions.[25]

The calculation of the parameters mentioned above involves the use of experimental data obtained in calibration measurements in a solution of a selected set of substances (ions) using the previously determined sensor materials the cross-sensitivity of which is to be studied. Even the most 'non-selective' sensor materials are sensitive only to a certain group of substances rather than to all ions in the solution.

The first and most important parameter of the cross-sensitivity is the average slope (S), which is determined in individual solutions of a selected set of substances as follows:

$$S = \frac{1}{n}\sum_i S_i,$$

where S_i is the slope of the sensor electrode response in calibration solutions that contain individual substances, with respect to which the cross-sensitivity of the sensor is studied, n is the number of substances studied. Thus, this parameter represents the averaged sensitivity of a sensor material toward a certain group of substances (ions).

The second parameter is the stability factor (K), which represents the signal-to-noise ratio for the sensor material averaged over all studied substances

$$K = \frac{1}{n}\sum_i K_i = \frac{1}{n}\sum_i \frac{S_i}{s_i^2},$$

where S_i is the slope of the sensor electrode response in solutions of chosen substances, s_i is the standard deviation of the electrode response in solutions of chosen substances. Apparently, the standard deviation is calculated in parallel measurements and characterises the reproducibility of the electrode characteristics of the sensor material in the solutions under study.

The third parameter, *viz.*, the non-selectivity factor (F), characterises the uniformity of the distribution of sensitivity of a sensor material with respect to the set of substances chosen for studies

$$F = \frac{S}{s^2},$$

where S is the average slope, s is the standard deviation of the average slope, which is calculated based on the slopes of the electrode response in solutions of individual substances.

The larger is the average slope, the higher is sensitivity of a sensor to the studied set of substances. The optimum value of this parameter is estimated in each particular case. Assume that the cross-sensitivity of a sensor material with respect to a set of doubly charged ions is considered. It this case, the electrode response slope is most likely to vary from 0 (the absence of sensitivity) to 29 mV $(\mathrm{pX})^{-1}$ (a response corresponding to the Nernst equation). Thus, the average slope close to 29 mV $(\mathrm{pX})^{-1}$ suggests the equally high sensitivity with respect to all ions under study. In practice, the same sensitivity with respect to a wide set of ions is virtually unknown. Therefore, it can be assumed that sensor materials with an average slope > 25 mV $(\mathrm{pX})^{-1}$ exhibit high cross-sensitivity and may be included into the multisensor system for determination of this set of ions. However, in certain cases the average slope of a material sensitive with respect to a set of doubly charged ions can exceed 30 mV $(\mathrm{pX})^{-1}$, which is associated with the supersensitivity with respect to one or several ions. In this situation, to assess whether the sensor has cross-sensitivity, one has to consider the non-selectivity factor, which describes the uniformity of distribution of sensitivity over ions. A factor of non-selectivity below 0.1 is typical of highly selective sensors that exhibit high sensitivity to only one primary ion. The factor equal to 0.1 points to the sensitivity with respect to several ions among those studied. For the materials with relatively uniform sensitivity with respect to all ions, this value should exceed unity. As a rule, it is assumed that the non-selectivity factor of 0.5 and higher suggests the presence of cross-sensitivity of a given sensor material with respect to the studied set of ions. It is evident that both parameters, the average slope and the non-selectivity factor, should be taken into account in practice. Thus a sensor that exhibits equally low sensitivity with respect to all studied ions will have a high factor of non-selectivity but a low average slope.

The stability factor is used for assessing the reproducibility of electrode characteristics of sensor materials. Although it is measured in solutions of individual substances, it is evident that the reproducibility of electrode characteristics of sensor materials in these solutions correlates with their reproducibility in mixed solutions containing these substances. The higher the stability factor the higher the reproducibility. It is shown that sensors with the stability factor $\geqslant 2$ can be used in a multisensor system.[24,25]

This set of parameters is representative and suitable, although other sets exist.

Summarising, it is essential to note that within the framework of the proposed approach no *a priori* assumptions are drawn on the mechanism of the response of sensors; therefore, this approach can be applied for assessing the cross-sensitivity of not only potentiometric sensors but also chemical sensors of other types.

3. Sensors used in the electronic tongue systems

Systems of the electronic tongue type can comprise any chemical sensors for analysing liquids regardless of what physical principle they are based on.

The 'taste sensor' was the first multisensor system analogous to the electronic tongue.[26] It included eight potentiometric sensors with the so-called lipid membranes [2,27,28] that exhibited cross-sensitivity with respect to substances of different tastes. The membranes had a polymeric (PVC) matrix. Thin-film sensors were also manufactured, with the aim of miniaturisation, by applying Langmuir–Blodgett films on semiconducting supports, based on the same sensor materials but using a different principle

of signal detection. Different authors used field effect transistors,[29] light-addressable potentiometric sensors (LAPS) and sensors based on the method of surface photovoltage (SPV)[30,31] as the sensitive elements (transducers).

An electronic tongue based on arrays of various potentiometric sensors including inorganic membranes was developed;[32] its measuring circuit and photograph are shown in Figs 1 and 2. It is the authors of this study who, together with their Italian colleagues from the University Tor Vergata (Rome), were the first to propose the term 'electronic tongue' as applied to cross-sensitive sensors in combination with the data processing based on pattern recognition methods.[33] The sensors were fabricated using a wide assortment of membrane materials, which included chalcogenide glass doped with different metals, plasticised polymers containing various active substances and also polycrystalline compositions.[1,24,25,32] Several hundred different sensors were studied, from which the compositions with the highest cross-sensitivity were selected. As a rule, an electronic tongue comprises from 5 to 30 sensors depending on the analytical problem. Microsensors based on thin nanofilms of chalcogenide glasses were prepared using pulsed laser deposition (PLD).[34] The composition and properties of the film materials and systems differed little from those of the parent chalcogenide glasses.

A flow-injection version of the electronic tongue system with multisensor detection was developed, which included from 3 to 11 sensors.[35] The possibility of performing repeated measurements including those in the automatic mode (due to the multichannel actuator) and the small sample volume (as a rule, 150 – 500 μl, which can be decreased to 50 μl) are among the advantages of flow-injection multisensor systems.

It was proposed to use electronic tongues built of potentiometric sensors the preparation of which involved the application of metalloporphyrins with different central atoms [Mn(III), Fe(III), Co(II), Ni(II)], and also tetraphenylporphyrin onto glassy carbon supports by means of the electropolymerisation technique.[36] An electronic tongue based on already existing and commercially available ISE was produced.[37,38]

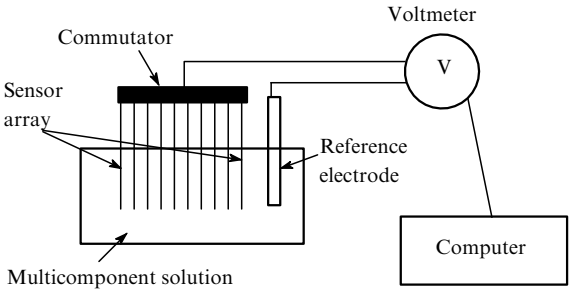


Figure 1. The measuring circuit of an electronic tongue based on potentiometric chemical sensors.[32]

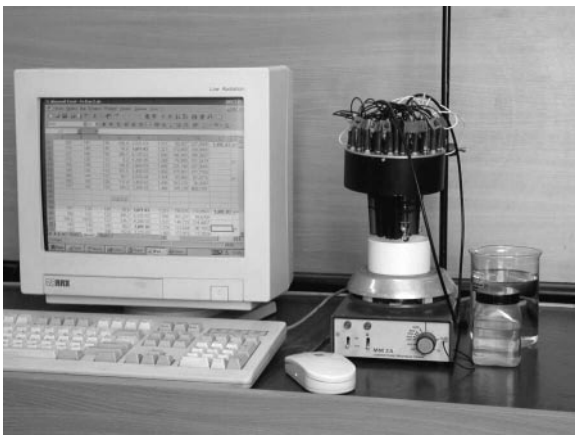


Figure 2. A photograph of a laboratory prototype of the electronic tongue based of potentiometric chemical sensors.[32]

The measurements using arrays of potentiometric sensors are by and large similar to those using individual ISE. In both cases, the emf of electrochemical cells formed by sensors of the array taken in turn and the reference electrode is measured. In these measurements, multichannel voltmeters with high input impedance ($\geqslant 10^{12}$ Ω) are used. As a rule, a computer controls the measurements and data recording.

In addition to potentiometry, it was proposed to use voltammetry in multisensor systems,[3,39–41] which is also based on a similar combination of measurements of non-specific electrochemical signals and their processing by pattern recognition methods. The polarographic wave becomes a non-selective analytical signal in those cases where several solution components are oxidised at the same or similar potentials. To resolve such a signal and retrieve certain analytical information, one has to use several working electrodes rather than one electrode, as in the classical scheme. Noble metals (platinum, gold, iridium, rhodium, rhenium) are used as the working electrodes.

A multisensor system based on electrodes modified with monophthalocyanine complexes of cobalt and copper, bis(phthalocyanine) complexes of europium, gadolinium, and lutecium and octakis(*tert*-butyl)-substituted bis(phthalocyanine) complex of praseodymium is described.[42] The modified electrodes were prepared either by applying Langmuir – Blodgett films on glass supports or with the use of the graphite paste electrode technology (by mixing 15 vol.% phthalocyanine with a graphite paste). Measurements with such voltammetric multisensor systems are carried out using a classical three-electrode circuit, which contains a reference electrode, a steel counter electrode, an array of working electrodes and a commutator for switching from one electrode to another. Large amplitude pulse voltammetry (LAPV) was chosen for the measurements with an array of electrodes made of noble metals. The potential was scanned in the range from -0.4 to $+0.6$ V with 100-mV steps.[3] Cyclic voltammetry with a scanning rate of 0.1 V s^{-1} was used[42] in the measurements with an array of modified electrodes.

An electronic tongue design was proposed that mimicked the biological prototype despite being based on optical sensors.[43] Sensors that mimicked taste receptors consisted of grains of poly(ethylene glycol) – polystyrene resin (PEG-PS) with various indicator molecules. The latter represented fluorescein, *o*-cresolphthalein complexone, alizarin complexone and resorufin-substituted galactoside boronate. The response of sensors was measured with respect to a control sensor, which represented a grain of a resin with acetylated terminal amino groups. The grains were located in microcavities fabricated by the micromachining technology in silicon/silicon nitride plates, which mimicked the arrangement of taste buds on the tongue. The changes in the light absorption by the grains in different solutions were detected using CCD (Charge-coupled Devices). The study was aimed at merely demonstrating the possibilities; therefore, the analytical applications of this tongue are yet unknown.

Different conducting polymers such as polyaniline, polypyrrolle, stearic acid and their mixtures are used in the preparation of sensors for electronic tongues.[44,45] Langmuir – Blodgett polymeric films are applied on metal supports. Measurements are carried out using the method of impedance spectroscopy at room temperature (20±3) °C in a frequency range from 20 to 10^5 Hz. The use of impedance spectroscopy is based on the fact that the low frequency range of such a spectrum describes the properties of the electrical double layer formed as a result of adsorption of substances from the analysed solution on the surface of a sensor.

Obviously, the possible sensor materials and detection methods are not limited to the versions mentioned above, and one can expect the appearance of reports on the use of other types of sensors.

4. Data processing

Although chemical sensors form the most important part of the multisensor system, the adequate methods of data processing also play an important role. The response of a cross-sensitive sensor in a multicomponent solution is complex and contains information on different components present in the medium. To gain this information, it is necessary to analyse the overall response of all sensors in the system. Under these conditions, the correct choice of the method of data processing and its application are of great importance. Different approaches including the methods of pattern recognition and multivariate calibration are used.

The choice of a particular method for the data processing depends on both the analytical problem and the parameters of sensitivity of sensors, *i.e.*, the non-linearity of the response, the degree of correlation between the responses of different sensors in the array, *etc*. The following three main problems are known in the data processing: the studies on the data structure and recognition; the classification and identification; the quantitative analysis (determination of concentrations of substances or other quantitative parameters).

The first stage of data processing always involves the data recognition and the studies on their structure, which allows one to initially assess the reproducibility and detect outliers, to visually study the data structure, detect data clusters, *etc*. For these purposes, the methods of unsupervised learning such as the principal component analysis and certain kinds of artificial neural networks are used.

The problems of classification and quantitative analysis are solved, as a rule, by the methods of supervised learning. For classification, such methods as (Soft Independent Modeling of Class Analogy) SIMCA, linear discrimination analysis, multidimensional regressions and artificial neural networks are used. In those cases where *a priori* information on the studied samples is absent, the classification can be accomplished by the methods of unsupervised learning. To obtain calibration curves for the determination of concentrations of solution components, multivariate calibrations are used, the most popular of which involve principal components regression and partial least squares as well as artificial neural networks. The detailed descriptions of the main methods of chemometrics, which are used to process the results of measurements with multisensor systems, are available in the literature.[46–48]

5. Advantages of sensor systems over individual sensors

Even the first studies devoted to the use of sensor arrays have demonstrated that the use of chemometrics for processing the response of sensors makes it possible to compensate to a certain extent the insufficient selectivity of ISE and quantitatively determine the activities of ions in multicomponent solutions. Subsequent experimental data implied that sensors with moderate selectivities or cross-sensitivities should be preferred for constructing the arrays.[19] Such arrays allow one to carry out quantitative measurements with smaller errors as compared with arrays including only highly selective sensors. Thus, there appears a possibility for extending the range of analysable substances or solution components.

In addition to the compensation of insufficient selectivity of sensors, the arrays of sensors with cross-sensitivity in relatively simple solutions make it possible to reduce the detection limit (with respect to concentration) by an order of magnitude.[49] In solutions of complex composition, this effect can even be more pronounced.

Yet another practically important feature of arrays of sensors is the possibility of carrying out potentiometric measurements without recourse to the reference electrode. In this case, the potential differences between all the pairs of sensors in the array are measured.[50] Evidently, some of potential differences obtained in this way will be excessive and should be rejected in the course of data processing. The analytical characteristics of the electronic tongue are shown to be independent of the reference electrode during the measurements.

The capability of systems of the electronic tongue type to recognise and identify multicomponent solutions in almost the same way as people do is very promising. In the literature, this is usually referred to as the fingerprint technique. Such an analysis is totally untypical of not only ion-selective electrodes but also all other conventional analytical methods. As a result, a multisensor system may produce an integral estimate, a chemical pattern of the analysed liquid, *i.e.*, its 'fingerprint'. This pattern either coincides or differs for different analysed liquids. This allows a conclusion to be drawn on their identity or difference. What is most unusual is that the electronic tongue can recognise liquids of unknown composition without any preliminary information on the qualitative or quantitative composition of samples. Apparently, the classification and identification by means of an electronic tongue require preliminary calibration of the instrument with respect to a series of known samples. This is a new and promising approach to the analysis of the quality of many foodstuffs and determination of its compliance with a chosen quality standard.

The ability of multisensor systems to recognise and quantitatively assess tastes is their most unusual property, which is the reason for their title 'electronic tongue'. The system is calibrated (trained) over a series of standard solutions or food samples, which have been characterised by professional tasters as regards the taste type and intensity. If a system can detect the key substances and the features that determine the taste, then, after such a training, the electronic tongue acquires the capability to analyse unknown food samples, producing the type and intensity of their taste as the result. The demand for the determination of taste by means of an analytical tool is the highest in the food and drug industries, which probably represents one of the most interesting practical applications of electronic tongues in future.

III. Certain analytical applications of multisensor systems of the electronic tongue type

To date, a great number of studies devoted to various applications of the electronic tongue multisensor systems are documented.[1, 32, 51] Many of them describe how to recognise different foodstuffs, determine the quality of one and the same foodstuff, confirm their correspondence to the quality standard and their authenticity and reveal counterfeit products. Currently, great attention is paid to the use of electronic tongues for monitoring industrial processes and the quality control, which involves the determination of concentrations of key components and the assessment of the correspondence of the overall quality of a process or a foodstuff to the standard. The taste of foodstuffs is assessed. For calibration of the system, the taste estimates made by professional tasters are used.

Electronic tongues are used most often in the analysis of foodstuffs. The performance of systems for the analysis of fruit juices,[3, 31, 52, 53] mineral water,[54–56] soft drinks,[56] coffee,[56, 57] tea,[58–60] milk and dairy products,[3, 39, 61, 62] wine,[55, 63, 64] miso (Japanese soy paste),[65] sake,[66, 67] vegetable oils,[68] fruit,[69] vegetables,[70] meat,[71] fish [56] is described. As a rule, the electronic tongue was used for recognition and classification of listed foodstuffs, less often, for their quantitative analysis. For instance, the use of the electronic tongue for recognition of different coffee brands was described.[56] Figure 3 shows the results of recognition for eight individual brands of coffee and three commercial mixtures. Data were processed by the Principal Component Analysis (PCA). As is seen, all the samples differ from one another except for samples 2 and 6, which represent one and the same coffee sample. This sample strongly differs from the rest samples in both the results of the analysis using the electronic tongue and its taste and scent.

The response of an electronic tongue towards the dilution of fruit juice with water or sugar solution was studied.[54] This problem was topical due to the appearance of faked foodstuffs obtained by excessive dilution of fruit juices with water, sugar

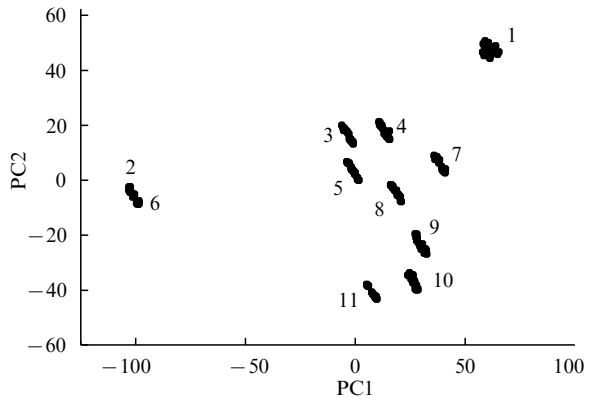


Figure 3. Results of measurements with an electronic tongue for eight individual brands of coffee (samples 1–8) and three commercial mixtures (sample 9–11). Data were processed using the principal component analysis.[56]
PC1 and PC2 are the first and the second principal components.

solution, or similar solutions. Figure 4 shows the results of measurements with a multisensor system for two samples of orange juice (freshly squeezed and prepared from a concentrate). The data were processed using the principal component analysis technique. The points in the upper part of the plot correspond to pure juice, those in the bottom part correspond to diluted juice. It was found that the multisensor system allows determination of just 1% water added to orange juice.

The use of the electronic tongue for the determination of concentrations of inorganic cations and anions, organic acid anions, amino acids, polyphenols, and also such parameters as the total and titratable acidity [55, 56, 64] and the number of bacteria in spoilt milk [39] is described. The electronic tongue can be used for the monitoring and determination of concentrations of key components in biotechnological processes for the synthesis of such substances as enzymes used in the production of cheese,[72] miso [65] and sake.[67] To evaluate this method in assessing the taste, solutions of substances with typical tastes were tested both separately and in mixtures with different foodstuffs and drugs. As a rule, several parameters were assessed in the taste, which were important for a given foodstuff, for example, the flavour, acidity,

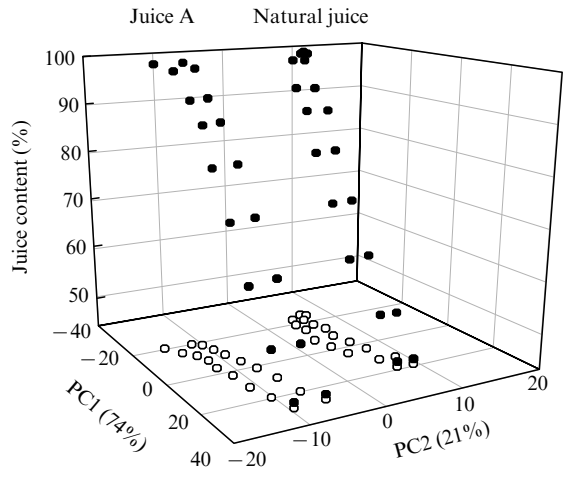


Figure 4. Monitoring of the dilution of orange juice with water carried out using a multisensor system.
The results of measurements with the electronic tongue for two orange juice samples: prepared from concentrate (juice A) and freshly squeezed (natural). Data were processed by the principal component analysis.[53]
PC1 and PC2 are the first and the second principal components. Open circles represent projections of the experimental points on a plane.

and texture of coffee,[56] the taste richness and the baked-milk flavour in milk,[62] 'dietness' (the difference between regular and light versions of beverages) of Pepsi-Cola,[56] *etc*. The main problem in the assessment of the taste of drugs was to measure the bitterness intensity in active substances and effectively mask it by different sweeteners and flavourings.[73–75] An electronic tongue (e.t.) based on potentiometric chemical sensors was used for the determination of taste characteristics of eight brands of coffee (Table 1).[56] The calibration was carried out using organoleptic estimates of the flavour and scent of coffee, which were made by professional tasters and provided by the manufacturing company. Four parameters were assessed on a ten-point scale. The calibration model was calculated using a neural network with back propagation of errors. A part of samples were used for calibration, the other samples were used in the tests. Table 1 shows the organoleptic estimates made by tasters and the values obtained by applying the calibration model to the control samples. All the cases demonstrate good agreement. The possibility of drawing correlations between the response of an analytical tool and human perception can be of great practical importance.

Table 1. Organoleptic tests of coffee made by tasters and calculated by applying the calibration model to the test samples.

Parameter	Method of estimate	Sample			
		5	6	7	8
Flavour	e.t.	4.8±0.2	7.8±0.1	3.1±0.3	4.1±0.4
	tasters	3–7	7–9	1–2	2–4
Acidity	e.t.	4.8±0.1	3.6±0.3	5.7±0.3	5.4±0.3
	tasters	5–8	2–5	5–8	5–8
Body	e.t.	7.0±0.1	8.5±0.01	8.4±0.1	6.0±0.1
	tasters	5–9	8–9	8–9	5–7
Smell	e.t.	5.3±0.2	8.4±0.01	3.8±0.3	4.7±0.3
	tasters	4–7	8–9	2–3	3–5

The application field of the electronic tongue is not limited to foodstuffs. Multisensor systems were used for the monitoring and determination of the principal components in the growth media used for growing microorganisms,[76] for recognition of various growth media,[77] for monitoring of cleaning of drinking water,[78] for determination of the contents of inorganic anions and transition-metal cations in model ground, mine and sea water,[24, 25, 79–83] and also in the smoke from incineration plants (after the absorption of smoke by a liquid);[35] for the quantitative analysis of the dialysis solutions used in the devices such as 'artificial kidney',[84] *etc*. The use of electronic tongues for simultaneous determination of iron and uranium in different oxidation states in model mine water is described.[81, 82] The need for such tests is associated with the control over the composition of water in deserted uranium mines in order to undertake timely measures on the radiation safety. Uranium in different oxidation states exhibits different solubility and, hence, the different ability to migrate under natural conditions. This is why the determination of the contents of uranium(VI) and uranium(IV) and also of iron(II) and iron(III), which accompany uranium, is among the most important problems in the analysis of mine water. Table 2 shows the results obtained by means of an electronic tongue. The possibility of simultaneous determination of the contents of iron and uranium in different oxidation states was also demonstrated.

The idea of simultaneously using liquid and gas sensors for the analysis of foodstuffs was born in analogy to the fact that people simultaneously assess tastes and smells. The sensitivity and selectivity of sensors used in electronic noses and tongues substantially differ from the characteristics of biological receptors; therefore, the role of artificial sensory systems and their contribu-

Table 2. Results of determination of the contents of iron and uranium in different oxidation states in solutions that model mine water (the results shown correspond to test solutions only).

The form of the element	Found /mol litre^{-1}	Added /mol litre^{-1}	Standard deviation
U(IV)	2.5×10^{-5}	3.0×10^{-5}	2×10^{-6}
	5.0×10^{-5}	5.4×10^{-5}	4×10^{-6}
	2.5×10^{-5}	2.7×10^{-5}	3×10^{-6}
	5.0×10^{-5}	5.0×10^{-5}	1×10^{-6}
	2.5×10^{-5}	2.9×10^{-5}	1×10^{-6}
	5.0×10^{-5}	5.5×10^{-5}	2×10^{-6}
	7.5×10^{-5}	6.4×10^{-5}	2×10^{-6}
U(VI)	5.0×10^{-5}	4.4×10^{-5}	7×10^{-6}
	7.5×10^{-5}	7.3×10^{-5}	7×10^{-6}
	1.0×10^{-4}	8×10^{-5}	1×10^{-5}
	5.0×10^{-5}	5×10^{-5}	1×10^{-5}
	7.5×10^{-5}	7×10^{-5}	1×10^{-5}
	1.0×10^{-4}	9.9×10^{-5}	3×10^{-6}
	2.5×10^{-5}	3.6×10^{-5}	3×10^{-6}
	5.0×10^{-5}	4.4×10^{-5}	3×10^{-6}
	7.5×10^{-5}	8.3×10^{-5}	7×10^{-6}
	1.0×10^{-4}	1.04×10^{-4}	8×10^{-6}
Fe(III)	1.0×10^{-5}	1.6×10^{-5}	3×10^{-6}
	3.0×10^{-5}	3×10^{-5}	1×10^{-5}
	5.0×10^{-5}	5×10^{-5}	2×10^{-5}
	1.0×10^{-5}	6.5×10^{-6}	2×10^{-6}
	3.0×10^{-5}	2×10^{-5}	2×10^{-5}
	5.0×10^{-5}	3×10^{-5}	3×10^{-5}
Fe(II)	1.0×10^{-5}	1.1×10^{-5}	2×10^{-6}
	3.0×10^{-5}	1.4×10^{-5}	4×10^{-6}
	5.0×10^{-5}	2.6×10^{-5}	4×10^{-6}
	1.0×10^{-5}	1.5×10^{-5}	1×10^{-6}
	3.0×10^{-5}	3.5×10^{-5}	6×10^{-6}
	5.0×10^{-5}	5×10^{-5}	2×10^{-5}

tions to the final result can differ from those of their natural prototypes. Nonetheless, the hybrid systems 'electronic nose + electronic tongue' were used in recognition of wines,[63] fruit juices,[41] milk and even urine samples.[61] The idea of using hybrid systems looks interesting, although to date it demonstrated no real advantages over the use of electronic tongue alone.

IV. Conclusion

Multisensor systems of the electronic tongue type represent a rapidly developing and promising interdisciplinary scientific field. At present, there is a possibility of using such systems for the quantitative analysis, quality control, recognition and classification in the food and pharmaceutical industries, medicine and also for environmental control. The existence of a correlation between the response of an electronic tongue and the human perception of taste is both unusual and promising from the viewpoint of practice. Today, the first commercial systems of the electronic tongue type are available.

Unfortunately, the knowledge in this young scientific direction is still largely empiric. The use of only limited number of sensor materials is a significant drawback of multisensor systems. In many cases, only a single type of sensors is used. For example, in certain studies only metalloporphyrins[36] or phthalocyanine complexes[42] or some other substances are used as the active components of sensor membranes. Naturally, the differences in the electrode characteristics of sensors containing homologues as the active substances are not great, and, in effect, such a multisensor system can be used for determination of only a limited group of substances and shows no serious promise for its extending. Consequently, the development of new sensor compositions and materials gains in importance. It is also necessary to extend the range of substances detectable by electronic tongues. For example, there are numerous problems on the determination of organic substances in mixtures. Without solving these problems, the extension of the application fields of this method and its further development are impossible.

Insufficient attention is also paid to studying the mechanism of the response of sensor materials used in multisensor systems. As a rule, the studies devoted to sensors are descriptive and empirical. The in-depth, more fundamental knowledge of the mechanism of the sensor response is the second prerequisite for the development of new compositions and the extension of the range of detectable substances.

An important task yet insufficiently reflected in the literature is the development of the objective criteria of the formation of a multisensor system to solve a given analytical problem. In particular, no methods exist which would allow one to *a priori* determine how many sensors and what sensor characteristics are required for the analysis of a given mixture of substances. At present, two major approaches to the formation of multisensor systems are distinguished. It is possible to take a redundant set of sensors sensitive to the analysed substances and then, in the stage of data processing, select those sensors that provide the greatest body of information, *i.e.*, exhibit the highest sensitivity with respect to the analytes and good reproducibility. Here, the requirement for the wide initial set of sensors is the key problem. Another approach consists of the use of a standard set of sensors. The weight of information provided by them is also assessed in the stage of data processing. It is evident that this approach is not always the optimum one.

Insofar as the electronic tongue represents an analytical tool, a question arises on its complex application. Despite the appearance of the first commercial instruments, most analytical results obtained with the electronic-tongue multisensor systems merely demonstrate their potentials rather than their practical analytical applications. There is the demand for the thorough development of the methodical grounds, in particular, aimed at providing the reproducibility of the responses of sensors, on the methods of calibration, conditioning and washing of sensors, *etc*.

Summarising, note once again that serious efforts should be undertaken in the studies of the mechanism of the sensor response to different analysed substances, in the development of new sensor compositions and also in the elaboration of methods for practical application of electronic tongues to solving particular problems. It is probable that rapid progress will be observed in this field in the near future.

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