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Tasting of beverages using an electronic tongue

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Abstract

An electronic tongue based on the sensor array of non-specific solution sensors together with pattern recognition tools has been applied to qualitative analysis of different beverages. It has been found that it is capable both to discriminate reliably between various sorts of the same type of beverages (tea, coffee, beer, soft drinks, juice, etc.) and to monitor the process of aging of juice. Correlations have been found between integral parameters produced by electronic tongue and quality of juice. Some conceptions and backgrounds used for electronic tongue development have been put forward and discussed. © 1997 Elsevier Science S.A.

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1. Introduction

The determination of quality of food stuffs, water and beverages and control of their correspondence to standards is an urgent problem. Usually, such studies are carried out with the help of sample preparation and rather complex and expensive laboratory analytical tools: various chromatographs, spectrometers, etc. These types of analysis may be finally profound and reliable but the necessary procedures can hardly be done rapidly and, moreover, on-site or on-line. Also, for quality control it is necessary to monitor the evolution of a group of certain components that reflect the process of ageing and spoilage of a food product. These components can be numerous or unknown and the problem appears to be quite difficult. Besides, it is very hard to compare the results of instrumental analysis to biological sensing.

One of the promising directions of development of different analytical methods, including chemical sensors, is the use of multicomponent measurements with the following extraction of information from the complex signal with the help of advanced mathematical methods. Electronic noses, the devices constructed according to the principles of the human olfactory system, based on sensor arrays with the following application of pattern recognition tools, are widely declared now for gas analysis [1]. They appeared to be capable of distinguishing between very complex and rather similar gas mixtures, such as odors of some foodstuffs and beverages [2,3], sometimes containing up to several hundreds components [4].

It is possible to come across at least two types of problems considering application of electronic noses to beverage analysis. The first ones are the difficulties related to the object of analysis, i.e. to complex liquid. Gas analysis in this case is a kind of indirect method that gives the final information about liquid phase via direct measurements of volatile components in gas. Moreover, one can easily imaging some matrix effects: for example, for mineral water the most readily evaporating component is water itself, for strong alcoholic beverages it would be presumably a combination of ethanol with water, for coffee—a complex mixture of organic compounds, about one third or one forth part of which is acetone, etc. When the problem is to distinguish between different liquids then it can be solved successfully in many cases due to significant differences in matrixes of main components. However, there is too little evidence that gas phase composition is always perceptibly dependent on the evolution of the

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liquid phase composition. A priori, one has no clear reasons to assume that all changes taking place in liquid, especially slowly, are reflected adequately by the detectable changes in the gas phase and, hence by an electronic nose output.

The second group of questions is related to sensing devices. There are several classes of gas sensing materials widely applied in arrays—solid-state compounds, conducting organic polymers, etc. Sometimes their stability and chemical durability are not sufficient and the problems of drift and parameters time dependencies are commonly urgent for gas sensors. Response time of a typical polymer gas sensor is not less than 60 s. Thus, it can be difficult to trace some processes in the gas phase, especially considering fast diffusion and chemical reaction rate. One can mention also rather vague mechanism of response reversibility and time-consuming recovering procedures for a number of gas sensors.

Multicomponent analysis can be done in complex liquids also [5]. The first attempts showed some perspectives but until the last few years they were neither developed into clear research directions nor applied for beverage control. However, recently researchers came closely to analysis of complex liquids and beverages using chemical sensor arrays.

Sensor array based on rather unusual materials—lipid membranes together with principal component analysis—have been used in [6,7] to distinguish between different kinds of mineral water, coffee, beer and also rice and tomatoes. The device is called the 'taste sensor' as far as attention is paid to qualitative analysis only and correlations between device output and human taste sense are considered.

Over 2 years ago the authors of the present paper joined their efforts in developing and evaluating of a set of devices based on a wide range of potentiometric chemical sensors and advanced mathematical methods of complex signal processing, including pattern recognition with the help of artificial neural networks [8]. Such a system mimics significantly organization (but not actual appearance!) of human taste sense and, also using analogies with electronic nose, can be called a prototype of electronic tongue. Earlier, it was applied successfully for quantitative and qualitative analysis of model complex solutions [9] and natural water [10].

One of the most promising fields of application of such instruments is an express on-site control of quality of complex products such as beverages and foodstuffs.

The present paper is devoted to analytical evaluation of the St. Petersburg–Rome electronic tongue capable of distinguishing between different sorts of the same type of beverages—tea, coffee, juices, soft drinks, beer, and to monitor the quality of fruit juices during storage and ageing.

2. Experimental

Two types of experiments have been carried out using an electronic tongue. At the first stage, system capability to distinguish between different types of beverages and between different sorts of beverages of the same type has been considered. The following objects have been studied: (1) four sorts of tea—two black ones, one flavored black and one green; (2) two sorts of instant coffee and two sorts of natural one; (3) three types of soft drinks—Coca-Cola, Pepsi-Cola and Sprite; (4) mineral water; (5) several kinds of orange and grape fruit juices; 6) four typical sorts of beer—light, classic, dark and porter. Juices, beers and soft drinks have been measured without any sample treatment during the first day after opening. One gram each of tea and coffee have been taken and extracted with 200 ml of distilled water. After filtration (except instant coffee) solutions were cooled to the room temperature and measured directly. The time of extraction of 5 min has been taken for coffee and 5, 30 and 60 min for tea.

At the second stage the evaluation of electronic tongue for quality monitoring of fruit juice has been carried out. Two sets of measurements have been taken. In the first set, two identical packages of grape juice were opened simultaneously and measured every hour during the first 4 h. For 2 weeks, one vessel has been stored in refrigerator and the other one at room temperature. Measurements have been taken two times a day to observe the differences in aging and spoilage processes. To consider some features of the juice evolution more in detail the second set of measurements has been performed. The first measurements were taken every hour for 5 h after opening and later 6 times a day for a week. The juice has been stored in a refrigerator.

Sensor arrays included two types of potentiometric sensors: (1) conventional ones, for example, chloride-, sodium-, potassium-selective sensors and pH sensor both on the basis of solid-state and plasticized organic membranes; (2) specially designed non-specific sensors with enhanced cross-sensitivities, estimated according to the method developed in St. Petersburg University [11]. The latter sensors have been based mainly on chalcogenide vitreous materials, which were not used widely, however, as ion-selective sensors, for example $AgI–Ag_2S–As_2S_3$.

In total, 18–21 sensors have been incorporated into sensor arrays. The certain array composition evolved during experiments, when some separate sensors appeared to be not enough stable or cross-sensitive. The details of sensor preparation can be found elsewhere [12].

Solid-state sensors have been stored in air between measurements while PVC membranes have been dipped into solutions of primary ions. To make potential values more standard, reproducible and comparable all sensors have been treated periodically by conditioner solution. The sensors have been washed with water before measurements to the constant potential, then the array have been exposed to analyzed solution. After short stirring repeated reading have been registered, usually with a 5-min interval. Technically, all measurements have been performed as conventional direct potentiometry.

Multicomponent data processing has been performed using principal component analysis and different kinds of artificial neural networks: back-propagation one and self-organizing map (Kohonen network).

3. Results

A number of complex beverages has been analyzed using multisensor systems. Some typical results are given below.

Four different sorts of beer from a famous bottling plant have been taken. Sensor array response in beer is shown in Fig. 1. Absolute potential values are normalized but the differences in sensor outputs are actual values. From 3 to 5 measurements have been performed with each sort of beer to evaluate and to ensure necessary reproducibility.

The behavior of a sensor array in different soft drinks is shown in Fig. 2. Potential values for Pepsi are taken as zero and deviations of sensor readings in Coke and Sprite are given. Different samples of Coca-Cola from different plants in various countries have been taken for measurements. Some discrepancies between them were supposed to be within the limits of experimental errors.

Sensor array response in all complex liquids appeared to be reproducible and stable enough to produce adequate integral information about analyzed media. Following daily reproducibility of potential values for different sensors has been observed: sodium sensor ± 2 mV, chloride sensor ± 1 mV, chalcogenide vitreous sensors ± 2– ± 5 mV depending on glass composition. Sometimes potential has been drifting, but mostly bi-directional deviations from an average value have been found. The most stable sensor array output has been observed in soft drinks. Potential stability in beers, coffees and juices is close to that in soft drinks. The most complicated sensor array behavior has been found during tea analysis.

Stability and long-term durability of sensor array output have been always sufficient enough to produce valuable information about analyzed complex liquid. After sensor array measurements data processing has been the following essential step.

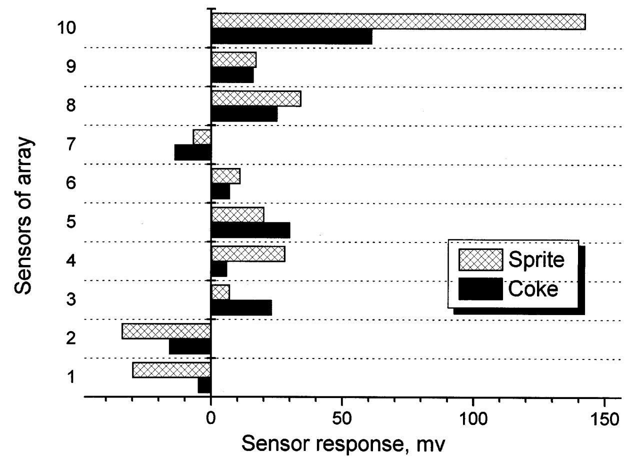

Fig. 2. A diagram of sensor array response, displaying the deviations between different branches of soft drinks. Pepsi readings are taken as zero.

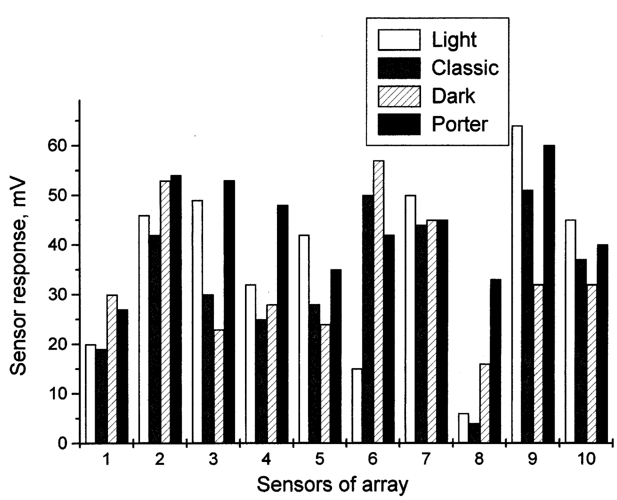

Fig. 1. Sensor array response in different sorts of beer. Average values for 3–5 sensor measurements are shown.

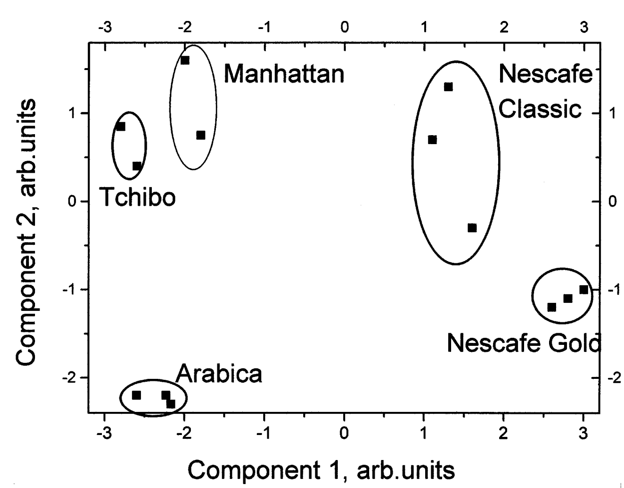

Fig. 3. PCA plot of different branches of natural and instant (Nescafe) coffee analyzed by electronic tongue.

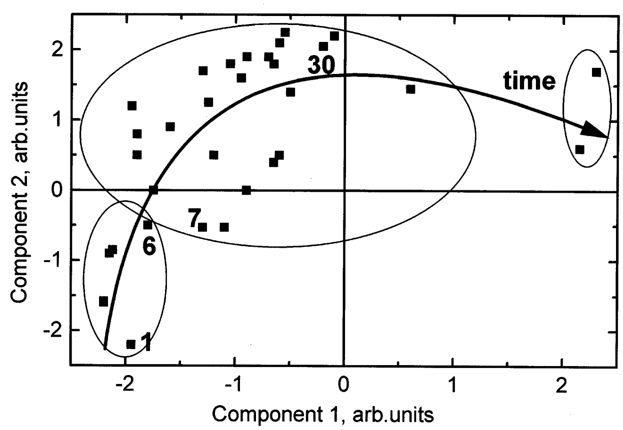

Fig. 4. The evolution with time of orange juice quality estimated by electronic tongue. Storage time in hours for some data points is commented in the text.

Fig. 3 presents the principal component analysis (PCA) plot discriminating different sorts of coffee, five types of which have been chosen. PCA enables to visualize the information produced by a 21-sensor array in a two-dimensional space. A good separation is observed between all types of natural coffee and two sorts of instant one (Nescafe) in spite of relatively small number of measurements (3–5 for each sample). On the other hand, there is no overlapping among different sorts within the same branch of coffee. It appeared possible to distinguish between Nescafe coffee prepared with the help of different technology: 'freeze dry' for Gold and 'spray dry' for Classic.

Principal component analysis together with SOM application has been performed for all measured beverages. Fine discriminating abilities of electronic tongue have been found.

The second part of the present work has been designed as an attempt to monitor quality evolution of fruit juices. In a preliminary experiment it was found that during the first 4 h after opening rapid evolution of grape juice occurs, which is observed distinctly using PCA. These data sets were clearly separated from the others. The following conclusion have been made: (1) the developed electronic tongue is able to trace evolution of an organic mixture such as a fruit juice; (2) the system appeared to be able to distinguish between different ambient condition of storage—room temperature and refrigerator, lower temperature decelerating spoilage.

After that, a detailed study has been performed. PCA plot displaying the results of orange juice analysis is shown in Fig. 4. A dependence of sensor array data on juice storage time can be observed. One can divide the whole plot in three parts.

During the first 5 h after package opening (measurements 1–6), data points are rather distant from each other. It can be evidence of rapid evolution of juice chemical composition in the starting period of storage.

The second data range (measurements 7–30, 25–122 h) is less evolving, thus indicating slow variations of juice integral composition. At the end of this period of about 5 days, juice should be near supposed limit of acceptable quality.

The last points are taken at the 7th day when the juice was surely spoiled. These points are quite distant from the others.

After performing of principal component analysis the data set has been divided in two groups. One of them (19 points) has been used for calibration of a neural network and the second group (13 points) as the test set. Estimated time values have been the aim network analysis. Fig. 5 shows the correlation between estimated and actual time of juice storage. The straight line corresponds to theoretical dependence while the points represent experimentally obtained values. The most of points are close to the line, demonstrating good reliability of sensor array analysis despite the limited number of calibration data.

Thus, the two series of experiments with juices revealed to be in a good agreement and displaying juice evolution features. The most rapid changes have been observed in the first 4–5 h after package opening, then a period of relative stability as long as 5 days in refrigerator has been observed. It was followed by juice spoilage also discriminated by electronic tongue. The period of 3 days for juice consumption recommended by manufacturers is surely within the limits of stability of the product and is estimated with some extra stock of reliability.

Of course, these experiments should be widened in future, however the first results are encouraging and observed correlations are likely to be reasonable.

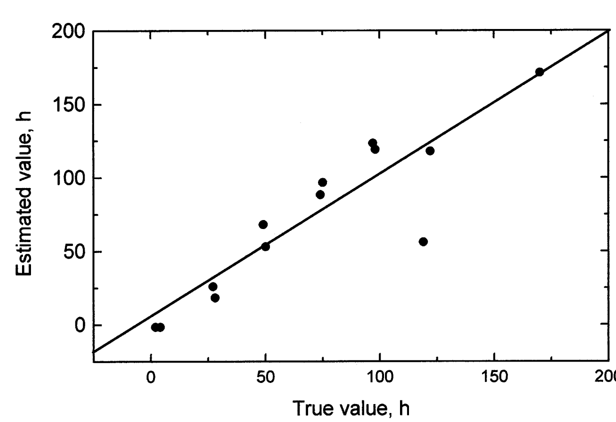

Fig. 5. Simulation of juice aging data with the help of artificial neural network.

4. Discussion

Along with promising results given above, it may be reasonable to present our point of view on the problems related to the electronic tongue in a wider aspect.

We can define an electronic tongue as an analytical instrument that includes an array of non-selective chemical sensors with partial specificity to different solution components and an appropriate pattern recognition tool, capable to determine quantitative and qualitative composition of simple and complex solutions.

Actually, such a system is based on the same organisation backgrounds as the taste system of human beings and is potentially capable for what can be called 'artificial tasting'. Special studies are surely necessary in this direction. At present time, however, using the word 'tasting' we are neither supposing to mimic closely the human tasting sense nor the real physical and chemical tasting systems of living beings. The problem to be solved in the present project, including this work, is to develop an electronic tongue displaying sensitivity, discriminating abilities, reproducibility and chemical durability as high as possible. It is reasonable to suppose that the final device should be able not only to substitute biological tongue in some obvious fields such as foodstuff quality, but to enhance significantly human sensing abilities by increasing the range of analysed media, including dangerous and non-eatable objects. Moreover, human sensing system is a unique and universal one. Electronic tongue can be produced in a wide number of more specialised versions, closely adapted to certain tasks.

Thus, as far as we are trying to mimic primarily structural principles of the sensing systems, the present work, devoted to beverage tasting and earlier reported ones dealing with multicomponent heavy metal analysis [9–11], must be considered as complementary parts of the same approach. Identical principles are used for different actual devices, their sensor array systems being significantly overlapping also.

Furthermore, the development of electronic tongue and sensor arrays for it has been done using the supposition that chemical sensitivity mechanism of separate sensors, even in complex solutions, is relatively simple and is finally based on ion, redox and functional group recognition. Some molecular processes at the sensor surface can also add to it. Considering overall sensor signal, however, it is normal that different additives from various sensing mechanisms are observed. And it is highly desirable for sensors of the array to display enhanced cross-sensitivity. Therefore, chemical sensors used for sensor arrays has been prepared using the most well-known and promising classes of solution sensing materials. This choice allows to get highest available sensitivity to certain species and significant chemical durability and signal stability of sensors. Also, on the basis of previous profound knowledge of dependencies of their sensing performance on composition it is possible to obtain a wide range of original non-specific sensing materials with high cross-sensitivities in multicomponent liquids. The study and array application of new sensing materials are an important part of the present work.

From the general point of view, various types of chemical sensors can be used for sensor arrays. However, applying new classes of sensing compositions, especially in complex media, one can face very common difficulties. For example, chemical sensitivity mechanism of lipid membranes used for taste sensors [6,7] can be simply interpreted in traditional terms of cation and anion response. Such response can be definitely produced by a number of conventional materials. On the other hand, the problems of reversibility, response stability and lifetime can appear quite serious for lipid membranes.

Anyway, the development of new solution sensing materials, especially for organic compounds, with reasonable durability and understandable and reproducible sensing mechanism is an urgent research problem.

The essential feature of our approach is the closest interrelation between application of appropriate sensor array and advanced complex signal processing by various available methods, especially by artificial neural networks. It is data processing that allows to get final information, either quantitative or qualitative, about complex systems and only harmonic combination of sensor array and pattern recognition tool makes the whole device performing as electronic tongue. Moreover, deep and profound data analysis gives the possibility to make new conclusions about sensing mechanism and behaviour features of various sensors and sensor arrays. At present time, the mechanism of reproducible sensitivity of some sensors in complex media, such as beer or fruit juice, containing a lot of organic components, is not clear. Further research in this direction is highly desirable.

One more item to discuss is as follows. Commonly, while discussing artificial olfaction [13], it is declared that it should give rather qualitative but not quantitative results, just like the corresponding human sense. While tasting, a human being can easily discriminate between quantitative differences in saltiness, bitterness or sweetness. But the results are still visualised in a qualitative way by the statement of more or less strong or weak taste. For an artificial sensing instrument, it is more natural to produce direct quantitative information about content of certain components regulating taste features. Therefore, the capability to determine quantitative characteristics and component content is likely to be an essential property of an electronic tongue and one of it doubtless advantages.

5. Conclusions

An electronic tongue has been applied to qualitative analysis of different beverages. The device is based on the sensor array of non-specific solution sensors combined with pattern recognition tools. A number of well-known classes of sensing materials have been used to produce potentiometric sensors included into array. Principal component analysis and artificial neural networks were applied for pattern recognition. It has been found that an electronic tongue is capable both of discriminating reliably between various sorts of the same type of beverages (tea, coffee, beer, soft drinks, juice, etc.) and to monitor the process of aging of juice. Correlations have been found between integral parameters produced by an electronic tongue and quality of juice. Some conceptions used for electronic tongue development and its applications for beverage analysis have been discussed.

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Biographies

Yu.G. Vlasov is the head of the Laboratory of Chemical Sensors and Solid Electrolytes and of the Radiochemistry Department at St. Petersburg University. He is a member of the editorial boards of Sensors and Actuators, Selective Electrode Reviews, the Journal of Applied Chemistry (Russia) and the Journal of Analytical Chemistry (Russia). He received his PhD degree from Leningrad University in 1964, and his DSc degree in 1986. Since 1987 he has been a professor of Leningrad University. He is also the Full Member of Russian Academy of Natural Sciences. His major research interests include the development of different solid-state chemical sensors for liquid media, their fundamental investigation and various applications.

A.V. Legin, senior research scientist at St. Petersburg University, received his PhD degree in 1985. His major research interests include the development of chalcogenide glass chemical sensors, investigation of bulk transport properties, ion-exchange processes and sensing mechanism of solid-state sensors and also the development of principles of analytical appliation of various sensors, including sensor arrays in liquids and electronic tongue.

A.M. Rudnitskaya is a final year post-graduate at the Chemistry Department of St. Petersburg University. She is doing research and preparing her PhD thesis in the field of analytical application of different types of chemical sensors, especially the development of multisensor arrays for liquid media and electronic tongue.