

Classification of beverages using a reduced sensor array

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Abstract

An electronic tongue based on the sensor array of ion-selective electrodes (ISEs) combined with pattern recognition tools is applied to qualitative analysis of mineral waters and apple juices. The procedure of reducing of total number of the sensors in the array is described. Before and after reducing of number of the sensors, this device is capable of reliable discrimination between different brands of mineral waters and apple juices.

Validation of this method is also confirmed using artificial neural networks as a classifier. The ability to recognize different brands of waters and juices after reduction of number of the sensors in the array is comparable to the ability to recognize the same samples by the system before reduction of number of the sensors.

This method enables to specify quantitatively the capability of a sensor to discriminate between different classes of samples and can be used for any electronic tongues and noses applications.

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1. Introduction

The use of multicomponent measurements together with pattern recognition tools for an extraction of information from sensor array responses is a new direction of qualitative analysis of complex liquid and gaseous media. Biological inspiration of smell and taste senses let scientists to build devices that can find wide applications in the field of medicine, environment monitoring, and foodstuff industry. It all started in 1982 from the work of Persaud and Dodd [1]. The term “electronic nose” became widely recognized in the late 1980’s and since then many sensing strategies were involved: metal oxide semiconductor [2], quartz crystal microbalance [3], conducting polymer [4] and surface acoustic wave sensors [5]. The sensor arrays were used together with various pattern recognition methods, such as Principal components analysis (PCA), back-propagation neural networks, learning vector quantization, cluster analysis, Kohonen network and more [6]. Some of these systems are now commercially available [7].

In 1985, first system for liquid analysis based on multisenor array was presented by Otto and Thomas [8].

Since then a few devices of this type, called “electronic tongue”, have been presented. A multichannel electrode with lipid–polymer membranes, known as “taste sensor”, was used for the classification of beers, coffee, tea and other foodstuffs [9,10]. This device was also able to differentiate between different amino acids, according to their taste [11] and to estimate some physical constants of analyzed compounds [12].

To classify mineral waters, wine and coffee, an array of non-selective potentiometric sensors based on chalcogenide glass membranes was used [13,14]. Also in this case, not only qualitative analysis was applied—estimation of alcohol and other organic substances concentration in wine samples [14,15] and metal concentration in artificially polluted water was possible [16].

To discriminate between different brands of orange and apple juices system based on voltammetry was used [17]. It was also applicable in monitoring of cleaning process of water in water plant [18].

Electronic tongues and noses usually consist of few-tens sensors. A method of reducing of number of the sensors in an array has not been discussed so far. After reducing, sensor array should perform specific task with the same or better capability to discriminate between different classes of samples. Quantitative specification of discrimination capability of the array before and after reducing of number of

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Table 1
Solutions and components used for electrodes preparation

An electrode number	An electrode type	Plasticizer	Liphophilic salt	Ionophore	Internal filling/conditioning solution
1, 2	Cl ⁻	<i>o</i> -NPOE	0.08 wt.% TDMAC	1 wt.% TPPCIMn	0.01/0.001 M NaCl
3, 4	F ⁻	<i>o</i> -NPOE	0.18 wt.% TDAB	1.5 wt.% uranyl salophene	0.01/0.001 M NaCl
5, 6	NO ₃ ⁻	<i>o</i> -NPOE	–	3.5 wt.% TDMAC	0.01/0.001 M NaCl
7, 8	HCO ₃ ⁻	DOS	0.15 wt.% TDMAC	1 wt.% ETH 6010	0.1 M NaH ₂ PO ₄ , 0.1 M Na ₂ HPO ₄ , 0.01 NaCl/0.01 M NaH ₂ PO ₄ , 0.01 M Na ₂ HPO ₄ , 0.001 M NaCl
9, 10	K ⁺	<i>o</i> -NPOE	0.4 wt.% KTFPB	1 wt.% valinomycin	0.01/0.001 M KCl
11, 12	Na ⁺	<i>o</i> -NPOE	0.15 wt.% KTPCIPB	1 wt.% ionophore X	0.01/0.001 M NaCl
13, 14	NH ₄ ⁺	BBPA	1 wt.% KTPCIPB	2 wt.% nonactine	0.01/0.001 M NH ₄ Cl
15, 16	Ca ²⁺	DOS	0.8 wt.% KTPCIPB	2 wt.% ETH 129	0.01/0.001 M CaCl ₂

the sensors is indispensable to perform further classification procedures.

The aim of this paper is to describe a procedure of reduction of number of the sensors in an array and to verify this method in the classification of water and juice samples.

2. Experimental

Redistilled water and chemicals of analytical-reagent grade were used for all experiments. Membrane components were supplied by Fluka Chemie AG (Buchs, Switzerland): TPPCIMn (chloride ionophore I, *meso*-tetraphenylporphyrin manganese(III)-chloride complex), ETH 6010 (carbonate ionophore I, heptyl 4-trifluoroacetylbenzoate), valinomycin (potassium ionophore I), ionophore X (sodium ionophore X, 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethyl ester), nonactin (ammonium ionophore I), ETH 129 (calcium ionophore II, *N,N,N',N'*-tetracyclohexyl-3-oxapentanediamide), TDMAC (tridodecylmethylammonium chloride), TDAB (tetrakis(decyl)ammonium bromide), KTFPB (potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), KTPCIPB (potassium tetrakis(4-chlorophenyl)borate), *o*-NPOE (2-nitrophenyl octyl ether), DOS (bis(2-ethylhexyl)sebacate), BBPA (bis(1-butylpentyl)adipate)). Fluoride ionophore—uranyl salophene derivative was synthesized in Laboratory of SMCT, MESA+ Research Institute, University of Twente [19].

The membranes for ion-selective electrodes (ISEs) preparation contained appropriate ionophores, 20–50 mol% versus ionophore lipophilic salt, 61 wt.% plasticizer, and 31–33 wt.% high-molecular-weight PVC (Fluka, Table 1). The method of the membranes preparation and the electrodes conditioning were the same as for standard ISEs. Compositions of internal filling and conditioning solutions are listed in Table 1. All the compounds used for preparing those solutions were supplied by Fluka. All electrodes were preconditioned at least 24 h.

Two electrodes (IS 561, Philips) for each membrane composition were prepared. One standard pH electrode

was also included (Mettler Toledo InLab 407 connected to pH-meter Mettler Delta 350), giving 17-sensor array. EMF measurements were carried out at room temperature using multiplexer (EMF 16 Interface, L-EMF DAQ 2.5 for Windows, Lawson Labs Inc., Malvern, USA) that allowed testing up to maximum 16 electrodes at the same time. All measurements were carried out with cells of the following type: Ag, AgCl; KCl 1 M/CH₃COOLi 1 M/sample solution//membrane//internal filling solution; AgCl, Ag.

To verify the performances of the sensors, potentiometric selectivity coefficients were determined using 10⁻¹ M buffered solutions of corresponding salts (Separate Solution Method). The solutions were buffered using 0.005 M MES (4-morpholineethanesulfonic acid monohydrate, Fluka). The final pH was adjusted with 0.1 M NaOH or 0.1 M H₂SO₄ solutions. Mean values of the selectivity coefficient for each two electrodes of the same type are presented in Table 2a (anion-selective electrodes) and Table 2b (cation-selective electrodes).

Table 2
Selectivity coefficients log $K_{(A,B)}$ for (a) anion- and (b) cation-selective electrodes

(a) Selectivity coefficients towards	An electrode type			
	Cl ⁻	F ⁻	NO ₃ ⁻	HCO ₃ ⁻
SO ₄ ⁻	-1.85	-0.76	-3.00	-1.10
Cl ⁻	0.20	0.57	-2.07	-1.12
Br ⁻	0.49	0.88	-1.18	-0.67
NO ₃ ⁻	0.00	0.00	0.00	0.00
H ₂ PO ₄ ⁻	-1.22	-0.22	-2.87	-0.67
F ⁻	-0.80	1.88	-2.58	-0.08
ClO ₄ ⁻	1.72	1.38	2.34	2.04
(b)	K ⁺	Na ⁺	NH ₄ ⁺	Ca ²⁺
K ⁺	0.00	-1.59	-0.52	-3.51
Na ⁺	-1.88	0.00	-1.67	-3.55
NH ₄ ⁺	-0.78	-2.35	0.00	-3.36
Ca ²⁺	-3.11	-2.92	-2.06	0.00
Li ⁺	-3.40	-2.81	-2.49	-1.45
Mg ²⁺	-3.75	-3.26	-3.00	-3.77

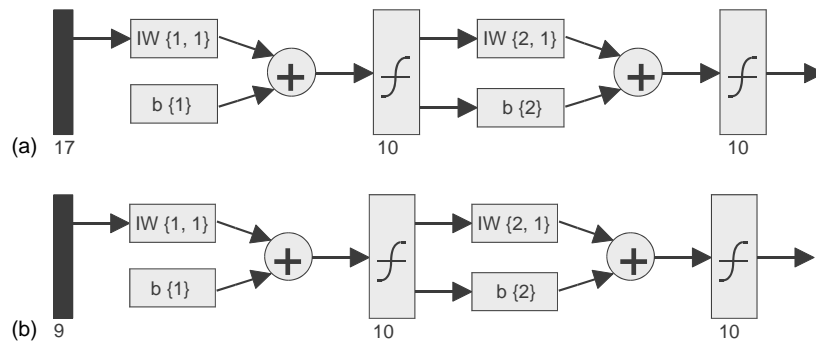


Fig. 1. Artificial neural network architecture in the case of: (a) 17-electrodes sensor array and (b) reduced, nine-electrodes sensor array.

All measurements of eight brands of mineral water, tap water, Oligocene water and 10 brands of apple juices were performed as conventional direct potentiometry, without any sample pretreatment. Sensor outputs were autoscaled to assure better performance of the following step, which was Principal components analysis.

Data obtained was processed by back-propagation neural network, consisted of three layers (17 or nine neurons in input layer, 10 in hidden layer and 10 in output layer, Fig. 1). The sigmoid transfer function and gradient descent algorithm to adjust weights and biases in the network (learning rate: 0.5, momentum coefficient: 0.8) were used. Network architecture arose from earlier work of Gardner et al. [20]. Details of training and performance of analysis can be found elsewhere [21]. Data processing was realized in Neural Network Toolbox working in MatLab environment (The MathWorks, Inc., Natick, USA).

3. Results and discussion

A sensor array generates data of high dimensionality, hard to handle and visualize. PCA is a linear feature-extraction technique, finding new directions in the pattern space, so that they explain the maximum amount of variance in the data set as possible. Usually the first two Principal Components (PC1 and PC2) are sufficient to transfer the majority of the variation of the samples.

Fig. 2 presents PCA plot discriminating different brands of waters (electrodes 1–16 and pH electrode were used). PC1 and PC2 together contain 60.6% of the variance of all data set. A good separation between all kinds of samples is observed. Similar discrimination capability in the case of apple juices is observed (Fig. 3, electrodes 1–16 and pH electrode were used), where PC1 and PC2 together contain 61.0% of the variance of the data set. To compare the ability of particular electrodes to distinguish between different classes of

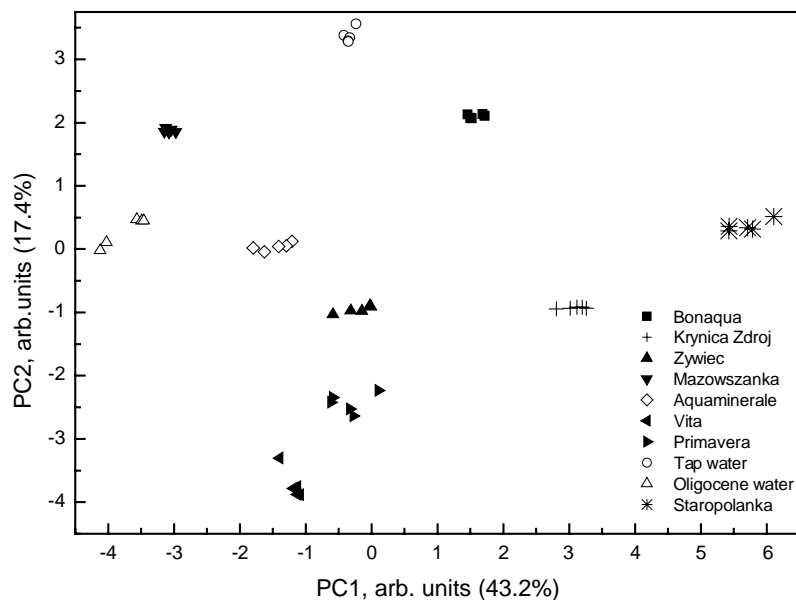


Fig. 2. PCA plot of different brands of mineral waters before reducing of number of the sensors in the sensor array.

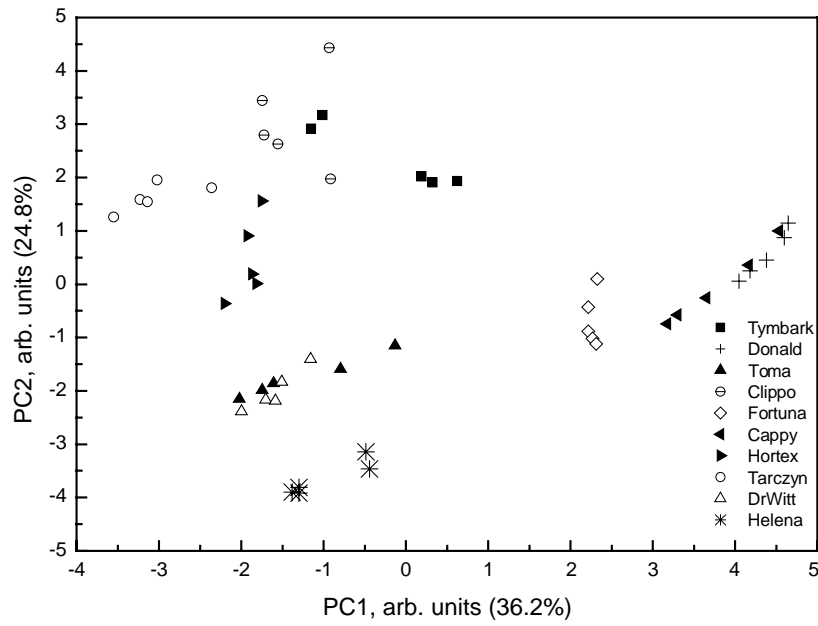


Fig. 3. PCA plot of different brands of apple juices before reducing of number of the sensors in the sensor array.

water and between different classes of apple juices, ratio of variances between classes and the sum of internal variance in all classes was calculated (so-called factor F) [22]:

$$F = \frac{\sum_{i=1}^k n_i (\bar{z}_i - \bar{z})^2}{k-1} \cdot \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} (z_{ji} - \bar{z}_i)^2}{\sum_{i=1}^k n_i - k}$$

where

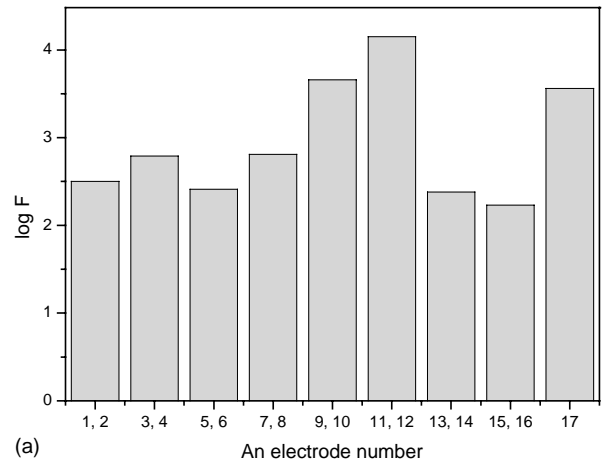
$$\bar{z}_i = \frac{\sum_{j=1}^{n_i} z_{ji}}{n_i}$$

is the mean value of sensor response in particular class of samples, k the number of classes, i the number of following class, j the following number of sample in i th class, z_{ji} the sensor response for j th sample in i th class, n_i the number of samples in i th class, and

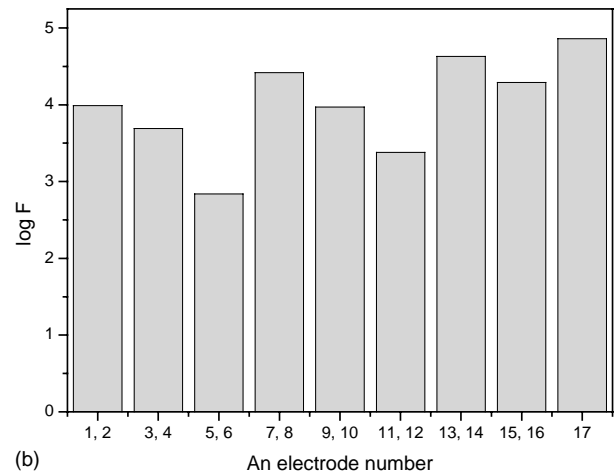
$$\bar{z} = \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} z_{ji}}{\sum_{i=1}^k n_i}$$

is the mean value of sensor response for all samples.

This factor is used as a standard procedure in analysis of variance for comparing precision of two independent ana-



(a)



(b)

Fig. 4. Plot of factor F values in the case of: (a) water and (b) juice samples.

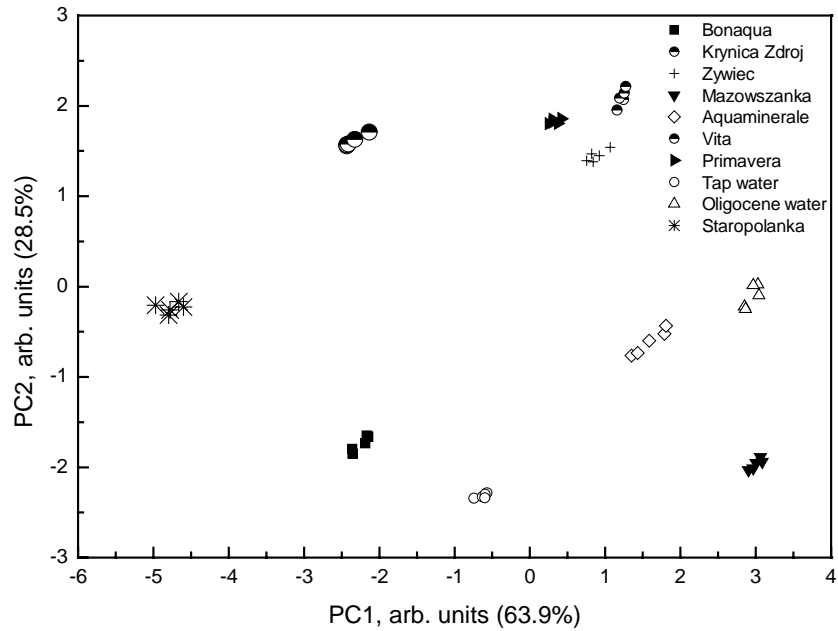


Fig. 5. PCA plot of different brands of mineral waters after reducing of number of the sensors in the sensor array.

lytical methods (statistics of Snedeckor), but it can also be used as a measure of capability of particular sensors to discriminate between different classes of samples in electronic nose and electronic tongue applications.

Mean values of factor *F* for each two electrodes of the same type was calculated and visualized in Fig. 4a in the case of water samples and in Fig. 4b in the case of juice samples. Electrodes displaying the highest values of *F* were chosen to create reduced sensor array (electrodes 3, 4, 7–12 and pH electrode for water samples, electrodes 1, 2, 7, 8,

13–16 and pH electrode for juice samples). Fig. 5 presents PCA plot for water samples of reduced, nine-electrode array. PC1 and PC2 together contain then 92.4% of the variance of all data set, which can be the result of reducing of the unsubstancial data and redundant information. Consequently the ability of PC1 and PC2 to discriminate between different brands of water is bigger. Factor *F* values before reducing was calculated as 8.8×10^2 for PC1 and 1.4×10^3 for PC2 compared to 2.5×10^3 and 2.0×10^3 , respectively, after reducing.

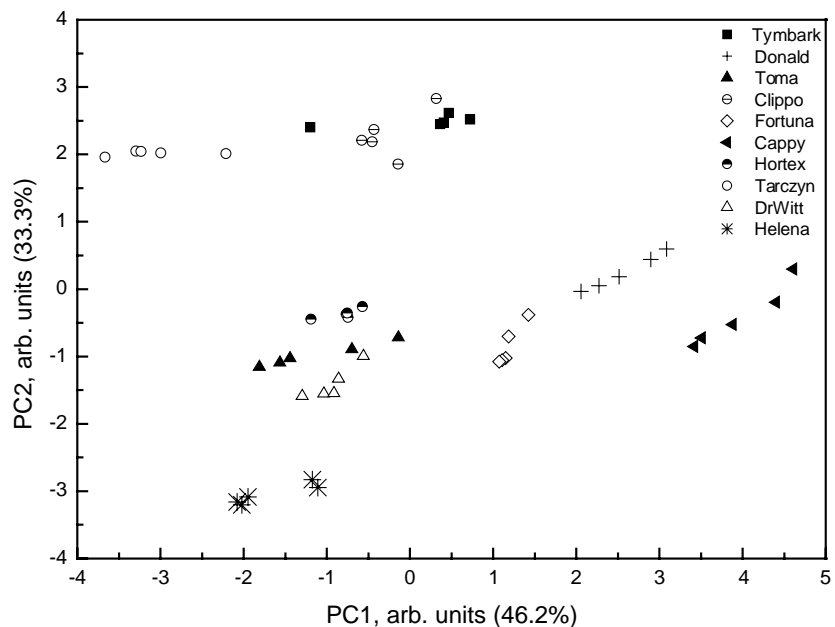


Fig. 6. PCA plot of different brands of apple juices after reducing of number of the sensors in the sensor array.

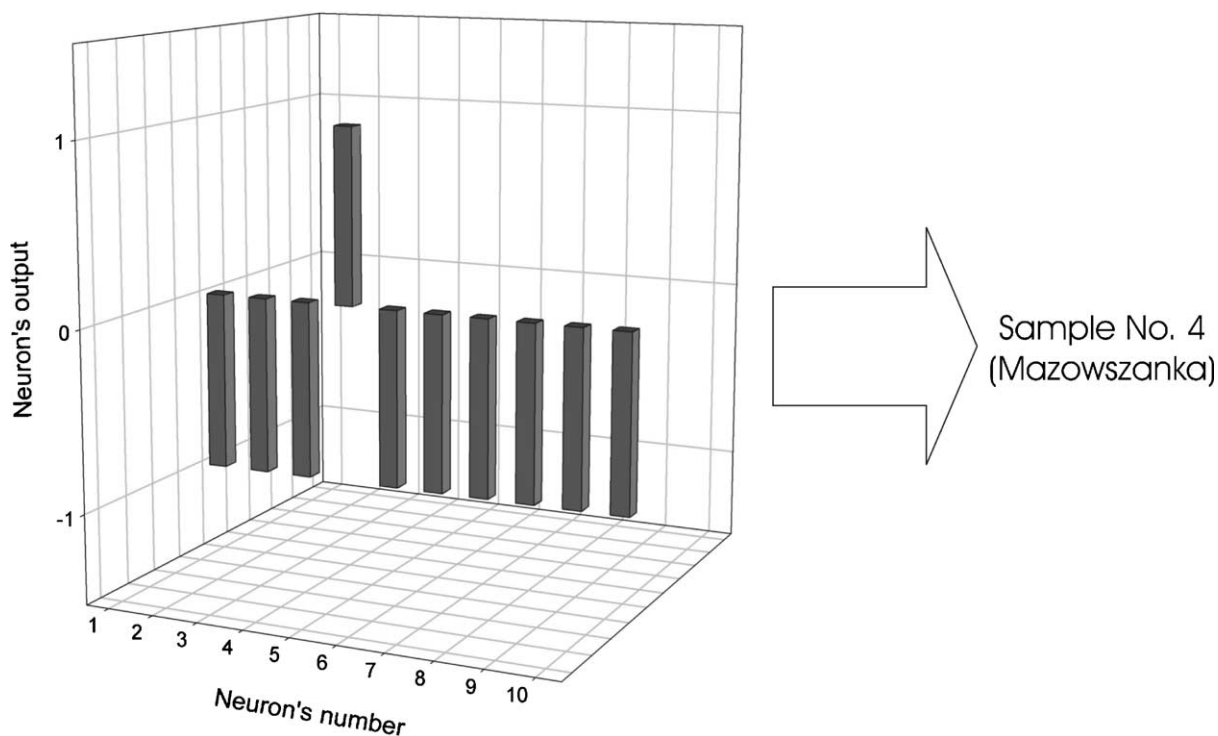


Fig. 7. Classification example of water sample using artificial neural network.

PCA plot for juice samples measured with reduced, nine-electrode array is presented in Fig. 6. In this case, PC1 and PC2 together contain 79.5% of the variance of the data set, compared to 61.0% before reduction of number of the sensors in the array. Consequently the ability of PC2 to discriminate between different brands of juices is much bigger. In the case of PC2 the value of factor F after reducing is almost four times bigger than before -2.6×10^2 compared to 6.6×10^1 obtained before reducing. The discrimination ability of PC1 becomes smaller (9.3×10^1), but it is still comparable to the value before reducing (1.3×10^2).

Validation of presented procedure of reducing of number of the sensors in sensor array was also realized using artificial neural network as a classifier. Network architectures for 17- and nine-electrode (reduced) sensor array are presented in Fig. 1a and b, respectively. Dataset obtained by measurements of water samples was divided in two parts—learning and testing set. Then both of them were autoscaled and processed using Principal components analysis. In this way, each sample was characterized by 17-dimension vector that made input for neural network. Each sample was also characterized by 10-dimension vector (target vector), which should appear at output of the net to properly classify the sample. Ten brands of water samples were used, so the simplest way of creating target vector was to put in order successive samples (1, Bonaqua; 2, Krynica Zdroj; 3, Zywiec; 4, Mazowszanka; 5, Aquamminerale; 6, Vita; 7, Primavera; 8, Tap water; 9, Oligocene water; 10, Staropolanka). Each of 10 outputs marked successive

number of the sample. If, for example, at fourth output +1 appeared and -1 at the rest of outputs, then it meant that the sample's number was four (the net classified the sample as Mazowszanka, Fig. 7). Process of learning involved adjusting value of weights and biases of each neuron ($IW \{1, 1\}$, $b \{1\}$, $LW \{2, 1\}$, $b \{2\}$, Fig. 1) according to the gradient descent algorithm. Process of learning was finished when the net was able to provide desired outputs corresponding to a determined input. Verification of the generalization capability of network was performed by means of testing set. The net could classify properly all the samples (Fig. 8).

In the case of juice samples, data was also divided in two parts—learning and testing set. Each sample was characterized by 17-dimension vector (result of autoscaling and PCA) and 10-dimension target vector. Samples were put in order in the following way: 1, Tymbark; 2, Donald; 3, Toma; 4, Clippo; 5, Fortuna; 6, Cappy; 7, Hortex; 8, Tarczyn; 9, Dr Witt; 10, Helena. After learning phase, testing set was processed by the net and appropriate result were achieved (Fig. 9).

The same network type characterized by the same parameters (learning algorithm, architecture of the net, learning rate and momentum constant) was used to process the data obtained by means of sensor array reduced to nine sensors. The only difference was the number of the neurons in the input layer—nine in spite of 17 (Fig. 1b). After the same sequence of operations, that is dividing dataset in two sets, autoscaling, PCA, learning of the nets, testing was performed. The classification of water samples is presented in Fig. 10.

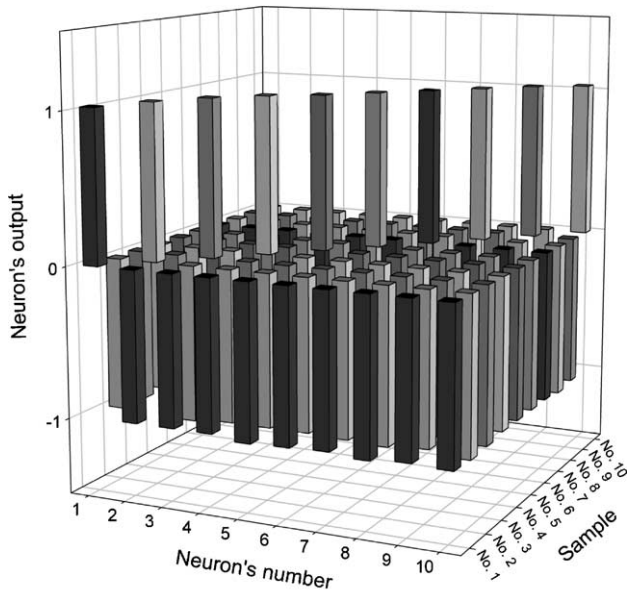


Fig. 8. Classification of water samples using 17-sensor array and artificial neural network.

In the case of eight brands of water results of network processing were almost the same as for model response. The response pattern for two water samples was enhanced. At fifth output in the case of Aquamminerale (Sample no. 5) and at ninth in the case of Oligocene water (Sample no. 9), values close to +3 in spite of +1 were obtained, but still the classification of these samples is clear and correct.

The capability of the network to recognize juices was similar as previously (Fig. 11). Results for nine juice samples were very close to the model response. Enhancing of output in the case of Toma (Juice no. 3)

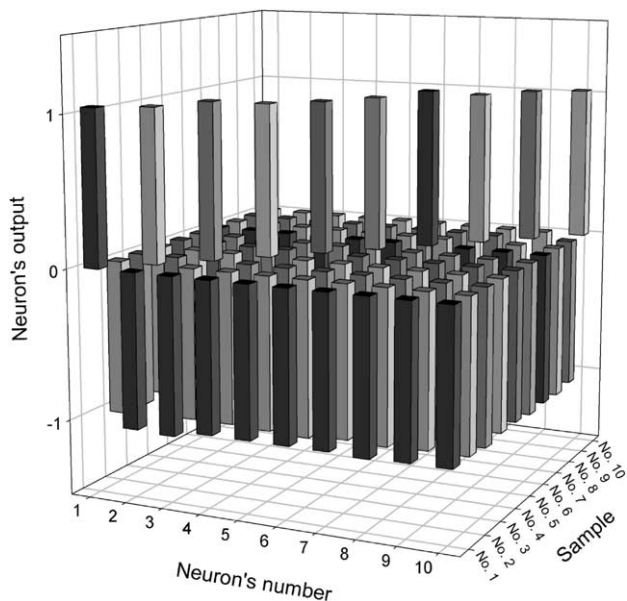


Fig. 9. Classification of juice samples using 17-sensor array and artificial neural network.

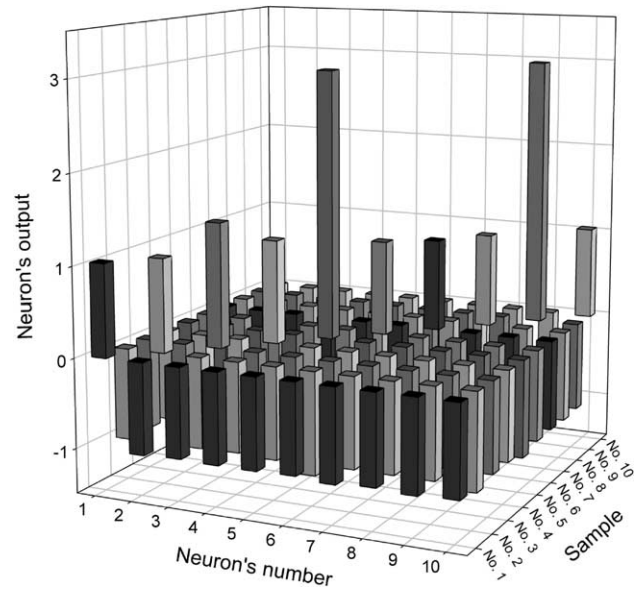


Fig. 10. Classification of water samples using reduced, nine-sensor array and artificial neural network.

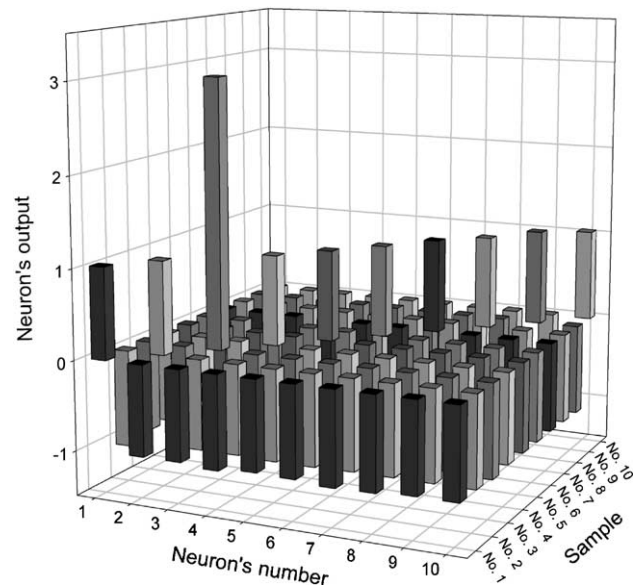


Fig. 11. Classification of juice samples using reduced, nine-sensor array and artificial neural network.

is observed, but the classification was also evident and appropriate.

4. Summary

This paper describes a procedure used to reduction of number of the sensors in an array. Ratio of variances between different classes of samples and the sum of internal variance in all classes—so-called factor F —lets to quantitatively specify the capability of a sensor to discriminate between different classes of samples.

Verification of the presented method gave satisfactory results. It was proved, that the choice of the most suitable sensors, characterized by the best discrimination capability, provides similar or even better discrimination of water and juice samples at PCA stage, which can be the result of reducing redundant and unsubstantial information. It was found, that classification performed by back-propagation neural network before and after reducing number of the sensors is comparable and provides satisfactory results.

The method presented in this paper could be used for any electronic tongues and noses applications.

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Biographies

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Wojciech Wróblewski received his PhD in analytical chemistry from the Warsaw University of Technology (WUT, Poland) in 1995, and his DSc degree in analytical chemistry from the Warsaw University of Technology in 2002. In 1992, he joined the Department of Analytical Chemistry (WUT) as an assistant professor. Since 2002 he has been associate professor at the Department of Analytical Chemistry (WUT). His current research interests are: ion recognition, ion-sensitive membrane, chemical sensors: electrochemical (ion-selective electrodes, solid-state electrodes, CHEMFETs) and optical (fibre optic chemical sensors), miniaturized chemical sensors, flow analytical systems with sensor detection.