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The recognition of beer with flow-through sensor array based on miniaturized solid-state electrodes

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Abstract

Flow-through electronic tongue based on miniaturized solid-state potentiometric sensors has been developed. A simple technique, i.e. membrane solution casting on the surface of the planar Au transducers was applied for the preparation of classical ion-selective and partially selective microelectrodes, introduced in the flow-through sensor array. The performance of the designed electronic tongue was tested in the qualitative analysis of various brands of beer. Samples of the same brand of beer but with different manufacture dates, originating from different manufacture lots, have been applied in the studies. The combination of PLS and ANN techniques allowed the discrimination between different brands of beer with 83% of correct classifications.

Keywords: Electronic tongue; Sensor array; Solid-state electrode; Flow-through analysis; Food classification

1. Introduction

Food quality, safety, and uniformity of products are emerging tasks in food industry. Characterization of complex samples in food industry is conducted with the application of various analytical techniques based mainly on efficient separation techniques, e.g. liquid chromatography coupled with spectroscopic detection systems. These techniques are time-consuming, expensive, and require specialized equipment and pre-treatment of sample. Chemical sensors can be used in modern analytical systems eliminating the necessity of a special sample preparation. Systems based on sensor arrays are especially powerful tools for the discrimination of characteristic properties of food samples, distinguishing among various types of them, and providing the recognition of their taste [1–5]. However, sophisticated chemometric methods are necessary to analyse the responses of the sensor array systems. Application of various pattern recognition tools, such as Artificial Neural Networks (ANN), Partial Least Squares (PLS), Soft Independent Modelling of Class Analogy (SIMCA), K-Nearest Neighbours (KNN) enables the analysis of measured data and the classification of multidimensional pattern spaces [6].

Brewery industry is a growing branch of foodstuff production. Nowadays, the consumption of the beer is growing at the cost of beverages with bigger alcohol content, such as wine. This is due to greater health consciousness and stricter law concerning driving and drinking. The characterization of beer flavour is complicated due to its complex composition and traditionally is performed with the combination of gas chromatography and organoleptic profiling panels or using HPLC methods [7]. These analytical procedures are usually expensive, time-consuming and demand the participation of specialized panellists. For these reasons there is a strong need for the development of fast methods and portable systems for product control and classification in brewery industry.

First attempts to construct sensor array systems for beer recognition were already presented. Pearce et al. [8] described the multisensor system (so-called electronic nose) based on 12 gas sensors, which could discriminate between various kinds of beer (Lager and Ale) according to their odour. High concentration of alcohol caused problems in such approach, so Heberle et al. proposed the combination of electronic nose with a pre-separation step, realized with gas chromatography column [9]. However, the analysis of the ionic and non-volatile

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components in the liquid phase is also important in the quality control of beer. Mineral components, which sources are cereals, hops, yeast, water can influence the brewering process and have nutritional importance [10,11]. Multielement characterization of beers, realized by inductively coupled plasma atomic emission spectrometry (ICP-AES) combined with pattern recognition tools was presented by Alcazar et al. [12]. They found that Mn, P, Mg and K elements were the most important variables for classification of 28 Lager beers and 4 dark beers.

The application of the system embracing ion-selective electrode arrays for the classification of various brands of mineral waters, fruit juices, and other foodstuffs was reported previously [1,3,6]. The development of the electronic tongue system for beer recognition should be based on sensor array approach, involving the ability to distinguish samples on the basis of their mineral content. Moreover, the introduction of the electronic tongue in continuous-flow systems would be especially favourable for automated sample monitoring in industrial control, leading to rapid and reliable results in real-time. However, only a few construction and performance of flow-through electronic tongue were presented in the literature [4,13].

In this work, miniaturized planar solid-state electrodes (SSEs) have been implemented in the flow-through sensor array. The designed flow-through electronic tongue, based on classical selective and partially selective microelectrodes, was applied to the recognition of brewery from which beer sample originated.

2. Experimental

2.1. Chemicals

All inorganic salts used were of analytical grade and were obtained from Fluka. The standard stock solutions (0.1 M) were prepared in redistilled water; working solutions were made by dilution of the stock solutions. The membrane components: 2-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis [3,5-bis (trifluoromethyl) phenyl] borate (KTFPB), bis (1-butylpentyl) adipate (BBPA), potassium tetrakis (4-chlorophenyl) borate (KTPClPB), ammonium ionophore I (nonactin), sodium ionophore X, 4-tert-butylcalix [4] arene-tetraacetic acid tetraethyl ester (ionophore X), potassium ionophore I (valinomycin), chloride ionophore I, meso-tetraphenylporphiryn manganese(III)-chloride complex (TPPClMn), bis (2-ethylhexyl)sebacate (DOS), tetrakis(decyl)ammonium bromide (TDAB) were purchased from Fluka. Fluoride ionophore and dihydrogen phosphate ionophore–uranyl salophene derivatives were synthesized in Laboratory of SMCT, MESA+ Research Institute, University of Twente (The Netherlands) [14]. Freshly distilled tetrahydrofuran (THF) from Fluka was used as a solvent for the membrane components.

2.2. Membrane composition

The membranes contained appropriate ionophores, 20–50 mol% versus ionophore lipophilic salt, 61 wt.% plasticizer, and 31–33 wt.% high-molecular-weight PVC. KTPClPB was used as lipophilic salt for the preparation of NH_4^+, Na^+/K^+ and Cl^--selective membranes, whereas TDAB was used in the case of $F^-/H_2PO_4^-$-selective membrane. *o*-NPOE was applied as plasticizer of Na^+/K^+, Cl^- and $F^-/H_2PO_4^-$-selective membranes and BBPA in NH_4^+-selective membrane. “Cation-selective” membrane contained only PVC, DOS as plasticizer and KTFPB as lipophilic salt. Following ionophores were applied: nonactine in NH_4^+-selective membrane, ionophore X and valinomycin in Na^+/K^+-selective membrane, TPPClMn in Cl^--selective membrane, and fluoride ionophore and dihydrogen phosphate ionophore in $F^-/H_2PO_4^-$-selective membrane. Details concerning membrane compositions and conditioning solution are listed in Table 1.

2.3. Electrode preparation

The membrane components (∼100 mg) were dissolved in 0.5 ml of freshly distilled THF. The resulting membrane solution (7 μl) was deposited on the surfaces of the back-side contact Au planar microelectrodes (5 mm × 5 mm), cleaned thoroughly with distilled water and methanol. The fabrication of the transducers based on a typical printed circuit board technology, used in this work, was previously described [15,16]. Two ion-selective electrodes were prepared for each membrane composition (Fig. 1a).

After the membrane solvent evaporation (24 h), the sensors were mounted in the flow-through cell (Fig. 1b) [17,18] and conditioned for 2 days in the conditioning solution (Table 1). Flow-through 10-sensor array was obtained, with 5 types of polymer membranes microelectrodes: selective (NH_4^+, Cl^-) and partially selective (Na^+/K^+, $F^-/H_2PO_4^-$, “cation-selective”). An additional, commercial pH-electrode (Mettler-Toledo) was also included in the measuring system.

2.4. EMF measurements

The potential of the microelectrodes, mounted in a flow-through cell, were measured in an automated measuring system

Table 1
Components used for electrodes preparation

	Electrode type	Plasticizer	Lipophilic salt	Ionophore	Conditioning solution
1.	NH_4^+	BPPA	1 wt.% KTPClPB	2 wt.% nonactine	10^{-3} M
2.	Na^+/K^+	*o*-NPOE	2.05 wt.% KTPClPB	3.5 wt.% ionophore X, 2 wt.% valinomycin	KCl,
3.	Cl^-	*o*-NPOE	0.07 wt.% KTPClPB	1 wt.% TPPClMn	10^{-3} M
4.	“Cation-selective”	DOS	1 wt.% KTPFPB	–	NaCl,
5.	$F^-/H_2PO_4^-$	*o*-NPOE	0.28 wt.% TDAB	1.5 wt.% ionophore $H_2PO_4^-$, 0.05 wt.% ionophore F^-	10^{-3} M
6.	pH	Glass electrode			NH_4Cl

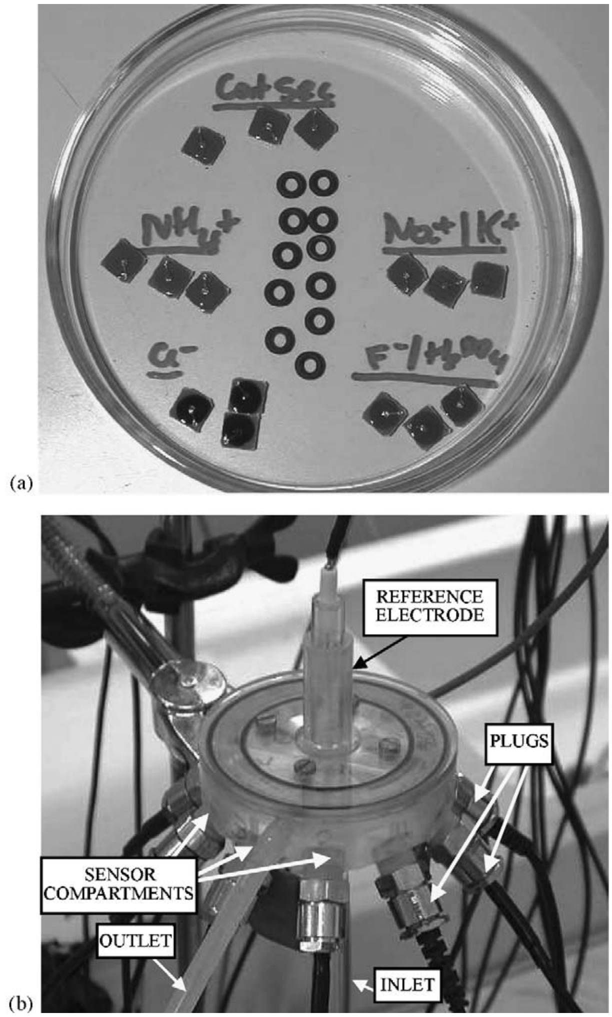

Fig. 1. (a) Solid-state polymer membranes microelectrodes; and (b) flow-through sensor head.

[19]. The system consisted of a peristaltic pump (Minipuls 3, Gilson), and a data acquisition PC-based system (with 16-channel amplifier: EMF-16, LawsonLab) with LabVIEW application (Fig. 2). A customized silver/silver chloride electrode, with a double junction containing 1 M CH_3COOLi, was used as a reference electrode. The measurements were carried out at 20 °C. The selectivity patterns of the microelectrodes were studied, and the values of the selectivity coefficients for each sensor were determined by the separate solution method (SSM), using 0.1 M solutions of inorganic salts. The activities of ions in aqueous solutions were calculated according to the Debye–Huckel approximation.

Mean values of potentials of electrodes of the same type were calculated for every measurement (i.e. every measurement was characterized by 6 features). They formed inputs for further data analysis, which was realized in MatLab environment (The MathWorks Inc., Natick, USA). ANN consisted of 6 neurons in the hidden layer and 5 in the output layer. The sigmoid transfer function and gradient descent algorithm were used to adjust weights and biases in the network (learning rate 0.5, momentum coefficient 0.8). Details of training and performance of analysis can be found elsewhere [20].

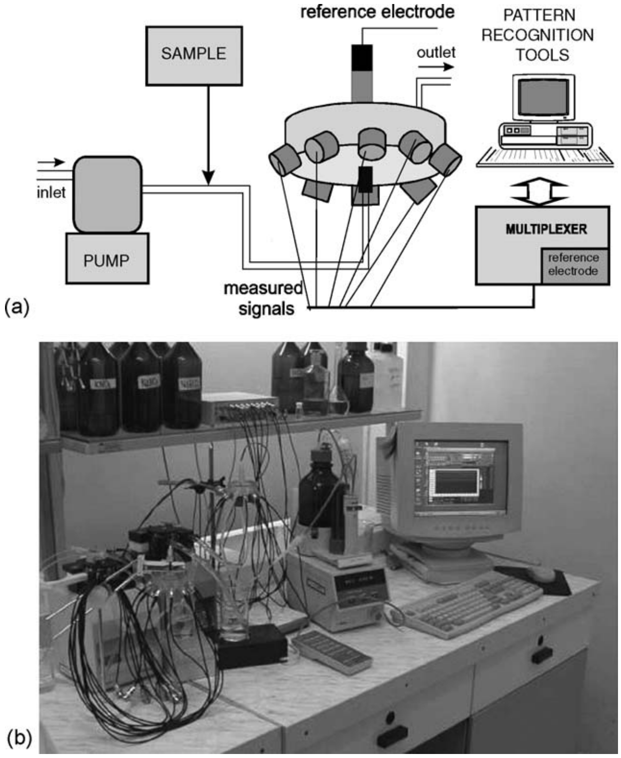

Fig. 2. (a) Scheme; and (b) photograph of the set-up for electronic tongue measurements.

2.5. Learn and test set

Ale beer originating from 5 Polish breweries: Tyskie (extract content 11.7 wt.%, alcohol content 5.7%, v/v), Tatra (extract content 12 wt.%, alcohol content 5.7%, v/v), Lech (extract content 11.1 wt.%, alcohol content 5.8%, v/v), Zywiec (extract content 12.5 wt.%, alcohol content 5.8%, v/v), Warka (extract content 12.5 wt.%, alcohol content 6.2%, v/v), were investigated with the flow-through electronic tongue system.

The results of the measurements were divided into 2 parts: the first one was used to create the patterns of the array responses (learn set), the second one to validate the correctness of the system work (test set). These sets differed in time of production and they originated from various manufacture lots. In this way, the reliability of the classification results was ensured and real working parameters of the system were evaluated.

Our previous studies showed [3] that the data base constructed of pattern vectors belonging to samples from only 2 manufacture lots is sufficient to achieve good performance of the recognition process of another lot's samples. In this work, this procedure of measurements was also applied. Each brand of beer samples originated from 3 manufacture lots. The database of "chemical image" benchmarks was constructed from data obtained by measuring 2 manufacture lots of each brand of beer. The samples from the third lot formed the test set. Six samples were collected from each lot. The role of the flow-through system coupled with pattern recognition tools was to compare their patterns with patterns forming the database and to estimate their class affinity (brand of beer). Percent of correct classifications was evaluated in this way.

3. Results and discussion

Preliminary studies on the construction of ion-selective miniaturized all-solid-state sensors, suitable for flow analysis, have been presented in our previous paper [16]. Plasticized PVC potassium-selective membranes with and without ion-electron conducting polymer additive (polypyrrole doped with di (2-ethylhexyl) sulfosuccinate) were deposited directly on the surface of the planar Au electrodes. Both types of microsensors exhibited comparable performance; the integration of the conducting polymer in the ion-sensitive membrane involved only the improvement of the standard potential stability. For this reason, membranes without any conducting polymer additive in membranes (coated-wire type electrodes) were applied to fabricate the flow-through electronic tongue. Similar technique, i.e. the membrane solution casting on the surface of the Au back-side contact transducers was used for the preparation of the solid-state electrodes.

In this work, two kinds of novel miniaturized solid-state sensors (selective and partially selective) were developed and tested in the sensor array of the flow-through electronic tongue. Classical ionophores and membrane compositions were applied to prepare the ion-selective microelectrodes (i.e. NH_4^+ and Cl^--selective). The ion selectivity of these sensors was checked; the values of their selectivity coefficients were in good accordance with the literature data and were presented in Table 2. Membranes containing mixtures of ionophores were used to obtain partially selective sensors ($F^-/H_2PO_4^-$ and Na^+/K^+ microelectrodes, see their selectivity coefficients in Table 2) [21]. "Cation-selective" polymer membrane contained only a lipophilic salt as an electroactive component in order to obtain sensor sensitive to cationic organic species, especially quinine, present in the sample [22].

Table 2
Selectivity coefficients log K(A,B) for (a) anion-; and (b) cation-selective electrodes

Selectivity coefficients towards	An electrode type	
	Cl^-	$F^-/H_2PO_4^-$
(a)		
SO_4^-	−2.38	−1.42
F^-	−0.97	−0.64
$H_2PO_4^-$	−2.00	−0.83
Cl^-	0.69	−0.29
Br^-	0.78	−0.43
NO_3^-	0.00	0.00
ClO_4^-	1.36	1.11

Selectivity coefficients towards	An electrode type		
	NH_4^+	Na^+/K^+	"Cation-selective"
(b)			
K^+	0.27	−0.62	0.82
Na^+	−2.27	0.00	0.00
NH_4^+	0.00	−1.36	0.62
Ca^{2+}	−3.45	−2.44	−1.79
Li^+	−3.41	−1.55	−0.03
Mg^{2+}	−3.36	−2.81	−1.80

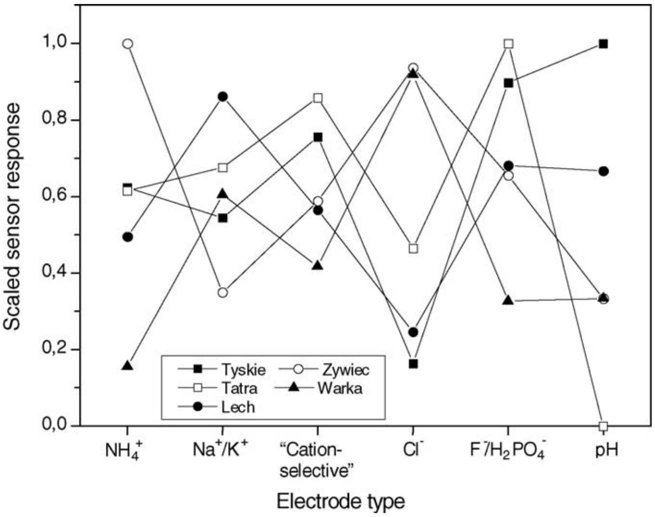

Fig. 3. Scaled responses for all brands of beer.

The responses of the sensor array were measured in the tested five brands of beer. Each sample was stirred for 15 min to remove the excess of CO_2. After this time the sample solution was transferred into the cell and the flow-through measurements were performed.

Scaling of electrode responses allowed visualizing the sensor array outputs (Figs. 3 and 4), according to the formula:

$$x'_{j,k} = \frac{x_{\text{meas}}^{j,k} - x_{\text{min}}^{j}}{x_{\text{max}}^{j} - x_{\text{min}}^{j}}$$

where $x'_{j,k}$, scaled response of jth sensor in kth sample; $x_{\text{meas}}^{j,k}$, measured response of jth sensor in kth sample; x_{min}^{j}, minimum of the measured responses of jth sensor in all samples; x_{max}^{j}, maximum of the measured responses of jth sensor in all samples.

All the brands were easily distinguished from each other because their pattern of responses were evidently different (Fig. 3). Similarity of pattern responses of the same brand

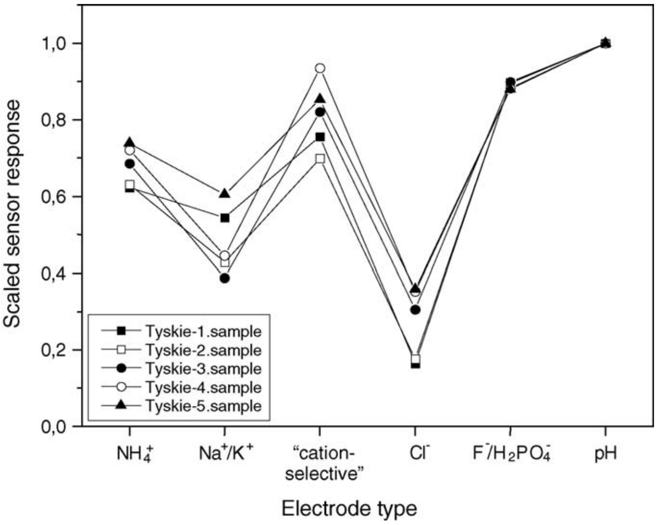

Fig. 4. Scaled responses for one brand of beer – Tyskie.

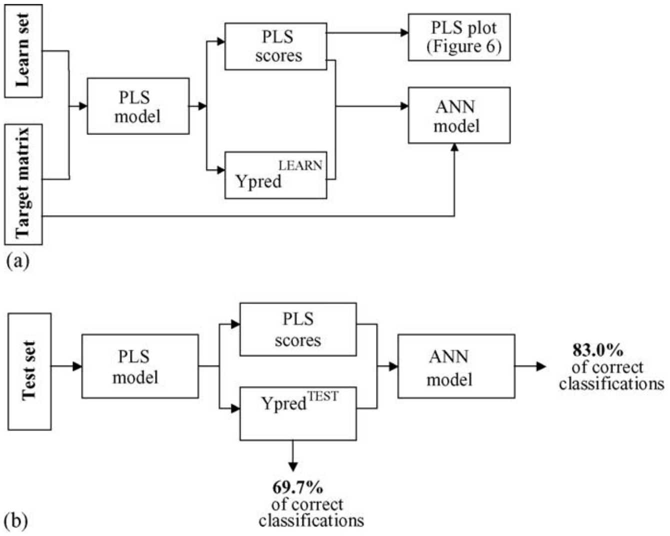

Fig. 5. Processing methods presented in the article: (a) establishing of the model (fitting); and (b) validation of the model with independent test samples.

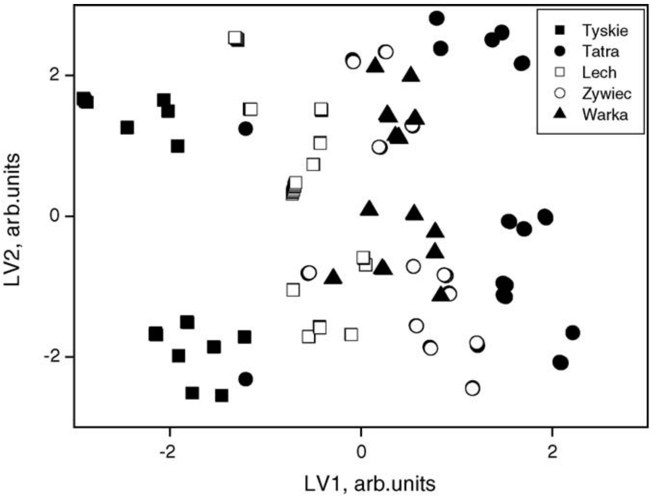

Fig. 6. PLS plot of all brands of beer (for each brand samples from 2 manufacture lots were presented).

samples (e.g. Tyskie) was presented in Fig. 4. Responses of two electrodes were almost the same ($F^-/H_2PO_4^-$, pH electrode), however Na^+/K^+ and "cation-selective" electrode exhibited more differentiated signals for the same brand samples. This effect is observed for the electrodes possessing worse discrimination capability, i.e. the sensors for which the range of the potentials measured in all brands tested is narrower (see Fig. 4). Therefore, the scaled responses of these sensors measured in the same brand sample are characterized by the greatest signal variability in the [0,1] interval.

PLS model was used to extract the information from multicomponent measurements and to remove redundant data. PLS is a supervised method, which models the relationship between two matrices, i.e. the data set obtained from sensor array measurements, and class affiliation matrix (target matrix composed of vector with true class affiliations, Fig. 5a). It can analyse noisy, uncompleted data and it is able to manage with multicolinearity problem, which often occurs in sensor array measurements [23]. The output of PLS are two matrices: the score matrix (PLS scores) and predictor matrix (Ypred – matrix of predicted affiliation to the particular class), which estimates the class affiliation (Fig. 5a). Matrix of PLS scores provides the visualization of the majority of significant data in two- or three-dimensional spaces. Respective clustering of measurement data coming from various manufacturers of beer was visible on PLS plot (Fig. 6).

The comparison of particular vectors of predictor matrix (Ypred) with respondent vectors of target matrix shows correctness or incorrectness of particular sample classification. When comparisons of all vectors are performed, the percent of correct classifications can be calculated. After PLS regression 69.7% of correct classifications were obtained (Fig. 5b).

The classification capability of the electronic tongue can be enhanced combining PLS and ANN, which was already described in the literature [24]. ANNs, a powerful tool for non-linear approximations, are widely used in artificial senses data analysis; among numerous network architectures, backpropagation neural networks have been frequently used [25]. In this way, a strategy based on supervised feature extraction for further neural network processing was employed. Both matrixes obtained by PLS: "PLS scores" and "Ypred" were used to establish the ANN model (Fig. 5a). In the case of two stage data processing, significantly better discrimination results were achieved, i.e. 83% of correct classifications (Fig. 5b). Two matrix produced by PLS represent the described sensors data (PLS scores) and the predicted class membership (Ypred). By using both of them, all the potentialities of PLS are taken into account as variables to be treated by the ANN. The role of ANN is to combine non linearly all the information provided by PLS, which is necessary for classification.

4. Summary

Multisensor systems, such as electronic noses and tongues, exhibit natural capability to measure attributes of samples: quality, condition, changes in time ("soft measurement technique" [4]), which can be exploited in foodstuff industry. However, the electronic nose systems are based mainly on flow techniques, while the electronic tongues are usually designed as a set of electrodes to be dipped in the sample solution. Only a few flow-through electronic tongues have been presented so far [4,5,13] and most of them were utilized for the determination of ion concentration [5,13].

This work presents the application of novel miniaturized solid-state electrodes in the development of the flow-through electronic tongue. The system was tested in the recognition of a brand of beer. The results obtained proved that the combination of ion-selective and partially selective microelectrodes in the flow-through sensor array and the combination of PLS/ANN techniques led to the recognition of beer with 83% correctness. Moreover, other miniaturized electronic tongue systems based on the proper choice of solid-state polymer membrane sensors can be developed for the quality control in foodstuff industry.

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References

[1] P. Ciosek, Z. Brzózka, W. Wróblewski, Sens. Actuators B 103 (2004) 76–83.

[2] K. Toko, Meas. Sci. Technol. 9 (1998) 1919–1936.

[3] P. Ciosek, E. Augustyniak, W. Wróblewski, Analyst 129 (2004) 639–644.

[4] F. Winquist, E. Rydberg, S. Holmin, C. Krantz-Rülcker, I. Lundström, Anal. Chim. Acta 471 (2002) 159–172.

[5] J. Mortensen, A. Legin, A. Ipatov, A. Rudnitskaya, Y. Vlasov, K. Hjuler, Anal. Chim. Acta 403 (2000) 273–277.

[6] P. Ciosek, W. Wroblewski, Sens. Actuators B, in press.

[7] K. Vermuza, I. Steiner, T. Glinsner, H. Klein, Eur. Food Res. Technol. 215 (2002) 235–239.

[8] T.C. Pearce, J.W. Gardner, S. Friel, Analyst 118 (1993) 371–377.

[9] I. Heberle, A. Liebminger, U. Weimar, W. Gopel, Sens. Actuators B 68 (2000) 53–57.

[10] M.J. Lewis, T.W. Young, Piwowarstwo, Wydawnictwo Naukowe PWN, Warsaw, Poland, 2001, pp. 8–29 (in Polish).

[11] D. Bellido-Milla, J.M. Moreno-Perez, M.P. Hernandez-Artiga, Spectrochim. Acta B 55 (2000) 855–864.

[12] A. Alcazar, F. Pablos, M.J. Martin, A.G. Gonzalez, Talanta 57 (2002) 45–52.

[13] J. Gallardo, S. Alegret, M. del Valle, Sens. Actuators B 101 (2004) 72–80.

[14] K. Wojciechowski, W. Wróblewski, J. Przygórzewska, G. Rokicki, Z. Brzózka, Chem. Anal. (Warsaw) 47 (2002) 335–346.

[15] A. Dybko, J. Zachara, J. Golimowski, W. Wróblewski, Anal. Chim. Acta 485 (2003) 103–109.

[16] R. Toczyłowska, R. Pokrop, A. Dybko, W. Wróblewski, Anal. Chim. Acta 540 (2005) 167–172.

[17] M. Chudy, A. Dybko, W. Wróblewski, Z. Brzózka, Anal. Chim. Acta 429 (2001) 347–355.

[18] M. Chudy, W. Wróblewski, A. Dybko, Z. Brzózka, Sens. Actuators B 78 (2001) 320–325.

[19] A. Dybko, Metrol. Meas. Syst. 8 (2001) 263–270.

[20] S. Osowski, Siecei Neuronowe do Przetwarzania Informacji, Oficyna Wydawnicza Politechniki Warszawskiej, Warsaw, Poland, 2000, pp. 38–78 (in Polish).

[21] M. Erdosy, V.V. Cosofret, R.P. Buck, K. Toth, Electroanalysis 14 (2002) 1433–1442.

[22] M.M. Zareh, E. Malinowska, K. Kasiura, Anal. Chim. Acta 447 (2001) 55–61.

[23] S. Wold, M. Sjostrom, L. Eriksson, Chemometr. Intell. Lab. Syst. 58 (2001) 109–130.

[24] P. Ciosek, Z. Brzózka, W. Wróblewski, E. Martinelli, C. Di Natale, A. D'Amico, Talanta 67 (2005) 590–596.

[25] P. Daponte, D. Grimaldi, Measurement 23 (1998) 93–115.