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Characterization of various drinking waters by new potentiometric taste sensor with lipid, lipid like-polymer membranes

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ABSTRACT

A new sensing system comprising five all-solid-state electrodes with lipid, lipid like-polymer membranes was applied for rapid qualitative and quantitative analysis of various drinking waters. The results elaborated by chemometric methods revealed sensitivity to CO_2 content in drinking water, suggesting that this sensing system could be used as a taste sensor. The ability of taste sensor to perform quantitative analysis of minerals content ($Ca^{2+,}$ Na^+, Mg^{2+}, K^+, F^-, Cl^-, HCO_3^-, SiO_2) concentration in water was also demonstrated. The developed sensing system seems to be promising solution for the analysis of treated drinking water.

Keywords: Drinking water quality; Taste sensor

1. Introduction

Almost 50% of inhabitants of developing countries suffer from health problems caused by unclean water and poor sanitation [1]. The study in 2010 revealed that there were 77 million of people exposed to toxic levels of arsenic in ground water supply in Bangladesh [2].

According to documents published by World Health Organisation (WHO) in 2000, drinking water should not bring any risk to health over a lifetime of consumption [3]. Drinking water quality needs to be monitored according to microbiological and physicochemical parameters, for example, chlorine residue, pH and turbidity. There are also sensory parameters (colour, taste and odour), which should be monitored [3].

Natural mineral water, being microbiologically wholesome, can be clearly distinguished from ordinary drinking water. It originates in underground water and emerges from a spring tapped at one or more natural or bore exits [4]. Unlike ordinary drinking water, natural mineral water is characterised by its original purity, natural minerals content and trace elements presence. Natural mineral waters can be divided according to mineral salt content indicated as a fixed residue (Table 1).

Apart from natural mineral water, mixed mineral water, natural spring water and table water can be distinguished.

Although water is very often listed separately from other food groups, its quality must be monitored. There are some analytical methods suitable for aqueous phase analysis (e.g., UV spectroscopy, liquid chromatography), which are very expensive [5].

There is an interest in low-cost methods enabling rapid analysis of food products quality. Due to this fact, application of various taste sensors for rapid, at site analysis, seems to be very promising. The concept is based on application of potentiometric sensors with global selectivity to many different components in the solution [6–8]. Such sensors transform the chemical signal related to the presence of different chemical species in the solution into potential response.

The first potentiometric taste sensors containing seven or eight sensing electrodes with lipid/polymer membranes and a

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Table 1
Division of natural mineral waters according to mineral salt content indicated as a fixed residue (based on [4])

Type of natural mineral water	Mineral salt content
With very low mineral content	Not greater than 50 mg l^{-1}
With low mineral content	Not greater than 500 mg l^{-1}
With medium mineral content	Between 500 and 1,500 mg l^{-1}
Rich in mineral salts	Greater than 1,500 mg l^{-1}

reference electrode was proposed by Toko [6]. These ion selective electrodes (ISEs) contain an inner electrolyte (KCl) as an ion to ion transducer and are covered with a lipid, modified PVC membrane [6]. Taste sensors with ISEs containing various lipid polymer membranes were used for determination of taste of such food products as milk, coffee, tomatoes, beer, sake, different amino acids and soybean paste [6,7,9]. Such kind of sensors was developed by Anritsu Corp Inc. in 1993 for commercial use (Taste Sensing System SA401) [10]. However, there were some problems with inaccuracy of information on taste qualities due to specific electrodes preconditioning. The latest improved model of taste sensing system (TS-5000Z) has been introduced by Insent Intelligent Sensor Technology, Inc. [10].

Legin et al. has successfully employed sensor array consisting of 29 different electrodes involving conventional ISEs for qualitative analysis of mineral water and wine [5,11]. The output data obtained from the device has permitted to determine every water sample. Polish group of Szpakowska has successfully applied lipid, lipid like-polymer membrane system, containing various lipids in matrices of polymeric membranes, as taste sensor with five ISEs dedicated to discrimination of tonic waters and lemonades [12]. This taste sensor has provided quite good stability and reproducibility and its output has allowed identification of tested samples.

Maintenance of ISEs as working electrodes in taste sensor involves preconditioning, which often results in adsorption of taste species to lipid polymer membrane and, hence, in imperfect results. Therefore, some attempts are made to replace ISEs with easier to maintain all-solid-state electrodes (ASSEs), where inner electrolyte is replaced with conducting polymer responsible for ion to electron transduction. Due to this, ASSEs are easier to miniaturize than ISEs [13].

There were already some attempts to construct taste sensor based on potentiometry involving ASSEs. This taste sensor was successfully applied for the analysis of taste quality of various sour solutions [14].

In this work, the feasibility of a new potentiometric taste sensor with five ASSEs with lipid, lipid like-polymer membranes dedicated for discrimination of mineral waters is demonstrated. The results of qualitative and quantitative analysis of selected mineral waters with different carbon dioxide content are presented.

2. Experimental

2.1. ASSEs preparation

ASSEs were prepared by deposition of polymerized 3,4-ethylenedioxythiophene (PEDOT), formed by galvanostatic electrochemical polymerization from a solution composed of 0.01 M PEDOT and 0.1 M poly (sodium 4-styrenesulfonate) (NaPSS) at 850 mV, on glassy carbon (GC) disc.

GC/PEDOT electrodes were coated with a PVC membrane modified with lipophilic compounds. Five different lipophilic compounds were used in particular electrodes: (1) benzyldimethyltetradecylammonium chloride, (2) dodecyltrimethylammonium bromide, (3) palmitic acid, (4) stearic acid and (5) phytol. The composition of lipophilic polymer membrane was as follows: 2.5 mg of appropriate lipophilic compound, 300 mg PVC, 483.5 mg dioctyl phenylphosphonate (DOPP) used as a plasticizer in 10 ml of tetrahydrofuran (THF). Lipid polymer membrane solution was put on GC/PEDOT electrodes and dried for 24 h. All ASSEs were conditioned in 10^{-3}M KCl for 24 h before measurement.

2.2. Experimental setup

Taste sensor was constructed of five ASSEs and a reference electrode (Ag/AgCl/Cl$^-$) immersed in a tested water sample. The electrode responses were obtained using high-input impedance voltmeter Atlas Solich 0961 Multiplexer at 23°C (Fig. 1). ASSEs were conditioned in 0.001 M KCl solution between particular measurements.

2.3. Tested mineral waters

Eight types of bottled waters and distilled water were analysed. The measurements were run for 2 weeks. A new sample was used each day. The results of independent standard analysis, obtained from the manufacturers of tested waters, were used as reference for calibration.

2.4. Calculation methods

The processing of data from the sensor array was performed using principal component analysis (PCA), agglomerative hierarchical clustering (AHC) and multiple linear regression (MLR). Calculations were made with XLStat computer software.

2.5. PCA

Data collected by five electrodes of the taste sensor may be correlated and a part of it might be redundant. PCA allows

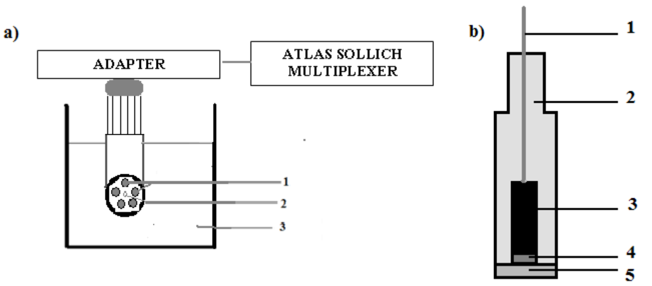

Fig. 1. (a) Experimental setup: 1 – five ASSEs with lipid/polymer membranes, 2 – Ag/AgCl/Cl$^-$ reference electrode, 3 – tested water sample; (b) All-solid-state electrode: 1 – copper wire, 2 – polytetrafluoroethylene, 3 – glassy carbon, 4 – PEDOT/PSS, 5 – lipid – polymer membrane.

representing data in a form of smaller number of uncorrelated variables called principle components [15]. Input data for PCA were prepared using correlation matrices.

2.6. AHC

AHC is a method enabling to build a hierarchy of clusters of data, starting from each observation in its own cluster, and then merging of pairs of clusters [16]. In this work, AHC was applied for classification of various mineral waters based on taste sensor response.

2.7. MLR

In this work, MLR was used to model the relationship between mineral content of tested waters given by producers and the taste sensor response in terms of mineral content. It was done by fitting a linear equation to the data set measured by the taste sensor [17].

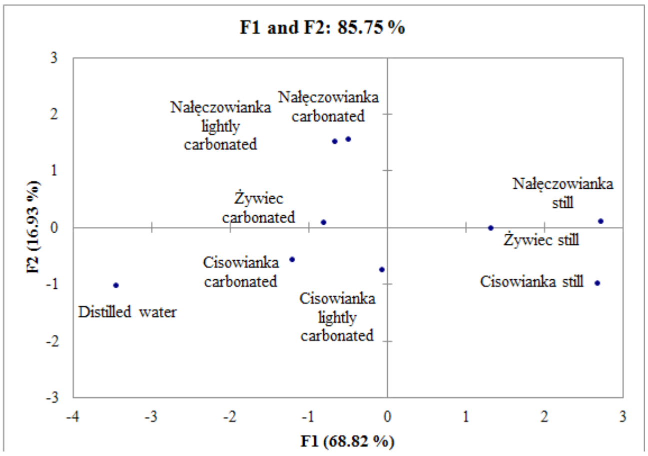

Fig. 2. Score plot for first principal component (F1) vs. second principal component (F2) for PCA of taste sensor responses to different water samples.

3. Results and discussion

Discrimination of different kinds of analysed bottled waters using potentiometric taste sensor with lipid, lipid like-polymer membranes is presented in the PCA score plot in Fig. 2.

The scores representing still waters (Żywiec, Cisowianka and Nałęczowianka) are situated together on the right hand side of F1 axe (Fig. 2). Carbonated and lightly carbonated waters are placed close to each other independently of mineral content around centre point of F1 and F2 axes. Distilled water is far from the rest of tested drinking waters (Fig. 2).

In order to provide a mathematical proof of grouping of water samples, AHC was performed. In Fig. 3, AHC dendrograms are presented.

Three classes of tested waters were identified by means of AHC (Table 2, Fig. 3(b)), in coherence with PCA results (Fig. 2). It seems that carbon dioxide content strongly affected the taste sensor response. Carbon dioxide is known to be responsible for orosensory excitation. Thus, the final perception of carbon dioxide was a combination of multisensory inputs [18]. It can be stated that taste sensor was capable of discrimination between water samples with and without carbon dioxide content. It confirms the possibility of application of this sensing system as a taste sensor.

The distinction of distilled water by PCA of taste sensor results (Fig. 2) might indicate its ability to discriminate between samples differ in mineral composition.

Besides the qualitative recognition of waters, the ability to perform quantitative analysis using taste sensor was investigated. Data obtained from taste sensor, together with calibration data, were processed using MLR. For each mineral

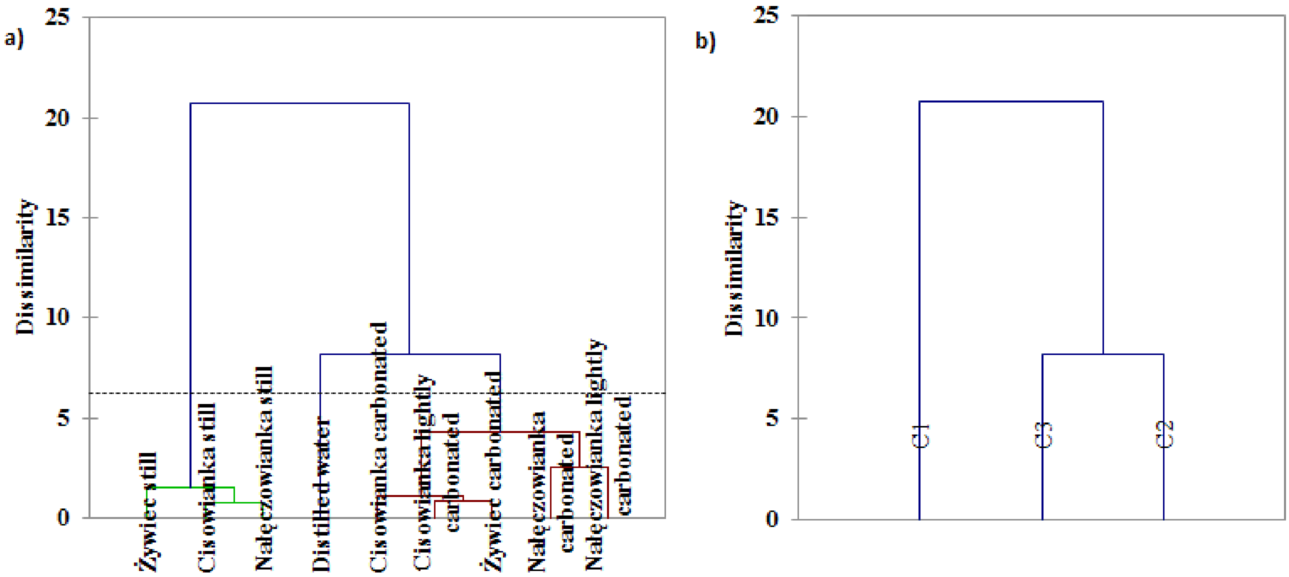

Fig. 3. Dendrograms from AHC of taste sensor responses to different water samples: (a) all tested water samples, (b) tested water samples in terms of three classes identified by AHC.

content, a separate model to predict mineral concentration in water was prepared (Table 5). The determination coefficients describing how well obtained data fit the model are presented in Table 3.

Data in Table 3 show that models for prediction of Cl^-, F^- ions and SiO_2 are the best fitted ones. Results of quantitative determination of mineral content of tested waters by the taste sensor are summarised in Table 4.

The greatest residuals (differences between real and predicted value) were observed for carbonated waters (Table 4, no. 3 and 6) in case of Ca^{2+}, $Na^{+,}$ HCO_3^-. In case of Cl^-, the greatest residual was only for Cisowianka carbonated water.

Nevertheless, it should be noted that the taste sensor provided quantitative measurements of different drinking waters with reasonable accuracy.

It can be stated that by the use of the taste sensor, concentration of different ions could be measured simultaneously in the multicomponent solution. The determination of concentration of minerals necessary for standard characterisation of mineral waters was also possible. The same measurement and data processing procedure could be applied for analysis of treated drinking waters.

The most important advantage of ASSEs in taste sensor is that they require much less maintenance than ISEs. Due to the replacement of inner electrolyte with solid conducting polymer, miniaturization of ASSEs is also easier. However, costs of ASSEs fabrication are higher than in case of ISEs due to application of expensive conducting polymers.

Table 2
Results of AHC of taste sensor responses to different water samples by class

Class	Type and brand of tested water
C1	Cisowianka still
	Nałęczowianka still
	Żywiec still
C2	Cisowianka lightly carbonated
	Cisowianka carbonated
	Żywiec carbonated
	Nałęczowianka lightly carbonated
	Nałęczowianka carbonated
C3	Distilled water

Table 3
Values of determination coefficient (R^2) of each mineral obtained by MLR

Mineral content	R^2
Ca^{2+}	0.782
Mg^{2+}	0.704
Na^+	0.767
K^+	0.784
HCO_3^-	0.733
Cl^-	0.880
F^-	0.857
SiO_2	0.809

Table 4
Results of MLR analysis of taste sensor responses in tested waters

Water	r.v.	p.v.	SD	r.v.	p.v.	SD
	Ca^{2+} [mg l^{-1}]			Na^+ [mg l^{-1}]		
1	130.30	132.10	27.81	11.00	11.32	2.61
2	131.26	136.51	27.43	10.71	9.85	2.57
3	**128.26**	**90.80**	25.19	**10.00**	**7.75**	2.36
4	114.50	101.29	27.00	12.70	11.77	2.53
5	108.20	127.19	33.19	10.00	11.29	3.11
6	**114.50**	**90.44**	31.17	**12.70**	**10.160**	2.92
7	42.62	60.59	32.80	9.73	10.72	3.07
8	62.12	90.44	18.28	4.00	8.16	1.71
	Mg^{2+} [mg l^{-1}]			K^+ [mg l^{-1}]		
1	21.90	23.01	6.52	5.00	4.45	1.16
2	22.48	21.48	6.43	0.78	2.07	1.14
3	21.26	14.14	5.91	2.50	0.79	1.05
4	23.10	19.92	6.33	5.40	5.39	1.12
5	21.90	25.85	7.79	2.20	2.84	1.38
6	23.10	16.83	7.31	5.40	4.75	1.30
7	5.52	14.96	7.70	n.a	n.a	1.36
8	6.08	8.92	4.29	n.a	n.a	0.76
	F^- [mg l^{-1}]			SiO_2 [mg l^{-1}]		
1	0.50	0.63	0.14	22.10	25.30	5.89
2	1.00	0.80	0.14	18.38	20.22	5.81
3	0.21	0.34	0.13	22.10	14.07	5.34
4	0.30	0.21	0.14	36.00	30.14	5.72
5	0.30	0.28	0.17	22.00	26.71	7.03
6	0.30	0.32	0.16	36.00	33.31	6.60
7	0.07	0.03	0.17	n.a	n.a	6.95
8	0.07	0.45	0.09	n.a	n.a	3.87
	HCO_3^- [mg l^{-1}]			Cl^- [mg l^{-1}]		
1	539.10	551.90	134.845	5.00	5.40	1.17
2	542.60	549.14	133.00	3.20	3.92	1.16
3	**518.70**	**350.58**	122.14	**5.00**	**3.33**	1.06
4	488.10	425.04	130.90	8.50	7.53	1.14
5	439.30	527.07	160.94	7.00	7.87	1.40
6	**488.10**	**358.73**	151.12	8.50	8.07	1.31
7	136.24	216.10	159.06	n.a	n.a	1.38
8	201.50	361.40	88.63	n.a	n.a	0.77

Note: r.v. – real value; p.v. – predicted value; SD – standard deviation; n.a. – not available; 1 – Cisowianka still, 2 – Cisowianka lightly carbonated, 3 – Cisowianka carbonated, 4 – Nałęczowianka still, 5 – Nałęczowianka lightly carbonated, 6 – Nałęczowianka carbonated, 7 – Żywiec still, 8 – Żywiec carbonated.
Source: self-elaboration based on water manufacturers data.

4. Conclusions

New potentiometric taste sensor with lipid, lipid like-polymer membranes was employed for simultaneous qualitative and quantitative determination of mineral content in drinking water. In quantitative analysis, the ability of taste sensor to estimate the concentration of ionic species and

Table 5
Mathematical models for prediction of mineral content in tested waters basing on the taste sensor response

Mineral content – equations of the models		
Ca^{2+}	=	8.63 + 2700.56 ∗ **El.1** – 35540.62 ∗ **El.2** + 3263.951 ∗ **El.3** + 26912.33 ∗ **El.4** + 2507.32 ∗ **El.5**
Mg^{2+}	=	2.06 – 75.725 ∗ **El.1** – 6504.41 ∗ **El.2** – 667.25 ∗ **El.3** + 6677.64 ∗ **El.4** + 556.22 ∗ **El.5**
Na^+	=	–1.03 + 994.38 ∗ **El.1** + 80.17 ∗ **El.2** + 3902.29 ∗ **El.3** – 158.33 ∗ **El.4** + 324.49 ∗ **El.5**
K^+	=	0.52 – 431.52 ∗ **El.1** – 5.79 ∗ **El.2** + 1405.10 ∗ **El.3** + 650.23 ∗ **El.4** – 117.95 ∗ **El.5**
HCO_3^-	=	44.14 – 2699.24 ∗ **El.1** – 161534.43 ∗ **El.2** – 11676.39 ∗ **El.3** + 136715.19 ∗ **El.4** + 8634.31 ∗ **El.5**
Cl^-	=	0.333 – 14.90 ∗ **El.1** + 391.182 ∗ **El.2** + 3007.25 ∗ **El.3** + 224.77 ∗ **El.4** + 220.80 ∗ **El.5**
F^-	=	–1.565E-03-4.20 ∗ **El.1** – 367.59 ∗ **El.2** – 17.77 ∗ **El.3** + 207.62 ∗ **El.4** – 14.10 ∗ **El.5**
SiO_2	=	0.747 + 466.88 ∗ **El.1** + 242.60 ∗ **El.2** + 13706.84 ∗ **El.3** + 364.32 ∗ **El.4** + 386.42 ∗ **El.5**

SiO_2 content with reasonable accuracy was proved. In qualitative analysis, the taste sensor was capable of discrimination between drinking water samples with different carbon dioxide content. Therefore, applied sensing system can act as a taste sensor because carbon dioxide content has a significant impact on drinking water taste. This sensing system might also be a promising solution for the analysis of treated drinking water.

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