The possibility of the application of a potentiometric sensor with all-solid-state electrodes for the quality control of different natural waters

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ABSTRACT

The quality of various natural waters was examined by a new potentiometric sensor with six all solid state electrodes containing an appropriate lipophilic compound in a polymer membrane. Physicochemical parameters such as conductivity and acidity of tested waters were also tested. All waters were neutral or slightly alkaline and contained different ions (e.g., Cl⁻) due to the place of their sampling (a coastal zone and a moraine plateau). They differed significantly in conductivity values. The results obtained by potentiometric sensor, elaborated by chemometric methods showed that tested waters (surface, subsurface, mix subsurface, mix groundwater, rain, and tap) could be grouped in terms of their conductivity values. It means that this sensor is capable of discriminating between waters of low, middle, and high conductivity and may be a good tool for the quality analysis of natural waters.

Keywords: Natural waters; Quality control; Potentiometric sensor; Chemometric methods; Conductivity

1. Introduction

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Water quality assessment is made on the basis of measurable quality indicators, which define the quality status of waters, that is, the amount and types of pollutants in water and the condition of aquatic biocenoses [1]. The interest in the quality of drinking water necessary for all human kind has recently grown rapidly [2,3]. There are several kinds of such a bottled water available on the market: natural mineral water, mixed mineral water, natural spring water, and table water. However, in many places it is recommended to drink tap water, since its quality is similar to bottled drinking water. It is probably due to good quality of treated surface or groundwater, which is delivered to municipal water supply systems [4]. Tap water is frequently a mixture of these two types of water. Water consumption forces continuous flow in the water supply systems, which demands continuous monitoring not only of tap water, but also of raw water [4].

There are several analytical methods suitable for drinking water analysis (e.g., liquid chromatography or spectroscopy). The use of these methods enables to estimate a water composition, detect its contaminants appearing in very small amount (i.e., micropollutants, e.g., heavy metals), etc. However, these methods are very expensive [5,6].

Due to this fact, the application of potentiometric sensors with global selectivity [7,8] to different components in the solution for rapid, in-place quality analysis of different kinds of water seems to be very promising [9,10]. Such sensors transform the chemical signal related to the presence of different chemical species in the solution into the potential response.

The potentiometric sensor containing seven or eight ionselective electrodes (ISEs) with lipid–polymer membranes

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and a reference electrode was proposed by Toko [7]. These ISEs contained an inner electrolyte as an ion to ion transducer and they were covered with a lipid-modified PVC membrane [7]. Potentiometric sensors with ISEs were used for quality determination of such liquids (e.g., milk, coffee, beer, sake, and wines). Legin et al. [9,11] employed a sensor array consisting of 29 different ISEs for quality analysis of mineral water and wine. Szpakowska et al. [12,13] successfully applied lipid, lipid like-polymer membrane potentiometric sensor with ISEs for the discrimination of tonic waters and lemonades.

ISEs with an inner solution have been found to be practically inconvenient in the maintenance. Therefore, all solid state electrodes (ASSEs), in which inner electrolyte is replaced with a conducting polymer responsible for ion to electron transduction, have been proposed [14].

A potentiometric sensor with five ASSEs containing lipid, lipid like-polymer membranes for discrimination of mineral waters with different carbon dioxide content was already used [10]. Each electrode contained one lipophilic compound in the lipid–polymer membrane: benzyldimethyltetradecylammonium chloride, dodecyltrimethylammonium bromide, palmitic acid, stearic acid, and phytol. It was shown that not only qualitative, but also quantitative analysis of selected soft drinks was possible [15].

Another type of potentiometric sensor with six ASSEs containing the following lipophilic compounds (each in one membrane electrode): hexadecyltrimethylammonium bromide, hexadecylamine, palmitic acid, lauric acid, decanoic acid, and cholesterol, was applied for discrimination of quality changes in red wines [16]. It was shown that wines produced by different vineyards could be divided into two groups of similar quality.

In this work, this potentiometric sensor with six ASSEs was used for the quality control by grouping tested waters of similar parameters. Natural waters such as: ground-water (ANGIELSKA GROBLA, treated LIPCE), surface water (raw and treated STRASZYN), subsurface water (BUDOWLANYCH), and rain water were tested. As references, distilled and tap waters were also examined. Selected physicochemical parameters such as conductivity and pH were also measured.

Raw STRASZYN water was sampled at the intake of the artificial reservoir on the Radunia river. The quality of this water is affected mostly by the activities of agriculture and tourism sectors. This water after treatment was also examined.

Sampling points for other natural waters are presented in Fig. 1.

Groundwater from LIPCE intake (no. 3, Fig. 1) was sampled in the point situated near the area of Vistula Delta Plain. Intake wells pump water from the Cretaceous level (over 100 m deep) and Quaternary aquifer (up to 50 m deep). The top layer of soil is a layer of poorly permeable peats and silts. There is no risk of salt intrusion from Dead Vistula River, including salt water withdrawn from the Gulf of Gdansk [17].

Mixed ground ANGIELSKA GROBLA (no. 4, Fig. 1) water is an example of excavation dewatering. It consists of mixed systems: 10 m deep wells and needle filters. This is water from shallow ground level containing a mixture of groundwater from the Quaternary outcrop aquifer, filtered



Fig. 1. The diagram of groundwater circulation in the Gdańsk area with marked sampling points: 3 - groundwater intake LIPCE, 4 - mixed groundwater excavation dewatering ANGIELSKA GROBLA, 5 - spring subsurface water BUDOWLANYCH, Aquifers: Q - Quaternary, Tr - Tertiary, and Cr - Cretaceous. The sampling points 1 and 2 are located outside the diagram.

rainwater, and snowmelt. It may contain the salt water withdrawn from the Gulf of Gdansk. The sampling point of this water was situated near Dead Vistula River, about 5°m below the sea level in the collecting well.

Water BUDOWLANYCH (no. 5, Fig. 1) is an example of subsurface water from spring areas supplying creeks in moraine plateau part of Gdansk agglomeration. The sampling point was situated about 160 m above sea level. Water at this point comes from natural processes of infiltration and filtration of rainwater.

2. Experimental

2.1. ASSEs preparation

The conductive poly(3,4-ethylenedioxythiophene) polymer (PEDOT) was obtained by electrochemical synthesis [10]. Each ASSE consisted of two layers (Fig. 2(b)). The layer containing PEDOT was put directly on glass carbon (GC). The outer layer was lipid–polymer membrane with PVC (~wt. 61%), plasticizer DOPP (~wt. 38.5%) and appropriate lipophilic compound (~wt. 0.5%). Each electrode contained one lipophilic compound in the lipid–polymer membrane: $e_1 - hexadecyltrimethylammonium bromide$, $e_2 - hexadecylamine$, $e_3 - palmitic acid$, $e_4 - lauric acid$, $e_5 - decanoic acid$, and $e_6 - cholesterol$. The layers put one by one on GC were dried for about 5 h. The electrodes were conditioned for 24 h in KCl (10⁻³ M) solution.

2.2. Experimental setup

Potentiometric sensor (Fig. 2(a)) consisted of: six working ASSEs with lipophilic compounds in polymer membrane (Fig. 2(b)), a reference electrode (Ag/AgCl/Cl⁻), and a voltmeter Atlas (Sollich Company, Gdansk, Poland) connected with a computer. The lipophilic compound present in a lipid–polymer membrane was responsible for the reaction with dissolved substances present in tested waters.

2.3. Tested waters

A series of water samples were taken from eight different sources (series I). This operation was repeated twice with 1 week interval (series II and III). The following kinds of natural water were tested: raw surface STRASZYN water from artificial lake situated on Radunia river (no. 1), treated STRASZYN surface water (no. 2), treated ground LIPCE water from deeper aquifer (no. 3), mixed ground ANGIELSKA GROBLA from a shallow aquifer (no. 4), and subsurface water BUDOWLANYCH (no. 5). The samples of tap water (no. 6) and rain water (no. 7) were taken from Gdansk University of Technology (GUT). Distilled water exposed to a 1 d contact with air (no. 8) was examined as a standard. All the samples were thermostated at 25°C and used without dilution.

2.4. Physicochemical measurements and calculations

Potentiometric measurements were made by using a sensor (Fig. 2(a)) with six ASSEs. They were conditioned in appropriate 10⁻³ M KCl solution prior to and between measurements. The mean values of voltages (in mV) of each ASSE



Fig. 2. (a) Experimental setup: 1 - a set of working electrodes with lipophilic compound-polymer membranes (ASSEs), $2 - Ag/AgCl/Cl^-$ reference electrode, and 3 - tested water, (b) single ASSE: 1 - copper wire, 2 - glassy carbon disc, 3 - teflon casing, 4 - conductive polymer layer, and 5 - lipophilic compound-polymer membrane.

in samples taken in three series (I–III) consisted of appropriate kind of water were analyzed by Principal Component Analysis (PCA). This method reduces information included in six-dimensional data space to ones in two-dimensional space. PCA method allows for representating the data in a form of smaller number of uncorrelated variables, so called principle components [18]. Input data for PCA were prepared using correlation matrices. The PCA calculations were done using Statistica v12 software. The cluster analysis (CA) for grouping of tested waters of similar composition was also applied [19]. The MS Excel 2015 program was used for other data elaboration.

Conductivity (σ) and *pH* values of all examined samples were measured in *T* = 25.0°C using CPC – 501 pH/conductometer after appropriate calibration. The conductometric electrode of CD-2 type, with *K* = 0.503 ± 0.01 cm⁻¹ was used after washing in distilled water.

3. Results and discussion

The conductivity (σ) results of tested natural waters (nos. 1–5) are presented in Fig. 3. Three samples for each water from series I, II, III are presented. It can be seen, the conductivity of each type of water slightly changed with sampling time and this could be a result of water flow processes. The mean value of results from three series was taken for further calculations.

The pH values for a given type of water taken with 1 week interval (series I–III) varied within 2%–4% (Fig. 4). There was no correlation between pH values and sampling time. In this case, the mean value of three series for each tested water was also taken for further calculations.

The physicochemical parameters (conductivity, σ , and pH) of tested waters obtained in our laboratory (mean values of samples from three series) and the content of selected ions determined in other laboratories [20] are given in Table 1.

The pH values of all tested waters were in the range of 6.30–7.98. Raw surface STRASZYN water (no. 1) and treated STRASZYN (no. 2) were characterized with alkaline pH values. Their conductivity values were in the same range. The treatment of this water resulted in diminishing of certain ions' content (e.g., NH_4^+).



Fig. 3. Conductivity values (σ) of tested natural waters for series I (∞), II (m), and III (∞): 1 – raw surface STRASZYN water, 2 – treated surface STRASZYN water, 3 – treated ground LIPCE water, 4 – mixed groundwater ANGIELSKA GROBLA water, and 5 – subsurface BUDOWLANYCH water.



Fig. 4. The pH values of tested waters for series I (1), II (1), and III (2): 1 – raw surface STRASZYN water, 2 – treated surface STRASZYN water, 3 – treated ground LIPCE water, 4 – mixed groundwater ANGIELSKA GROBLA, and 5 – subsurface BUDOWLANYCH water.

The conductivity of treated LIPCE water (no. 3) was almost twice higher than in discussed STRASZYN waters (nos. 1 and 2). It was due to a greater amount of ions (e.g., SO_4^{2+} and Ca^{2+}) present in this water in comparison with STRASZYN water (no. 2) (Table 1).

Mixed groundwater ANGIELSKA GROBLA (no. 4) was characterized with more than six times greater conductivity value in comparison to raw surface STRASZYN water (no. 1). This was due to the presence of large amount of Cl⁻ ions, which originated from salt water of Dead Vistula River.

The content of Cl⁻ ions in subsurface BUDOWLANYCH water (no. 5) was higher in comparison with treated STRASZYN water (no. 2) and treated LIPCE water (no. 3), which resulted in higher conductivity value. However, it was much less than in case of mixed groundwater

ANGIELSKA GROBLA (no. 4), in which salt water leakage from Dead Vistula River (Table 1) was noted. Subsurface BUDOWLANYCH (no. 5) water had no hydraulic contact with salt water from the Dead Vistula River.

The GUT tap water (no. 6) was a mixture of water produced at intakes in Czarny Dwór and Zaspa. Therefore, its conductivity was in the same range (702 μ S/cm for Czarny Dwór and 725 μ S/cm for Zaspa intake [20]).

Distilled water (no. 8) was characterized with very low conductivity as it was expected. The pH value (6.3) indicated on the dissolution of some amount of CO_2 from air. The conductivity of GUT rain water (no. 7) was 10 times larger in comparison with distilled water (no. 8). It was due to air pollution in vicinity of GUT.

The ASSEs responses of potentiometric sensor (mean value of three series) are given in Figs. 5(a) and (b).

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Table 1

Physicochemical parameters of natural, distilled and tap waters

No.	Kind of water	Mean σ	Mean pH	Cl-	SO ₄ ²⁻	NH_4^+	Ca ²⁺	Total hardness
		$(\mu S/cm),$ T = 25°C	<i>T</i> = 25°C	(mg/dm³)			(°N)	
1	Raw surface STRASZYN	316 ± 25	7.84 ± 0.05 7.85ª	-	_	0.13ª	-	-
2	Treated surface STRASZYN	378 ± 31 (392 ^a)	7.98 ± 0.05	20.5ª	22.3ª	<0.05ª	63.0ª	-
3	Treated ground LIPCE	617 ± 32 (644 ^a)	7.60 ± 0.05	13.0ª	29.0ª	<0.05ª	67.0ª	16.0ª
4	Mix ground ANGIELSKA GROBLA	$2,024 \pm 83$	7.12 ± 0.05	347.0 ^b	124.6 ^b	0.1 ^b	_	16.2 ^b
5	Subsurface BUDOWLANYCH	854 ± 25	6.87 ± 0.05	134.7°	-	-	_	27.0 ^c
6	Tap GUT	709 ± 32	7.49 ± 0.05	-	-	< 0.05	_	_
7	Rain GUT	29 ± 2	6.92 ± 0.05	-	-	-	_	_
8	Distilled	2.1 ± 0.05	6.30 ± 0.05	0	0	0	0	0

^aSNG laboratory [20], ^bBarg M.B. laboratory [20], ^cFC&EE GUT laboratory [20], GUT – Gdańsk University of Technology.



Fig. 5. Mean values of three series (I, II, III) of electric potential (in mV) of six ASSEs containing: $e_1 - hexadecyltrimethylammo$ $nium bromide, <math>e_2 - hexadecylamine$, $e_3 - palmitic acid$, $e_4 - lauric acid$, $e_5 - decanoic acid$, and $e_6 - cholesterol for water$, (a) 1 – raw surface STRASZYN water, 2 – treated surface STRASZYN water, 3 – treated groundwater LIPCE, 4 – mixed groundwater ANGIELSKA GROBLA, and 5 – subsurface BUDOWLANYCH water and (b) 6 – tap GUT water, 7 – rain GUT water, 8 – distilled water.

It can be concluded that e_2, e_3, e_4, and e_5 electrodes were more sensitive to the kind of water used in comparison with electrodes e_1 and e_6 (Fig. 5(a)). The shapes of radar plots for tap water GUT, rainwater GUT, and distilled water (Fig. 5(b)) were different in each case. Again the responses of four electrodes (e_2, e_3, e_4 and e_5) differed significantly for each tested water.

The contribution of each ASSE in PC1 and PC2 coordinates is shown in Fig. 6. PCA analysis of the results obtained by the potentiometric sensor of tested waters is presented in Fig. 7 and Table 2.

As it can be seen, the first two principal components (PC1 and PC2) explain 95.50% of variability of this model, which shows the presence of a strong pattern, according to which data are arranged.

The greatest contribution to PC1 was given by e_2 (factor loading = 0.99). The e_1 electrode had a similar contribution

to the PC 1 (factor loading = 0.97). On the other hand PC2 was mainly defined by e 3 (factor loading = 0.74).

The points representing waters of low conductivity (nos. 7 and 8) are situated on the right side of Fig. 7. The other water samples are situated at left-hand side of Fig. 7. The point for water of the highest conductivity, that is, of very high content of Cl⁻ ions (no. 4) characterized with the smallest PC1 values.

In order to provide mathematical evidence for the grouping of the water samples, the CA was performed (Fig. 8). The obtained results showed that the tested waters might have been divided into several groups. They are marked by circles in Fig. 7 and by dotted line in Fig. 8.

Three water samples: mix groundwater ANGIELSKA GROBLA (no. 4), rain GUT water (no. 7), and distilled water (no. 8) created three separate groups. They characterized with a different level of conductivity. Subsurface BUDOWLANYCH



Fig. 6. Biplot of PCA analysis of potentiometric sensor responses to different water samples, 1 – raw surface STRASZYN water, 2 – treated surface STRASZYN water, 3 – treated groundwater LIPCE, 4 – mixed groundwater ANGIELSKA GROBLA, 5 – subsurface BUDOWLANYCH water, 6 – tap GUT water, 7 – rain GUT water, and 8 – distilled water. e_1 – hexadecyltrimethylammonium bromide, e_2 – hexadecylamine, e_3 – palmitic acid, e_4 – lauric acid, e_5 – decanoic acid, and e_6 – cholesterol.



Fig. 7. The results of potentiometric sensor responses by PCA for tested waters, 1 – raw surface STRASZYN water, 2 – treated surface STRASZYN water, 3 – treated groundwater LIPCE, 4 – mixed groundwater ANGIELSKA GROBLA, 5 – subsurface BUDOWLANYCH water, 6 – tap GUT water, 7 – rain GUT water, and 8 – distilled water.

Table 2

Eigenvalues and variability explained by principle components in PCA analysis

	PC1	PC2	PC3	PC4	PC5
Eigenvalues	5,819.06	515.95	241.27	34.78	22.28
Variability	87.72	7.78	3.64	0.52	0.34
explained (%)					
Cumulative	87.72	95.50	99.14	99.66	100.00
variability					
explained (%)					



Fig. 8. The cluster analysis (CA) of the results obtained by the potentiometric sensor with six ASSEs, 1 – raw surface STRASZYN water, 2 – treated surface STRASZYN water, 3 – treated groundwater LIPCE, 4 – mixed groundwater ANGIELSKA GROBLA, 5 – subsurface BUDOWLANYCH water, 6 – tap GUT water, 7 – rain GUT water, and 8 – distilled water.

water (no. 5) and tap GUT water (no. 6) were in the same group (Figs. 7 and 8). A separate group (Fig. 8) was created by raw surface STRASZYN water (no. 1) treated surface STRASZYN water (no. 2), and treated groundwater LIPCE (no. 3) resulting of the similar range of conductivity.

Taking into account the discussed results, it can be stated that potentiometric sensor with six ASSEs can be successfully used for grouping tested waters according to their conductivity caused by the presence and the content of different ions.

4. Conclusions

Physicochemical parameters such as conductivity and acidity (pH) of several tested waters: mixed groundwaters (AGIELSKA GROBLA, treated LIPCE), surface waters (raw and treated STRASZYN), subsurface water (BUDOWLANYCH), and rain and tap waters were measured. The pH values obtained for all tested waters were in the range of 6.30–7.98. The mixed groundwater ANGIELSKA GROBLA contained salt water from Dead Vistula River, so its conductivity was very high. It constituted a separate group in PCA and CA analyses.

Subsurface BUDOWLANYCH and tap GUT water created the separate group since their conductivity was of the same range. The points representing other waters (raw surface STRASZYN, treated surface STRASZYN, and treated ground LIPCE) were also collected in one group. It was due to similar range of conductivity. It means that the potentiometric sensor with six ASSEs is capable of discriminating between water samples of low, middle, and high conductivity. Such sensor may be used for qualitative analysis of different types of natural waters.

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