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All solid state electrodes taste sensor with modified polymer membranes for discrimination of mineral water with different CO_2 content

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ABSTRACT

A potentiometric taste sensor with All Solid State Electrodes containing five all solid state electrodes with appropriate lipophilic compounds (benzyldimethyltetradecylammonium chloride, dodecyltrimethylammonium bromide, palmitic acid, stearic acid, and phytol) embedded in a polymer membrane was applied for discrimination of mineral water samples differed in CO_2 content. Samples of still, slightly sparkling, and sparkling Naleczowianka mineral water were examined. The investigation of CO_2 content in the sparkling Naleczowianka mineral water in time lapse after opening the bottle was also performed. It was shown by Principal Component Analysis and Agglomerative Hierarchical Clustering that the taste sensor could discriminate between samples of similar CO_2 content. Distances between principal component points representing samples of tested water as a function of time after opening the bottle created a power curve. These distances could be a measure of CO_2 content in tested water samples. The shape of the obtained power curve was in agreement with sensory perception of major CO_2 release during openings of the bottle of carbonated water.

Keywords: Polymer membrane; Drinking water quality; Taste sensor

1. Introduction

Nowadays, the quality of human life is, among others, closely related to access to freshwater. There exists the strong linkage between poverty and scarcity of water resources [1]. World water resources and the way their use are a great challenge of world's food security. "Ensure availability and sustainable management of water and sanitation for all" is one of the sustainable development goals until 2030 announced by The United Nations [2].

There is a debate on the adequate quantity and quality of water in humans health protection [3–5]. Ground water, as a main source of drinking water, may be contaminated with heavy metals, for example, arsenic. Remediation of such metals from water for drinking purposes may be achieved by pressure-driven membrane processes [6,7].

Nowadays bottled water is a global commodity with an annually increasing consumption level [8,9]. Bottled water has achieved unquestionable commercial success despite its 240–1,000 times higher price comparing with tap water. It is so, even despite the fact that the quality of tap water is rapidly increasing in developing countries [10]. Restaurants and supermarkets all over the world offer a wide variety of both, still and sparkling bottled water. Sparkling water drinking causes a wide range of sensory experiences. The candidate, that is, CO_2 receptor has been identified in *Drosophila melanogaster* [11]. It is known that in case of humans CO_2 activates the cells responsible for sour taste sensing. However, the final perception of CO_2 is not a simple sour taste, but it is a multiple orosensory feeling with "tingle" and "fizz" being a part of it [12]. Hence, dissolved CO_2 is a key parameter to be monitored in sparkling beverages. Conventionally, total pressure and temperature need to be measured in order to estimate dissolved CO_2 content in a liquid. This technique,

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based on Henry's law, does not provide accurate results [13]. The direct measurement methods are still searched. Among them, there are laboratory methods based on an infrared spectroscopy and a membrane gas-diffusion flow injection analysis system involving spectrometry detection with pH indicators [13,14]. There is also a commercial in-line dissolved carbon dioxide analysis system D-CO_2 [15]. The principle of its operation is based on free flow of CO_2 across the selective membrane straight to a mass flow device. With this analyzer, dissolved CO_2 content above 1.0 g/L can be measured [15].

The interest in low cost methods for rapid, at site complex water analysis does not expire. One of the types of instruments enabling such analysis is a potentiometric taste sensor, also called an electronic tongue [16–18]. The principle of operation of such taste sensors with global selectivity is based on the transformation of the chemical signal due to various chemical species in the solution into measurable potential signal. The first potentiometric taste sensor with sensing electrodes with lipid–polymer membranes containing an inner electrolyte was proposed by Japanese scientists [16]. Since then, there have been many modifications of taste sensors. Various electrodes in different numbers were applied in the set of taste sensors for liquid food analysis, including qualitative analysis of water [19–22].

It was observed that the potentiometric taste sensor with electrodes containing the inner electrolyte and the lipid–polymer membranes could be applied for classification of selected soft drinks into groups with respect to CO_2 content [23]. In taste sensor elaborated in our laboratory, the electrodes with the inner electrolyte were replaced by all solid state electrodes (ASSEs) containing a conducting polymer as an ion to electron transducer and membranes modified with lipophilic compounds. The replacement of the inner electrolyte with the conducting polymer simplified application and maintenance of instrument [24]. Such taste sensor was applied to quantitative and qualitative analyses of drinking water [25].

In this paper the application of the elaborated in our laboratory potentiometric taste sensor with five ASSEs containing membranes modified with lipophilic compounds for the discrimination of selected drinking mineral water samples of varying CO_2 content was demonstrated. The effect of CO_2 content on ASSEs' taste sensor responses was also examined in the time lapse after opening the bottle of tested mineral water.

2. Experimental

2.1. Materials

Benzyldimethyltetradecylammonium chloride (BDMTACl) (98%, Sigma-Aldrich, Poznań, Poland), dodecyltrimethylammonium bromide (DTMABr) (98%, Sigma-Aldrich), palmitic acid (PA), stearic acid (SA) (>99%, Fluka, Poznań, Poland), phytol (P) (97% – mixture of isomers, Sigma-Aldrich) were used as compounds modifying polymer membranes. Dioctyl phenylphosphonate (DOPP) (Sigma-Aldrich) was used as a plasticizer. The monomer 3,4-ethylenedioxythiophene (EDOT) (Sigma-Aldrich, Poznań, Poland) and poly (sodium 4-styrenesulfonate) (NaPSS) (Aldrich) were used for ASSEs conducting polymer layer preparation.

2.2. Experimental set-up

The essential element of the taste sensor (Fig. 1) was a set of five ASSEs with different lipophilic compound – polymer membranes and a reference electrode (Ag/AgCl/Cl$^-$). They were immersed in a sample of the appropriate tested water. The potential responses of all electrodes were measured by the high-input impedance voltmeter Atlas Solich 0961 Multiplexer at 23°C ± 0.5°C. Measurement data were collected by computer.

2.3. ASSE electrodes preparation

The core of each ASSE was glassy carbon (GC) disc electrode. Polymerized 3,4-ethylenedioxythiophene (PEDOT) was deposited on the GC by the galvanostatic electrochemical polymerization from a solution composed of 0.01 M PEDOT and 0.1 M NaPSS at 850 mV. Subsequently, the GC/PEDOT layer of each electrode was coated with appropriate polyvinyl chloride membrane modified with lipophilic compounds: El.1 – benzyldimethyltetradecylammonium chloride, El.2 – dodecyltrimethylammonium bromide, El.3 – palmitic acid, El.4 – stearic acid, and El.5 – phytol.

The exact composition and ASSEs preparation with lipophilic compounds is given in Ref. [25]. The set of five ASSEs and reference electrode (Fig. 1) was conditioned for 24 h before measurement in 10^{-3} M KCl solution.

2.4. Tested samples

The mineral water Naleczowianka was chosen for the analysis by our potentiometric taste sensor. Two series of experiments were done. The first one involved qualitative analysis with the taste sensor of three types of Naleczowianka mineral water differed in CO_2 content: still, slightly sparkling (max. 1,500 mg CO_2/L) and sparkling (approx. 4,000 mg CO_2/L) [26].

The second type of the experiment concerned the investigation of CO_2 escape after opening the bottle of sparkling Naleczowianka. The measurements were run 0.1, 6, 24, 48, 72, 96, and 120 h after opening the bottle of tested water. Between measurements, the tested water was stored in the original polyethylene terephthalate bottles closed with the screw cap.

2.5. Calculation methods

The following mathematical methods were applied for the analysis of data collected by the sensor array: Principal

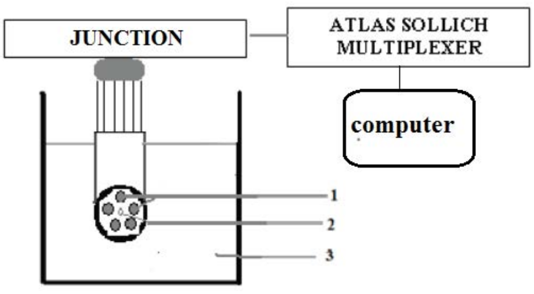

Fig. 1. Taste sensor experimental set-up: 1 – five ASSEs with appropriate lipophilic compound–polymeric membranes, 2 – Ag/AgCl/Cl – reference electrode, and 3 – tested water sample.

Component Analysis (PCA) and Agglomerative Hierarchical Clustering (AHC). Calculations were made with XLStat 19.7 computer software.

3. Results and discussion

The raw data obtained by ASSEs of the taste sensor for distilled water and Naleczowianka mineral water with different CO_2 content are presented in Fig. 2. Each axis represents responses of the particular electrode. As it can be seen the shapes of curves in the radar plot of each tested water are different. However, slight similarity in shape of curves of distilled water and Naleczowianka still mineral water could be noticed.

The most sensitive to composition of tested waters was electrode 5, while the electrode 3 was the least sensitive (Fig. 2).

The raw data (Fig. 2) were analyzed by PCA. The first two principal components explained 85.9% of the variability of the model (Table 1). The values of the variability explained by both PC 1 and PC 2 suggested that both components played a significant role in the model explanation.

Naleczowianka sparkling (no. 1) and Naleczowianka slightly sparkling (no. 2) waters were both characterized by negative PC 1 and positive PC 2 values (Fig. 3, Table 2). Naleczowianka still (no. 3) was positively correlated with PC 1 and PC 2. The point representing distilled water (no. 4) was characterized with the smallest, negative correlation with PC 1 and the highest, negative correlation value with PC 2 (Fig. 3, Table 2).

Factor loadings for ASSEs are also presented in Fig. 3. Electrodes El.2 and El.4 were positively correlated with both principal components (PC 1 and PC 2). El.1 was positively correlated with PC 1 and negatively correlated with PC 2 on the contrary to El.3 and El.5.

Table 1
Eigenvalues and variability explained by principle components in PCA analysis

Principal components	PC 1	PC 2	PC 3
Eigenvalues	2.485	1.811	0.705
Variability (%)	49.694	36.212	14.094
Cumulative (%)	49.694	85.906	100.000

Taste sensor electrodes' potential responses in tested carbonated mineral water in the time lapse after opening the bottle are presented in Fig. 4. It can be observed that ASSEs' responses differed significantly for water sample 0.1 h after opening the bottle (Fig. 4(a)) in comparison with other tested samples. The value of potential measured by El.1 decreased significantly for samples, which were exposed to longer contact with air (up to 24 h). However, this was not the case of El.1 responses for the latter type samples (Fig. 4(b)). The changes in responses of each of electrodes slightly differed in the range of 2%–5% and were significantly lower in case of samples having longer air contact time (Fig. 4(b)).

The raw values of potential responses of each ASSE were analyzed by PCA in order to identify the grouping of tested samples. The first two principal components (PC 1 and PC 2) explained 98.71% of the variability of this model (Table 3). This indicated on the existence of a strong pattern according to which data were arranged.

The results of PCA analysis of raw data (Fig. 4) are presented in Fig. 5(a). Groups are marked basing on the results of AHC analysis (Fig. 5(b)).

The point representing tested mineral water samples 0.1 h after opening the bottle (no. 1 in Fig. 5) was the only one located at the positive side of the axis PC 1 and negative side of PC 2 (Table 4). This point was at the considerable distance from the other points representing samples, which had longer contact time with air. Points representing tested mineral water 6 and 24 h after bottle opening (no. 2 and 3 in Fig. 5)

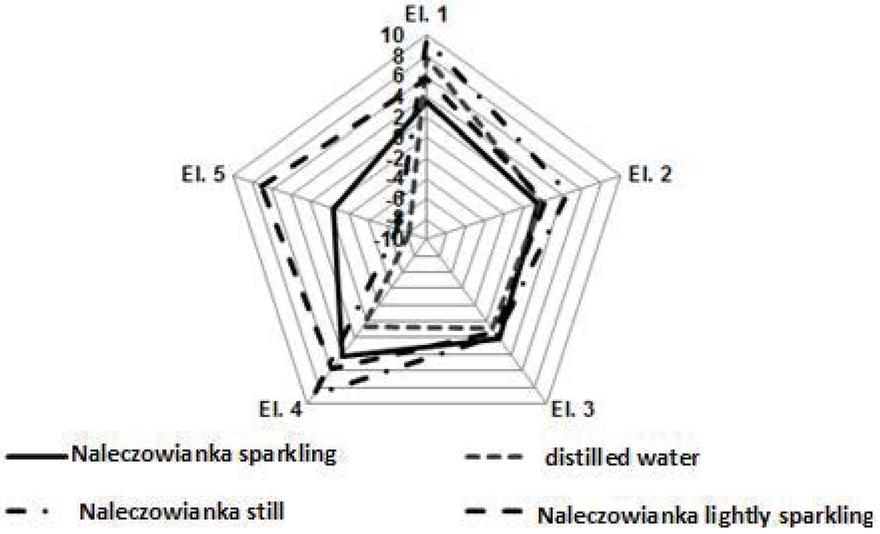

Fig. 2. ASSEs' responses in distilled water and Naleczowianka mineral water with different degree of CO_2 content; ASSEs with appropriate lipophilic compound: El.1 – benzyldimethyltetradecylammonium chloride, El.2 – dodecyltrimethylammonium bromide, El.3 – palmitic acid, El.4 – stearic acid, and El.5 – phytol.

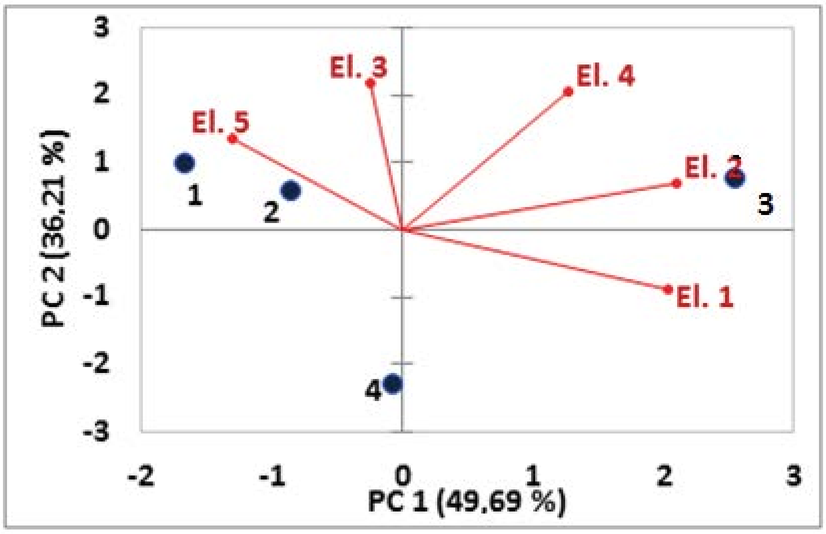

Fig. 3. Biplot for Naleczowianka of different CO$_2$ content and distilled water; 1 – Naleczowianka sparkling, 2 – Naleczowianka slightly sparkling, 3 – Naleczowianka still, 4 – distilled water; El.1, El.2, El.3, El.4, El.5 – ASSEs with appropriate lipophilic compound.

Table 2
Factor scores in PCA

	Tested waters	PC 1	PC 2	PC 3
1	Naleczowianka sparkling	–1.648	0.986	–0.983
2	Naleczowianka slightly sparkling	–0.843	0.562	1.338
3	Naleczowianka still	2.551	0.768	–0.196
4	Distilled water	–0.060	–2.316	–0.159

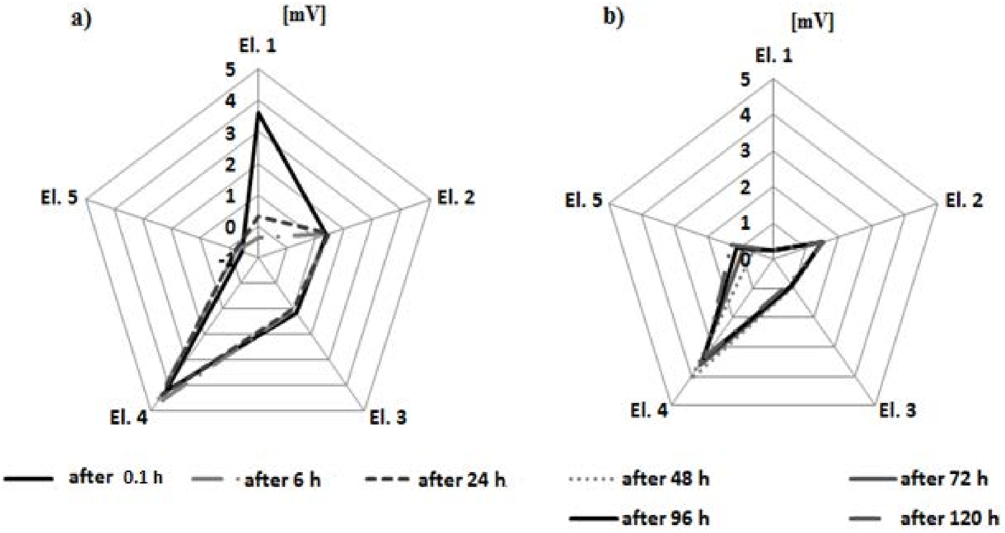

Fig. 4. ASSEs' responses in Naleczowianka sparkling mineral water in the time lapse after opening the bottle; El.1, El.2, El.3, El.4, El.5 – ASSEs with appropriate lipophilic compound: (a) after 0.1, 6, and 24 h; (b) after 48, 72, 96, and 120 h.

were grouped at the positive side of PC 1 and PC 2 axes (Fig. 5(a), Table 4). Other points (no. 4, 5, 6, 7 in Fig. 5(a)) representing samples of water with longer air contact time were located at the negative side of PC 1 axis.

According to AHC analysis, tested water samples were assigned to four groups (Fig. 5). The sample of the tested sparkling mineral water 0.1 h after opening the bottle (no. 1 in Fig. 5) created single one group. The samples of tested

Table 3
Eigenvalues and variability explained by principle components in PCA analysis

Principal components	PC 1	PC 2	PC 3	PC 4	PC 5
Eigenvalues	3.77	1.17	0.03	0.02	0.01
Variability explained (%)	75.37	23.34	0.63	0.45	0.21
Cumulative variability explained (%)	75.37	98.71	99.34	99.79	100.00

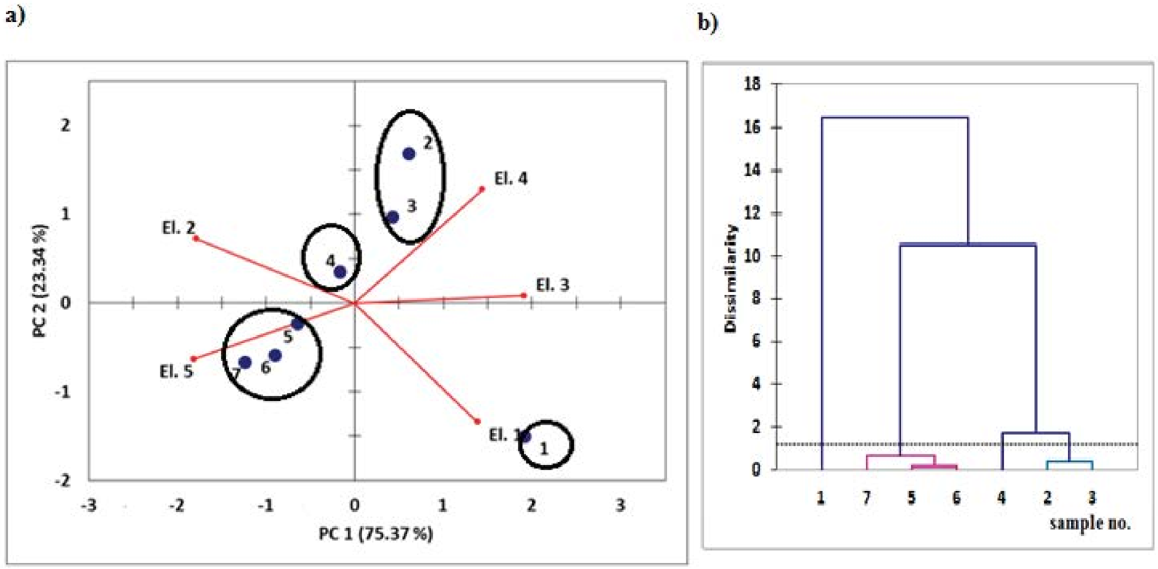

Fig. 5. (a) PCA biplot for Naleczowianka sparkling water in the time lapse after opening the bottle: 1 – 0.1 h, 2 – 6 h, 3 – 24 h, 4 – 48 h, 5 – 72 h, 6 – 96 h, 7 – 120 h; El.1, El.2, El.3, El.4, El.5 – ASSEs with appropriate lipophilic compound; (b) AHC analysis.

Table 4
Eigenvectors in PCA analysis

Sample no.	Time after opening the bottle (h)	Eigenvectors				
		PC 1	PC 2	PC 3	PC 4	PC 5
1	0.1	3.72	–1.63	–0.02	0.03	–0.01
2	6.0	1.18	1.81	–0.02	0.16	–0.13
3	24.0	0.83	1.05	–0.17	–0.27	0.07
4	48.0	–0.33	0.38	0.20	0.14	0.18
5	72.0	–1.25	–0.26	0.19	–0.10	–0.01
6	96.0	–1.75	–0.64	0.12	–0.09	–0.14
7	120.0	–2.40	–0.72	–0.31	0.13	0.03

water 6 and 24 h after opening the bottle belonged to the same group (no 2 and 3 in Fig. 5), which meant that their compositions were similar to each other. Tested water 48 h after opening the bottle (no. 4 in Fig. 5) created a separate group. The last group was created by the remaining samples (no. 5, 6 and 7 in Fig. 5). It suggested that the content of CO_2 in these samples of water did not differ significantly.

It should be also noted that the longer the time after opening the bottle was, the distances between points representing appropriate samples decreased.

Mean value of PC1 and PC2 distances between two neighboring samples from Fig. 5(a) as a function of time after opening the bottle are presented in Fig. 6.

The dependence between distance and time after opening the bottle in Fig. 6 could be described by the power curve (R^2 = 0.936). The decreasing distance between the points representing samples of tested water in PC 1 and PC 2 coordinates (Fig. 5(a)) as a function of time after opening the bottle corresponded to decreasing CO_2 relative content of the tested samples. For example, the mean relative content of CO_2 obtained at 0.1 and 6 h after opening the bottle was about eight times larger than that obtained at 96 and 120 h.

These results are in agreement with orosensory feeling that the most of CO_2 is released during the initial opening of the bottle of sparkling water.

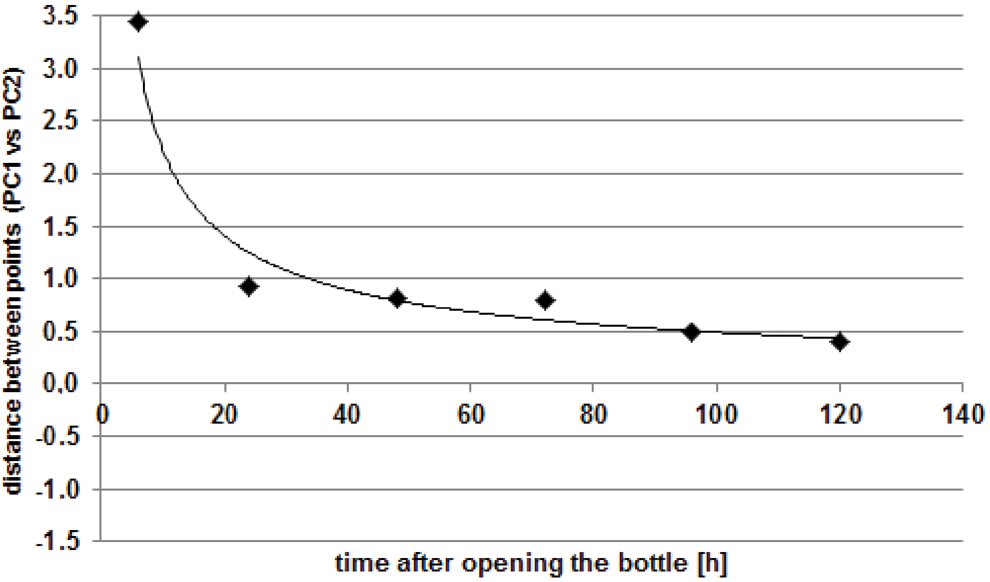

Fig. 6. Distance between the points representing samples of tested water in PC 1 and PC 2 coordinates (from Fig. 5(a)) as a function of time after opening the bottle.

4. Conclusions

The potentiometric taste sensor with ASSEs elaborated in our laboratory was applied for the discrimination of mineral water samples differing in CO_2 content. Three types of mineral Naleczowianka water were examined: still, slightly sparkling, and sparkling. Samples of sparkling Naleczowianka mineral water in the time lapse after opening the bottle were also investigated.

PCA and AHC analyses showed that samples of similar CO_2 content created the common groups. Distances between the points representing samples of tested water in PC 1 and PC 2 coordinates as a function of time after opening the bottle could be described by the power curve ($R^2 = 0.936$). These distances could be a measure of CO_2 content in tested water samples. The shape of obtained power curve was in agreement with sensory perception of CO_2 content after openings of the bottle of sparkling water.

This approach offers the opportunity to indicate on a sparkling water sample deviating from the standard due to, for example, poor storage conditions or a defective packaging, when an exact gas content is not necessary.

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