

Paper-Based Electronic Tongue

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Abstract: We present a low cost paper-based electronic tongue capable of discriminating forged water samples. System comprises of 4 paper-based potentiometric sensors (sensitive to Cl^- , Na^+/K^+ , $\text{Ca}^{2+}/\text{Mg}^{2+}$, NO_3^-) and a traditional Ag/AgCl reference electrode. Different electrode materials and methods of insulation were tested with best results obtained for pencil graphite and lamination. The

presented electronic tongue was able to distinguish tap and lake water from mineral water samples (PCA – Principal Component Analysis and KNN – K-nearest neighbour). In total 14 different water samples were used in this study. Sensors presented good signal repeatability, selectivity and reasonable sensitivity.

Keywords: Electronic tongue • Ion-selective electrodes • Lab-on-paper • Paper-based analytical device • Potentiometry

1 Introduction

Soft drink market worldwide is currently dominated by mineral waters [1]. Unfortunately bottled water can be easily tainted, by neglectful packaging, storage, or intentional substitution with tap water. Problems with bottled water not meeting generally accepted standards were already described in Asia including Bangladesh [2], India, China [3], Middle East: Iran [4], Africa: Tanzania [5], Nigeria [6] and South America: Brazil [7].

As the problem impacts mainly individual households and tourists and the samples are low cost and abundant sensing system that has the biggest chance of implementation should be inexpensive, easy to handle and widely applicable. Mineral waters from different sources can considerably differ in composition, also the type of contamination can be bacterial, inorganic or organic therefore it is difficult to name one sensor that could indicate adulteration. Electronic tongues comprising of several sensors can be trained to automatically distinguish samples from certain groups, and partially selective sensors make the analysis more robust. Potentiometric electronic tongues were already applied for the classification of beverages (milk, orange juices, beers) [8], analysis of fermentation process [9,10], even growth of cell cultures [11]. Numerous reviews about electronic tongue and electronic nose systems are already available in the Literature e.g. [12–14].


We chose paper as a base for our sensor matrix because of its unique structural and mechanical properties (lightness, flexibility, capillary action, high surface-to-volume ratio) and natural origin (biodegradability)[15]. Paper as a substrate for sensors has already become a subject of few review articles that include recent advances, methods of fabrication as well as the history of paper-based analyt[15–17]. Several paper-based potentiometric sensors were already presented, including: ion-selective electrodes for K^+ , NH_4^+ and pH[18], sensor for analysis of lithium ions in blood [19] and a potentiometric immunoassay [20].

Our work focuses on developing low-cost paper-based working electrodes, that is why we used a miniaturized Ag/AgCl reference electrode of traditional architecture. Having a stable, well characterized system we plan to include a paper-based reference in our future studies. During last year, few paper-based reference electrodes were proposed in the literature, including Ag/AgCl [21–24] and membrane electrodes [18]. Electrodes presented in this study are of solid-contact type(SCE) with polymer membranes, their advantages are the possibility of miniaturization and low-cost fabrication process but they can suffer from side reactions (chemical species penetrating the polymer) and may require intermediate transduction layer (e.g. conducting polymer) [25].

Accordingly to our knowledge no paper-based electrochemical electronic tongue was described until now, a fluorometric sensor array was presented recently by Feng et al. [26]. Ion-selective electrodes based on pencil graphite are already available [27] but till now not on paper. Our work presents a novel sensor matrix assembled from low cost, readily available substrates (paper, pencil, lamination sheet).

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2 Experimental

2.1 Chemicals and Equipment

Detailed composition of membranes is described in Table 1. $\text{Ca}^{2+}/\text{Mg}^{2+}$ selective electrode composition was elaborated and optimized basing on cited references for Ca^{2+} and Mg^{2+} membranes. Other electrodes were prepared without changes.

0.5 mL of tetrahydrofuran (THF) from Fluka was used as a solvent for the membrane components. *o*-NPOE (2-nitrophenyl octyl ether), DOS (bis (2-ethylhexyl)sebacate), TDMAC (tridodecylmethylammonium chloride), KTFPB (potassium tetrakis [3,5-bis (trifluoromethyl) phenyl] borate), TDMAN (tridodecylmethylammonium nitrate), PVC (polyvinyl chloride), TPPCIMn (*meso*-tetraphenylporphyrin manganese(III)-chloride complex), ETH 129 (calcium ionophore II), ETH 1117 (magnesium ionophore I), ETH 500 (tetradodecylammonium tetrakis(4-chlorophenyl)borate) were purchased at Sigma Aldrich.

A home-made Ag/AgCl reference electrode was used for all measurements. A Pt wire was inserted in the tip of a 3.5 cm glass capillary during its sealing, electrode was filled with a saturated KCl solution. Fabrication of the electrode was completed by immersing of a Ag wire with electrochemically deposited layer of AgCl in the KCl solution and affixing it in the capillary with a rubber stopper.

Preliminary experiments intended to optimize electrode architecture were conducted using a Metrohm Autolab Potentiostat. For the electronic tongue measurements we used a home-made system that consists of a multiplexer fabricated in our laboratory connected to a standard pH meter (Corning model 350). Together with a PC this system allows electrode multiplexing, control over agitation velocity and data acquisition. The multiplexer is based on an acquisition card (model ACL-8111 ADLink Technology) and an analogic switch (ADG201) with software written in VISUAL BASIC 4.0. Detailed architecture, schematics, and logical structure can be found in Reference [32].

2.2 Electrode Architecture

In each case membrane components as described in Table 1 were thoroughly mixed until homogenous (30 min to 2 hours) before casting on the electrode. Preliminary experiments were conducted with potassium selective membrane electrode.

Water samples are abundant thus it was not necessary to develop a flow through system. Sensor comprised of a paper slip with electrode and electrical path drawn on top. Membrane was spotted on the round electrode and the electrical contact was insulated by means of: wax, different types of glue, commercial liquid insulator, scotch tape or lamination. Basically, two architectures were tested, one where the tip of the paper slip was not insulated and dipped in membrane solution (Figure 1A), and another where membrane was spotted in an \varnothing 5 mm orifice in the insulation (two layers of membrane mixture 5 μL each) (Figure 1B). Architecture A proved to be difficult to insulate at the junction of membrane and electrode thus architecture B was chosen for further tests as the more reliable.

Silver ink and pencil graphite were used as the electrode material, but as the silver trail was prone to break on the flexible surface of paper, pencil was chosen. Electrodes

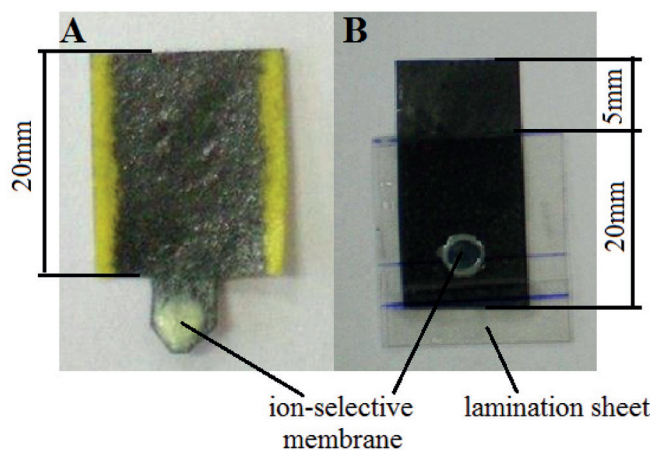


Fig. 1. Architecture of paper-based electrodes.

Table 1. Components used for electrode preparation.

Electrode type	Plasticizer	Lipophilic salt	Polymer	Ionophore	Conditioning solution	Calibration curve	Reference
Cl^-	<i>o</i> -NPOE 66.0 mg	TDMAC 0.08 mg	PVC 33.0 mg	TPPCIMn 1.0 mg	0.01 M NaCl	0.01 M $\text{NaNO}_3/0.1$ M NaCl	[28]
Na^+/K^+	<i>o</i> -NPOE 62.0 mg	KTFPB 2.05 mg	PVC 30.7 mg	valinomycin 0.2 mg; Ionophore X 5.15 mg	0.01 M NaCl, 0.01 M KCl	K: NaNO_3 0.01 M/ KNO_3 0.1 M; Na: KNO_3 0.01 M/ NaNO_3 0.1 M	[28]
$\text{Ca}^{2+}/\text{Mg}^{2+}$	<i>o</i> -NPOE 63.8 mg	KTFPB 0.6 mg	PVC 30.4 mg	ETH 129 1.3 mg; ETH 1117 1.0 mg	0.01 M CaCl_2 , 0.01 M MgCl_2	0.01 M NaCl, /0.1 M CaCl_2	[29,30]
NO_3^-	DOS 59.6 mg	TDMAN 0.4 mg	PVC 33.3 mg	ETH 500 6.67 mg	0.001 M $\text{NaNO}_3/0.01$ M NaCl	0.01 M NaCl/0.1 M NaNO_3	[31]
K^+	<i>o</i> -NPOE 65.0 mg	KTFPB 0.4 mg	PVC 32.6 mg	valinomycin 2.0 mg	0.01 M KCl	NaNO_3 0.01 M/ KNO_3 0.1 M	[29]

were drawn with a standard 6B pencil for several minutes to obtain steady resistance. Too long electrodes resulted in higher resistance and were more susceptible to insulation failures thus 20 mm was chosen as the path length.

As it comes to insulation, lamination was our method of choice as it is more easily available than liquid insulator, and easier to apply. We used standard office lamination sheets and hot roll laminator. Wax barrier would brake upon bending of paper. Different types of glue did not provide satisfactory insulation or in case of instant glue broke the electrical connection. Scotch tape would detach upon prolonged submersion in water.

To prevent absorption of water throughout the paper we impregnated the paper slips with wax before drawing the electrical connections.

From different types of paper used (office paper, Whatman no 1, Whatman no 3, carbon paper) best results were obtain for Whatman no 1. Thicker Whatman no 3 was prone to absorb water even when treated with wax, carbon paper suffered from problems with adherence of insulation. From office paper and Whatman no 1 the latter presented better sensitivity of K⁺ ion-selective sensors. We presume that better results were caused by higher surface of the graphite contact on the more fibrous Whatman no 1 paper.

The final electrode after optimization was constructed as follows:

- Wax was printed on both sides of Whatman no 1. paper by means of a Xerox Phaser printer;
- Sheet was heated to evenly spread the wax throughout the whole structure of paper;
- 25 × 10 mm slips were cut;
- Slips were drawn with a standard 6B pencil for several minutes to obtain steady resistance;
- 25 mm wide slip of the lamination sheet was cut and holes were made with a Ø 5 mm punch 8 mm from the bottom;
- Slips of paper were inserted in the lamination sheet and subjected to lamination;
- Separated electrodes were cut;
- Two layers of membrane mixture 5 µL each, were deposited in the orifice;
- Electrodes were conditioned in their respective solutions for at least 12 hours before measurement; Electrical connection was made by means of standard mini alligator clips.

3 Results and Discussion

3.1 Electrode Characterization

4 electrodes of each type (sensitive to Cl[−], Na⁺/K⁺, Ca²⁺/Mg²⁺, NO₃[−]) were prepared and left to condition in their respective solutions overnight (Table 1).

Types of ion-selective electrodes were chosen basing on highest differences of composition of mineral waters available on the market. Apart from that as it was already

reported by Ciosek et al. [28] better discrimination capability can be obtained in case of arrays containing both ion-selective and cross-sensitive sensors. Therefore we decided to use two ion-selective (Cl[−], NO₃[−]) and two cross-sensitive sensors (Na⁺/K⁺, Ca²⁺/Mg²⁺) thereby reducing the size and complexity of our system.

Four sensors of each type were prepared and a separate calibration curve was constructed for each sensor according to conditions resumed in Table 1. A representative dynamic response for each electrode type is presented in Figure 2, with respective sensitivities and standard deviation resumed in Table 2.

Sensitivity of our sensors is rather low as compared to theoretical (59.16 [mV/log(*a_x*)]), and to other paper-based potentiometric sensors presented by Novell et. al. [18,19] and by Whitesides group [23] (results resumed in Table 2). This fact can be attributed to rather high resistance of pencil graphite as compared to carbon nanotubes and silver used in aforementioned work. Sensors present good linearity in the range 10^{−5}–10^{−2} (higher range than sensors presented in [23]).

Selectivity coefficients were determined by the (SSM) separate solution method using 0.1 M solutions of inorganic salts: nitrates of appropriate cations and sodium salts in the case of anions. The solutions were buffered using 0.005 M MES (4-morpholineethanesulfonic acid monohydrate, Sigma Aldrich) with final pH adjusted with solutions of 0.1 M NaOH or 0.1 M H₂SO₄. The activities of ions in aqueous solutions were calculated according to the Debye–Hückel approximation. Tables 3 and 4 present selectivity coefficients of our electrodes together with examples from the literature. Our results are with good accordance with data obtained from other systems. It is also noteworthy that all sensors present cross-sensitivity, desired when working with electronic tongue systems. Sensors of this type mimic the taste buds of animals gen-

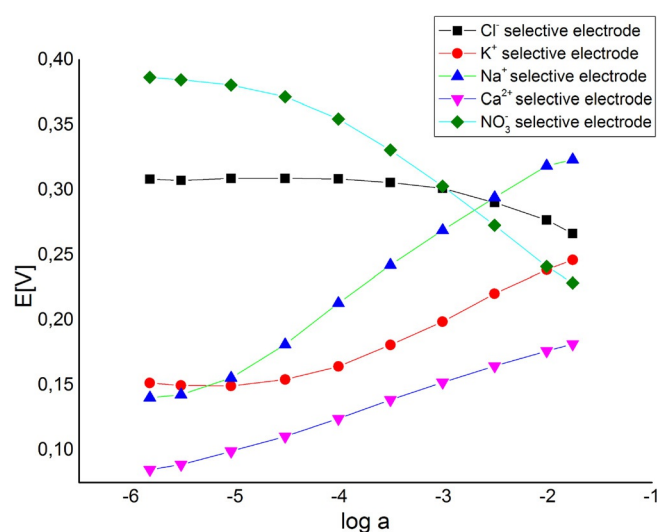


Fig. 2. Dynamic response of paper-based ion selective electrodes.

Table 2. Sensitivity of studied sensors. *SD* = standard deviation

Ion	Range (M)	Selectivity coefficients (mV/dec)	<i>SD</i> (<i>N</i> =4)	Sensitivity [23]
Na ⁺	1.2×10^{-5} – 1.3×10^{-2}	27.6	2.3	54.8
K ⁺	4.0×10^{-5} – 2.3×10^{-2}	18.8	0.9	54.9
Ca ²⁺	4.0×10^{-6} – 1.3×10^{-2}	12.6	1.2	22.9
NO ₃ [−]	4.0×10^{-5} – 2.3×10^{-2}	−25.5	2.1	–
Cl [−]	4.0×10^{-4} – 2.3×10^{-2}	−18.8	4.9	−61.8

Table 3. Selectivity coefficients of anion-selective paper electrodes.

Selectivity coefficient towards	Electrode type		Selectivity coefficients [29]	
	Cl [−]	NO ₃ [−]	Cl [−]	NO ₃ [−]
Cl [−]	0.00	−2.76	0.20	−2.07
Br [−]	0.14	−0.30	0.49	−1.18
NO ₃ [−]	0.72	0.00	0.00	0.00
F [−]	−1.57	−1.50	−0.80	−2.58
ClO ₄ [−]	1.49	3.28	1.72	2.34
SO ₄ ^{2−}	−1.53	−4.46	−1.85	−3.00

Table 4. Selectivity coefficients of cation-selective paper electrodes.

Selectivity coefficient towards	Electrode type		Sensitivity	
	K ⁺ /Na ⁺	Ca ²⁺ /Mg ²⁺	K ⁺ /Na ⁺ [35]	Ca ²⁺ [29]
Na ⁺	−0.17	−6.24	0.00	−3.79
K ⁺	0.00	−3.77	−1.20	−3.81
NH ₄ ⁺	−0.96	−5.42	−1.05	−3.66
Li ⁺	−0.68	−1.74	−1.55	−1.56
Mg ²⁺	−2.01	0.39	−2.05	−3.38
Ca ²⁺	−1.67	0.00	−1.85	0.00

erating great amount of complex data which are later analyzed using chemometric techniques [33,34].

Signal repeatability was also tested. In this case for each type of electrode two solutions of distinct activity of ion in question were prepared and measured alternately 3 times. Table 5 shows the medium of standard deviations for each electrode type. The calcium-magnesium selective electrode shows the lowest variations (~1 mV).

Signal repeatability test were conducted during a period of 4 weeks and no significant change in the electrode performance was noted, attesting their stability.

3.2 Electronic Tongue

9 different mineral waters from natural springs in Caxambu, Minas Gerais, Brazil and 2 commercial bottled mineral waters were obtained. As it can be seen in Supporting Information those samples show a great diversity with regard to the chemical composition. Apart from those, we obtained water from a lake in the city of Caxambu and two samples of tap water from distinct places in Campinas, Sao Paulo, Brazil that would represent the forged samples. Each from the 14 samples was divided in three parts and each part was measured separately. No recalibration of the sensors was necessary during the measurements. Samples were stored frozen until the day of mea-

Table 5. Signal repeatability for each sensor type. *SD* = standard deviation

Electrode type	Cl [−]	Na ⁺ /K ⁺	Ca ²⁺ /Mg ²⁺	NO ₃ [−]
SD (<i>N</i> =3) log <i>a</i> = −3.25	6.8 mV	10.8 mV	1.5 mV	4.2 mV
SD (<i>N</i> =3) log <i>a</i> = −2.25	4.6 mV	3.5 mV	0.6 mV	4.1 mV

surement and analyzed without pretreatment in random order during 3 consecutive days.

During measurement all 4 sensors (multiplexed) and reference electrode were placed in the sample, under stirring, signal was measured for 5 minutes to guarantee its stabilization.

Principal Components Analysis was conducted with the mean result obtained for each sample. Initial potential data was mean-centered to equalize the relevance of each factor. Chemometric analysis was conducted in Pirouette 3.11 (Infometrix).

PCA 1, 2 and 3 presented 86.7%, 9.5% and 2.3% of total information respectively. As it can be clearly seen on Figure 3 tap, and lake water samples present a separate cluster from mineral waters (more negative Factor 1). Samples similar in chemical composition are grouped close as in case of Mayrink I and III shown in the lower part of the graph. As it can be seen bottled mineral water

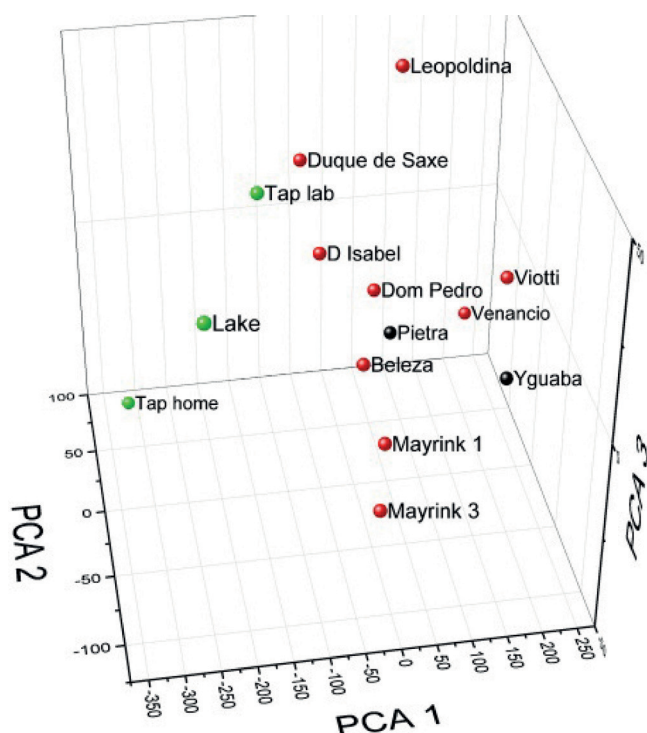


Fig. 3. PCA scores plot for all water samples, and all electrodes (green –tap and lake water, black –commercial, bottled mineral water, red –mineral water directly from spring).

and the one obtained directly from the spring do not form separate clusters.

Modeling power of all electrodes was almost equal ($K^+/Na^+ \sim 0.5$, other ~ 0.6). In scaled sensor response (graph not shown) NO_3^- sensor presented lowest standard deviation between the samples. PCA1 vs. PCA2 loadings plot (graph not shown) showed that NO_3^- electrode directs

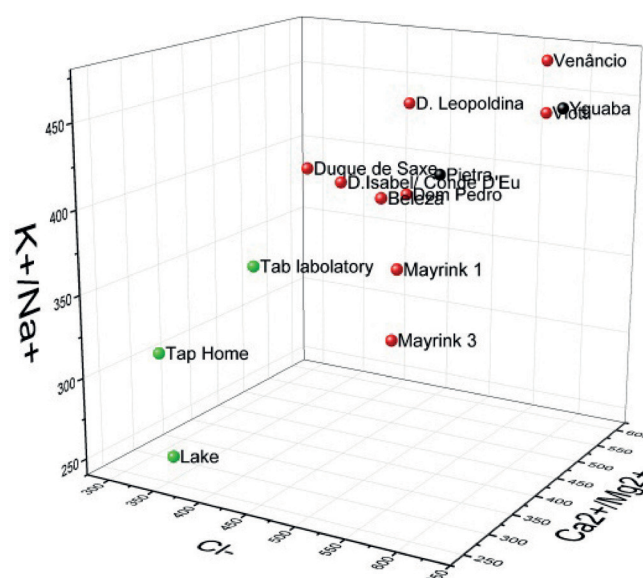


Fig. 4. 3D plot for all water samples, data without NO_3^- sensor (green –tap and lake water, black –commercial, bottled mineral water, red –mineral water directly from spring).

samples similarly to Cl^- , thus by removing this sensor more impact would be given to the other two.

Therefore data was analyzed without the NO_3^- sensor. With only 3 sensors left there is no need for dimensionality reduction and 3D graph can be constructed directly. As it can be seen in Figure 4 separation was not only still possible, but clusters became more pronounced without NO_3^- selective electrode.

To guarantee the correct classification of adulterated and not adulterated samples, KNN analysis was performed. Data was divided in two parts, first KNN analysis

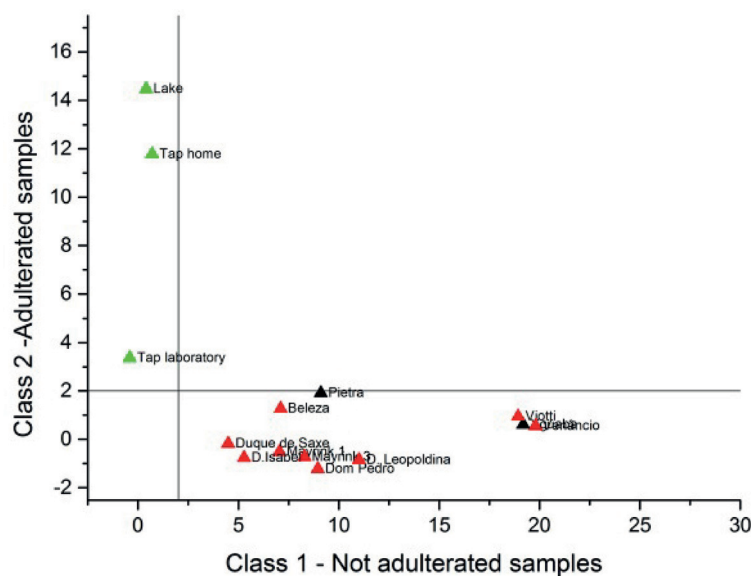


Fig. 5. KNN Class fit plot, data without NO_3^- sensor (green –tap and lake water, black –commercial, bottled mineral water, red –mineral water directly from spring).

was performed with 2/3 of the total data (28 samples, 3 variables, data mean-centered). In the next step this model was used to classify the remaining 14 samples. As presented in Figure 5 all samples were classified correctly.

4 Conclusions

We present a method of fabrication of potentiometric paper-based sensors, revising a wide range of materials. Those miniaturized sensors formed a paper-based electronic tongue capable of distinguishing different mineral waters and discriminating mineral water from tap or lake water samples. This kind of system would allow to verify adulteration of bottled water, even in cases when the type of possible adulteration is not known. Sensors presented in this work use readily available materials (paper, wax, lamination sheet, pencil). The sensitivity presented was not very high but sufficient for presented application. During the course of experiments it was noted that even better classification can be obtained with a reduced 3 sensor matrix (Cl^- , Na^+/K^+ , $\text{Ca}^{2+}/\text{Mg}^{2+}$) making the system even simpler and less expensive. All samples were correctly classified as adulterated or not adulterated by means of KNN algorithm. Potentiometry requires rather simple equipment as comparing with other electrochemical techniques, thus we can imagine that this kind of electronic tongue could use a smartphone based equipment as a reader. In the future necessary sensors could be integrated in a card that together with a connector and a smartphone application would allow to easily discriminate adulterated mineral water.

Supporting Information

Composition of mineral water samples used in this study is available in the Supporting Information

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