

REVIEW PAPER

## Evaluation of Tap Water Based on Sensor Array and Conducting Nanostructured Polymers

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### ABSTRACT

A sensor system, adapted to evaluate tap water, was fabricated and tested. Interdigitated gold-coated microelectrodes were covered with various conducting polymers, single or mixed, under several different conditions. Polymer films were laid down by a self-assembly technique and their impedance was analyzed over a range of frequencies from 1Hz to 1MHz. Samples collected from different localities at São Paulo state (Brazil) were used. The results of sensorial system analyzed by Principal Component Analysis had allowed completing discrimination of tap water samples. Good discrimination between the sensors was observed when there was obtained a PCA with different samples, obtaining the total variance (PC1 = 62.03%; PC2 = 37.97%) of the observations. The sensorial system based in global selectivity using interdigitated electrode and nanostructured conducting polymers allowed a statistical discrimination of sample waters of different locations. The future expectations are the upgrading of the system and implementation of a monitoring of tap water systems based nanostructured sensors.

**KEYWORDS:** *Nanostructured Conductive Polymer ; Sensorial System; Tap water*

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## INTRODUCTION

Concerning to management of aquatic resources, the importance of evaluation of water quality is undeniable. Electronic system using ultra-thin films of conducting polymers are generally fabricated by depositing a polymeric film onto interdigitated electrodes of predetermined configuration [1]. High sensitivity is achieved when interdigitated electrodes are coated with nanostructured thin films (~2 nm thick per deposited layer), which are able to detect very small changes in conductivity and dielectric properties of the materials comprising individual sensing units in contact with a liquid medium [2]. It was shown that low levels of impurities in water could be detected and

discriminated [3-6].

The sensor array in these systems produces signals, which are not necessarily specific for any particular species in the environment, but a signal pattern is generated, which can be related to certain features or qualities of the sample. These qualities can be determined by a computer programmed to recognize the class of response patterns related to the sample, environment, etc. [3].

The use of electrochemical sensors (“electronic tongues”) based on the concept of global selectivity to analyze the composition of the beverage [7] has been presented as a promising tool, discriminating characteristics proper to the human palate as acidity, salt, candy and bitter taste. Sensors based on this

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concept have been used in environmental analyses [8] and water quality control [9], being an efficient tool of monitoring. Consolin Filho et al. (2008) [10] showed a sensor system as a new method to identify and classify water samples according to their level of eutrophication. Carvalho et al. (2006) [11] presented the sensitivity of conducting polymers in the fabrication and assembly of a sensor system capable to detect by-products of water disinfection, such as chloroform, that exhibit carcinogenic properties.

The objective of this work was the use of electrochemical sensors for tap water discrimination based on electrochemical impedance. Waters samples collected from different localities and regions at São Paulo state (Brazil) were used. This paper describes a new proposal for evaluation and differentiation of the tap water from different locations, through a sensorial system based on global selectivity observed by an array of interdigitated microelectrodes coated with ultra-thin films conducting polymers.

## MATERIAL AND METHODS

### Ultra-thin Films of Conductive Polymer

The polymers used for film fabrication were polyaniline (PANI), poly(o-ethoxyaniline) (POEA), aquatic humic substances (AHS) and sulfonated lignin (SL). PANI and POEA were chemically synthesized as described in references [12-14]. The PANI was synthesized analogously to the synthesis method of MacDiarmid, A.G. et al. [12]. The POEA was synthesized using ammonium peroxydisulfate, 1.0 mol L<sup>-1</sup> hydrochloric acid at 0 °C and excess of monomer according to the method described in the literature [13-14]. The sulfonated lignin (SL) was obtained from Melbar (Brazil). The solution was prepared under the same conditions of concentration, volume and pH of the solution of POEA. The AHS were isolated from a water sample collected from River João Pereira, which is a tributary of the River Itapanhaú, close to the city of Bertioga, on the south coast of São Paulo state, Brazil [15]. The extraction and fractioning were made according to procedures established by the International Humic Substances Society [16], as well as recommendations by Malcolm [17]. The AHS solutions were prepared in the concentrations of 5, 10 and 30 mg L<sup>-1</sup>. All the aqueous solutions of POEA, SL and AHS were prepared using ultra pure water from a Milli-Q system (Millipore®). The pH

was adjusted by adding amounts of HCl 0.1 mol L<sup>-1</sup> or NH<sub>4</sub>OH 0.1 mol L<sup>-1</sup>. The substrate used to obtain the SA film of POEA was Suprazil® quartz previously washed according to the method described by Kern [18]. The details for film deposition for the sensing units are presented in Table 1, while the experimental setup for sensing is depicted in Fig. 1. Ten sensing units were produced as follows: i) Sensor 1 (S1): without film; ii) Sensor 2 (S2) had one layer of POEA deposited from a pH = 5 solution onto the electrode; iii) Sensor 3 (S3): a bilayer of POEA and SL (POEA/SL), with each layer being deposited for 3 min.; iv) Sensor 4 (S4): one layer was deposited from a complexed mixture of POEA and SL (in the same solution) (POEA+SL); v) Sensor 5 (S5): one layer of SL deposited for 3 min. (SL); vi) Sensor 6 (S6): one bilayer of AHS and POEA, with each layer being deposited for 3 min. (AHS/POEA); vii) Sensor 7 (S7): one layer obtained from a complexed mixture of POEA and AHS (POEA+AHS); viii) Sensor 8 (S8): one layer deposited from a PANI solution at pH = 5.0 (PANI); ix) Sensor 9 (S9): one layer deposited from a AHS solution (AHS); x) Sensor 10 (S10): one bilayer of PANI and SL, with each layer being deposited for 3 min. (PANI/SL).

Table 1. Sensing units in the sensor array to analyze drinking water

Sensing Unit	Type of Material
S1	Without film
S2	POEA
S3	POEA/SL
S4	POEA+SL
S5	SL
S6	AHS/POEA
S7	POEA+AHS
S8	PANI
S9	AHS
S10	PANI/SL

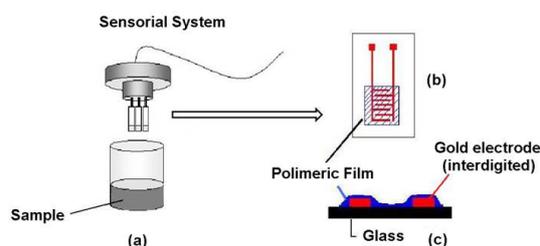


Fig. 1. (a) Diagram illustrating the sensing system [8] and schematic representation of a pair of interdigitated electrodes covered with polymeric film for use as a sensor. (b) front view; (c) side profile

### Experimental Details

The polymer nanostructured films with different architectures were deposited onto the interdigitated microelectrodes of glass-coated gold using the layer-by-layer (LbL) technique [19-23].

The layer-by-layer (LbL) technique [21-22], corresponding to immersion of treated substrate in the solutions of interest: solution containing POEA to obtain layers of POEA; POEA and LS solution alternately to obtain bilayer POEA / LS, and so on with other solutions. The layers were deposited with an immersion time of 3 min. per layer, from aqueous solutions at pH = 5.0 and concentration  $10^{-3}$  mol L<sup>-1</sup>, with the exception of PANI that was dissolved in NMP (N-Methyl-2-Pyrrolidone), with concentration of  $10^{-3}$  mol L<sup>-1</sup>. In the drying the substrate was used air or nitrogen. The analysis was carried through by electrochemical impedance using the Solartron impedance analyzer, SI 1260, being this interface to a microcomputer for the data acquisition. The frequency and the amplitude of the signal had been fixed in 1 kHz and 50 mV, respectively, after a study of performance of each sensor.

The treatment of the electrochemical data had been made by principal component analysis (PCA). PCA is a mathematical transform that is used to explain variance in experimental data. This mathematical tool allows discriminating different samples of origin in bi-dimensional graphs, locating each sample in a specific quadrant. This discrimination allows creating a database where the electrochemical characteristics will be associated

to the physicochemical results [24-26]. The data were interpreted with an equivalent circuit, from which the capacitance of the film was chosen as the variable to be treated with principal component analysis (PCA), using StatSoft Statistica version 10.0. Values are determined for pH, dissolved oxygen, conductivity and temperature of the samples using a WTW probe Multiparameter Multi340i model. The turbidity was determined using a portable microprocessor turbidity meter HI 93703 model (Hanna Instruments) and the residual chlorine was determined using a portable meter HI-95711 model (Hanna Instruments).

### Hydrographic Conditions and Location of Collection Areas

The tap water samples were collected at different locations in the state of São Paulo, Brazil. One sample was collected in the Pardo River (URGHI 4), localized in the Caconde municipality (21°31'44" S and 46°38'38" W), while others were collected in São Carlos (22° 01'04" S and 47°53'27" W) and Araraquara (21°47'38" S and 48°10'33" W) municipalities, in the Tietê-Jacaré watershed (UGRHI 13, Fig. 2). According to the Sao Paulo Environmental Sanitation Technology Company (CETESB), the Pardo watershed showed in 2011 ultraoligotrophic and oligotrophic characteristics, whereas Tietê-Jacaré basin presented also super-eutrophic characteristics in the same period [27]. Water samples were stored in plastic bags, refrigerated, and taken to the laboratory for subsequent analysis. All analysis occurred in triplicate.

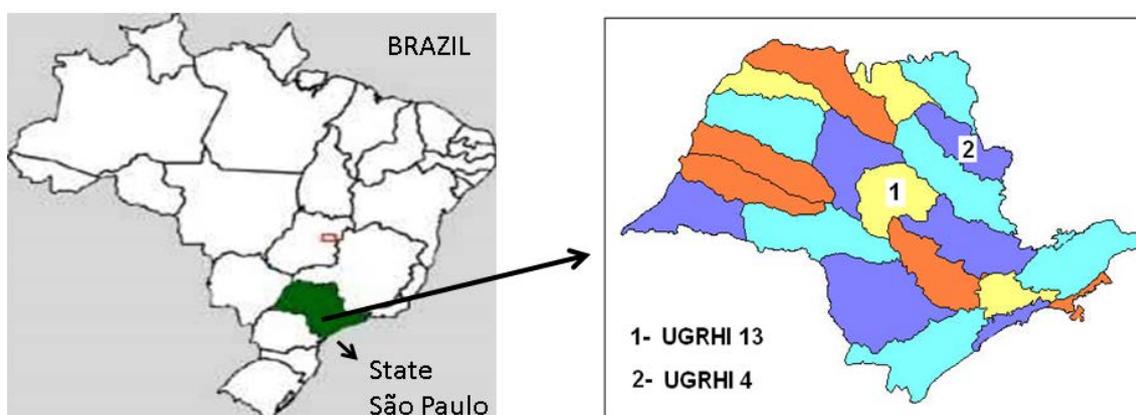


Fig. 2. Basin Management Units Water Resources (UGRHI) of the State of São Paulo – Brazil

## RESULTS AND DISCUSSION

### Physical Chemical Parameters of Water Samples

The physical chemical characteristics obtained for the tap water samples collected in different localities are describe in Table 2.

Comparing the data in Table 2, there was little variation for different parameters analyzed and between samples. In all samples the results demonstrated situations in accordance with Ordinance No. 2,914, of 12/12/2011 - Ministry of Health, given the quality standard required [28].

The disinfection method used in the samples in question is chlorine. It is observed in the data of Table 2, different values for the residual chlorine, which is greater for the samples from the city of Caconde / SP. Comparing these data with those obtained for the redox potential, it is observed that the sample with the highest concentration of disinfectant residual, also showed a higher value for the redox potential. When placed in a solution containing an oxidizer, such as chlorine, a measureable potential develops, which varies with the concentration of the oxidizer. This factor is dependent on the ratio of oxidized to reduced species of chlorine in solution. These results are in agreement with literature data [29-30].

### System Response to the Various Water Samples Water Analyses

Fig. 3 shows the response of the sensor system to the sample of ultrapure water. Plotting the score factors on the same PC1-PC2 plan, Fig. 3, we can observe excellent discrimination between the sensors. It was observed the formation of two distinct groupings in Fig. 3. To the grouping I, are the sensors of polymer nanostructured films with architectures deposited especially with mixtures complexed and bilayers. In grouping II, the sensors with architectures deposited natural polymers isolated of sulphonate lignine and humic substances, sensors 5 and 9 respectively. Sensor S1 corresponds to the reference microelectrode, that is, without film.

The PCA analysis showed values for first and second component representing about 100% of the total variance (PC1 = 85.91%; PC2 = 14.09%) of the observations. These results suggest that the sensors respond in a selective form, when in contact with samples water. With the application of the PCA, it was possible to notice a clear separation between the different types of polymer deposition and conditions, on the interdigitated microelectrodes. The sensors present good stability, reproducing the results.

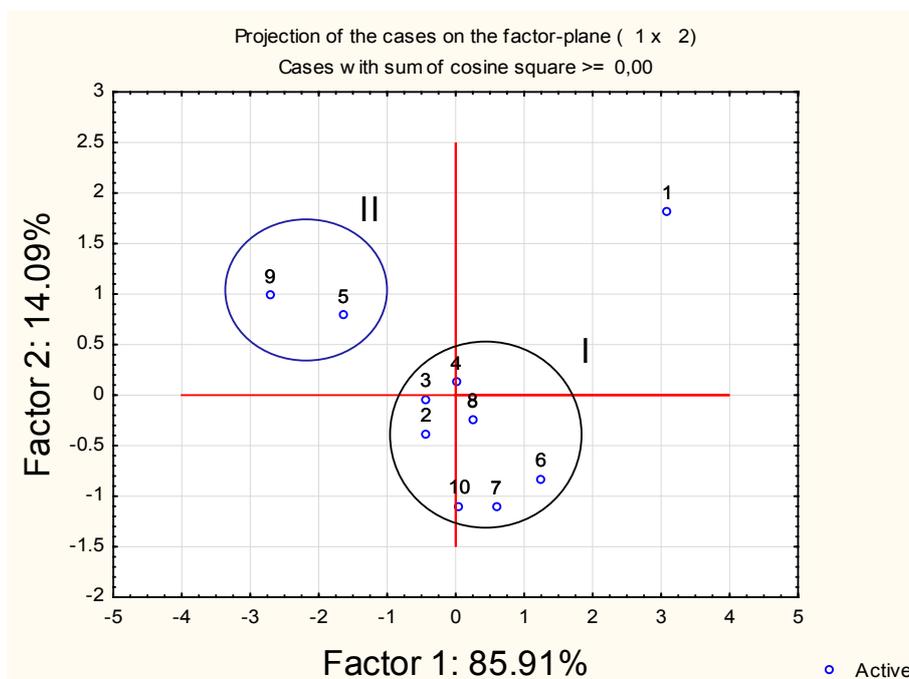


Fig. 3. PCA obtained for the sample of ultrapure water, regarding sensors with different polymeric complexes deposited over the interdigitated microelectrodes

Table 2. Physico-chemical variables from water samples collect at three different localities

Variable	MPV*	São Carlos	Araraquara	Caconde
Temperature (°C)	-----	21.90 ± 2.12	20.40 ± 1.35	19.50 ± 2.55
pH	6.0 - 9.5	7.6 ± 1.13	7.5 ± 1.24	7.2 ± 1.13
Electrical Conductivity ( $\mu\text{S cm}^{-1}$ )	-----	75.2 ± 1.32	69.9 ± 1.21	83.8 ± 1.31
Residual chlorine ( $\text{mg L}^{-1}$ )	0.2-5.0	0.38 ± 0.09	0.33 ± 0.07	1.05 ± 0.12
Turbidity (FTU)	5.0	0.25 ± 0.09	0.19 ± 0.06	0.38 ± 0.09
Dissolved Oxygen ( $\text{mg L}^{-1}$ )	$\geq 6$	7.84 ± 0.12	8.47 ± 0.08	6.85 ± 1.05
Redox Potential (mV)	+380	222,13±0,44	228,22±0,65	265,26±0,98

\* Maximum permitted value (MPV), according to the Brazilian rules (Conama Resolution, # 357) [27]

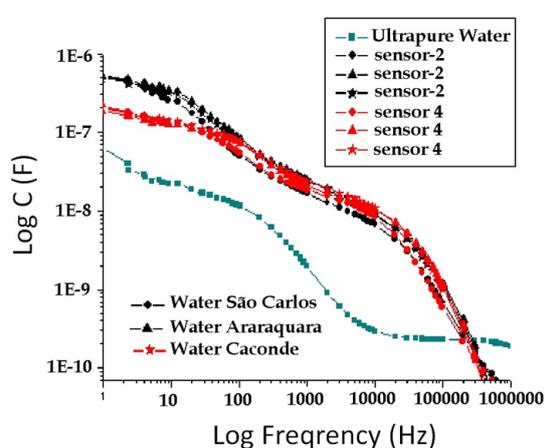


Fig. 4. Log of Capacitance (C / Faraday) as a function of the log of Frequency (Hz) for the sensors 2 and 4, as examples

Fig. 4 shows the frequency dependence of film capacitance for some of the sensing units (numbered according to the specifications in Table 1) immersed into tap water samples. As expected for films immersed into liquid samples, the capacitance decreases monotonically with the frequency [31]. Especially at lower frequencies, the electrical response of the sensing units differs from each other, which is useful for building a sensor array with high discriminating power for similar liquids. The low frequency region is dominated by the double-layer effect, while at the region between  $10^2$  and  $10^4$  Hz appears to be dominated by the effects from the nanostructured thin film used to coat the gold interdigitated electrodes. At frequencies higher than  $10^5$  Hz, the impedance of the system is dominated by electrode geometric capacitance [3].

The coating of the interdigitated gold electrodes with different materials resulted in the formation of a distinct electrical signal pattern, which is

characteristic of the substance being investigated. Therefore, to optimize the performance and specificity of the sensor array, it is essential to obtain the electrical impedance in various frequencies ranges and plot the data in a way that facilitates identification of main features such as the relaxation peaks in the loss tangent versus frequency [32]. The frequency and the amplitude of the signal had been fixed in 1 kHz and 50 mV, respectively, after a study of performance of each sensor.

Each electrode coating has a specific electrical response for a water sample and gives a distinct signal. Consequently, the sensor array can be used as a fingerprint to detect waters with different composition. The samples had been evaluated using ten sensors and the results of impedance analyzed for PCA. The sensorial set was capable to differentiate the three samples due the varied chemical composition of the sample that interacts of different form with the polymeric films, producing different values of impedance in each sensor as observed in the Fig. 4. The principal component analysis showed that the eigenvalues of the two first principal components represent 100% of total variance ( $PC_1 = 74.15\%$ ;  $PC_2 = 25.85\%$ ) of the observations.

Plotting the factors scores on a  $PC_1$ - $PC_2$  axes plane (Fig. 5), can be observe excellent discrimination of the water samples. Possibly groups have been constituted on the basis of electrical conductivity (proportional to ion concentration in medium) of the samples (concentration of nutrients and other chemicals). The sensor array have good stability, reproducing the results of water samples collected. The sensors allowed discrimination of the samples from different locations, subjected to the same type of treatment, i.e. with chlorine as the disinfecting agent. The discrimination is possibly associated

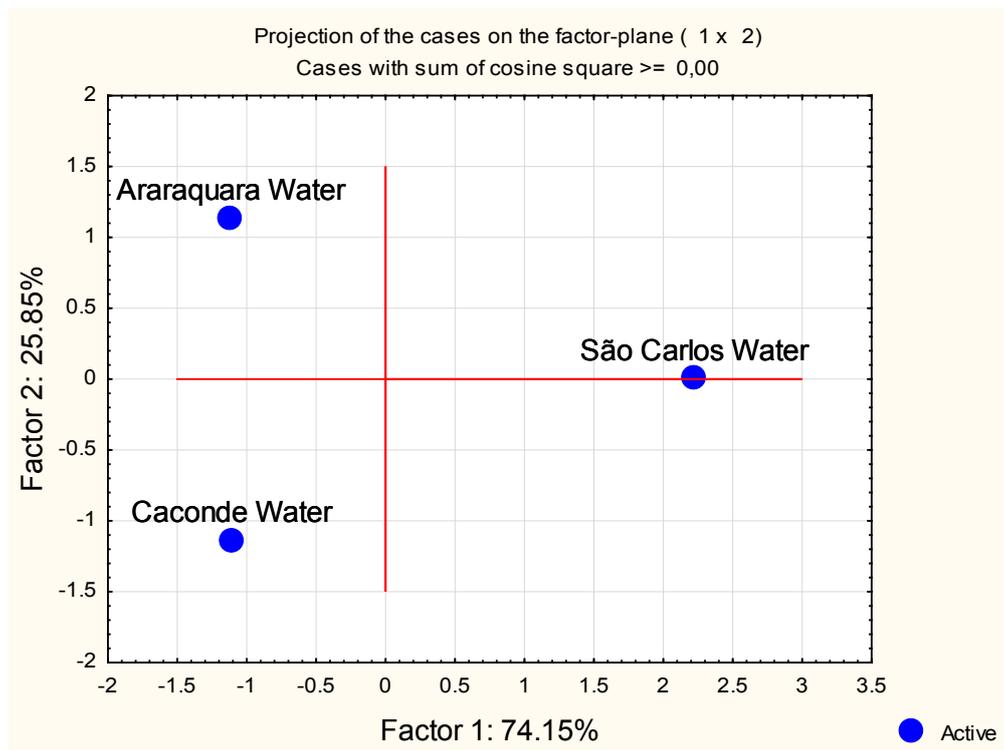


Fig. 5. PCA for the 3 samples tap water, using capacitance data at 1 kHz

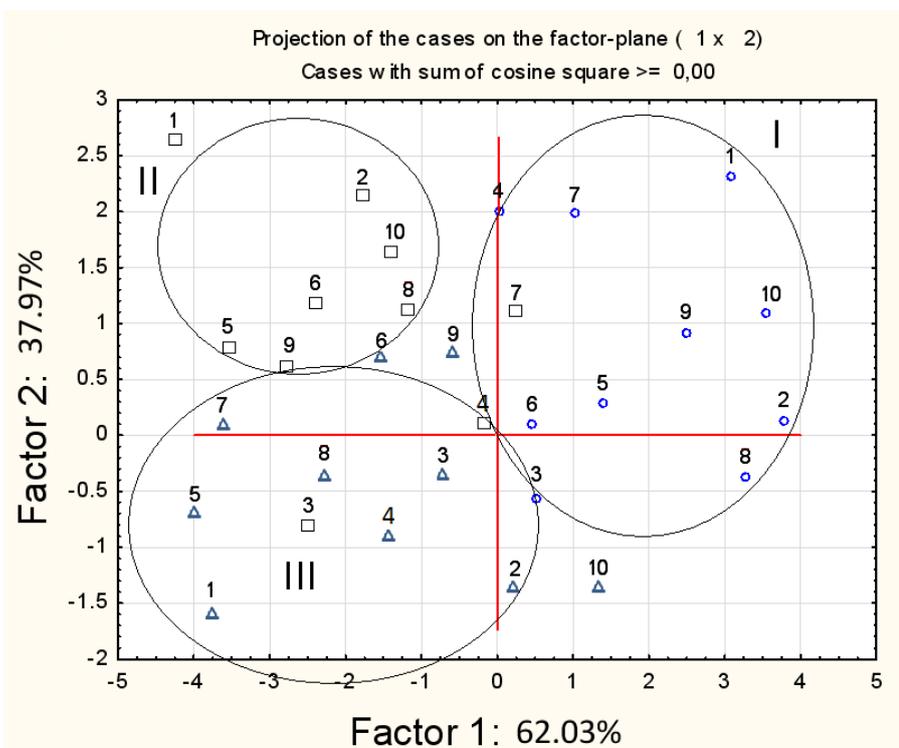


Fig. 6 PCA obtained for the sensors relative to the different polymeric complexes deposited over the interdigitated microelectrodes with the physical-chemical parameters obtained for each sample

with the physical-chemical characteristics of each sample of tap water.

Fig. 6 shows the PCA obtained taking into consideration the physico-chemical variables presented in Table 2 for the different samples. Plotting the score factors on the same PC1-PC2 plan (Fig. 6), we can observe good discrimination of the sensors. The PCA analysis showed that the values for first and second component represents 100% of the total variance (PC1 = 62.03%; PC2 = 37.97%) of the observations. According to the results, we can observe the formation of the three (3) distinct groupings. In grouping I, are the sensors of polymer nanostructured films with the sensory response corresponds to the physical-chemical parameters relating to the water sample São Carlos; in grouping II, to the water sample Caconde and grouping III of the Araraquara respectively. Possibly groups have been constituted on the basis of electrical conductivity (proportional to ion concentration in medium) of the samples (concentration of nutrients and other chemicals).

## CONCLUSIONS

The sensorial system based in global selectivity using interdigitated electrode and nanostructured conducting polymers allowed a statistical discrimination of sample waters of different locations. The polymeric films interact differently with each compound present in the water, and allow different signals for each sample. The use of electronic tongue for evaluation the sample water appears promising. Further tests are required but, future expectations are the upgrading of the system and implementation of a monitoring of tap water systems based nanostructured sensors.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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