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Detection of Soluble Organic and Inorganic Compounds with an Array of Pure and Blended Optical Reporters

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Abstract

The issue of detecting harmful compounds in water may be approached in different ways, ranging from analytical methods to chemical sensor arrays. Optochemical sensors offer the advantage of being a simple and effective method for online monitoring of the parameters of interest in water solution. The core of an optochemical sensor is represented by a dye that changes colour upon the interaction with analytes. In this work, we used porphyrins, pH indicators and their mixtures to prepare the colorimetric sensor array for the analysis of ionic salts and organic compounds in water. The colour changes of sensing dyes exposed to an aqueous solution containing target compounds were read out with a system consisting of a computer screen (light source) and a digital camera (detector). Beyond the detection of metallic salts, nitrites, nitrates, phosphates, and organic compounds, we found that the array can recognize creatinine and urea, two markers of kidney functionalities.

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Keywords: colorimetric sensor; porphyrin; pH indicator; water;

1. Introduction

The matter of environmental pollution is increasingly felt in our everyday life, and from this arise the need for simple methods that may be available for the community to detect the presence of toxic or noxious compounds in

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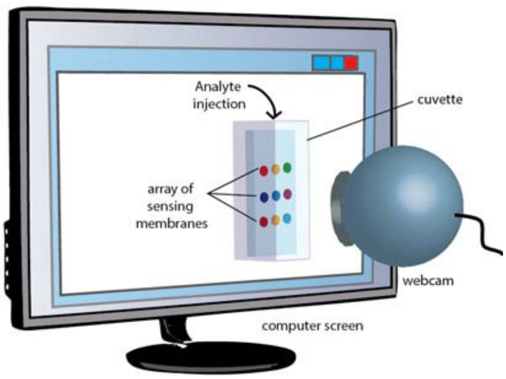
the surrounding environment. Chemical sensors may represent the solution, as they allow for evaluating the composition of gas and water. Depending on the transduction principle, these sensors offer different advantages. Optical transduction offer a straighforward way for the continuous monitoring of target parameters in gas and water [1]. Among those, we already demonstrated that a computer screen used as light source and a webcamera that serves as detector can become an effective transducer for arrays of colorimetric dyes [2]. This setup is known as Computer Screen Photoassisted Technique, and its core is represented by an array of chromophores that undergo a colour change when interact with chemicals. Porphyrins and their many metal complexes have been widely used as ionophores in potentiometric ion selective electrodes (ISEs) [3], and due to their peculiar optical properties and ligand characteristics are versatile molecules for opto-chemical sensors [4]. On the other hand, pH indicators are extensively used for measuring through the colorimetric change alkaline or acid ions [5]. However, these dyes may not provide a sufficient pattern of selectivity for certain types of samples. Then, our research was addressed to find out novel sensing dyes in order to enlarge the number of detectable chemical molecules. In this work, beyond the sensing features of porphyrins and pH indicators, we complemented the array with hybrid materials formed by blends of porphyrins, pH indicators, and lipophilic salts. As a proof of concept, the array was tested with a set of inorganic salts, whose cations are potentially dangerous for human health, and with organic molecules of interest for clinical diagnosis such as urea, creatinine and amines. As demostrated by the final data analysis, the array can detect both ionic metals and organic compounds, providing a method to design specific sensor array with enhanced sensing capabilities.

2. Experimental

In our experimental arrangement, the colorimetric array consists of a set of eigth sensing dyes in a polymeric solid state layer onto a glass substrate. The glass slide is inserted in a 3 ml plastic cuvette, containing the solution to be analyzed. During the measure, the cuvette is illuminated by means of the computer screen, meanwhile a webcamera captures the pictures of the sensing layers and records them in a video stream. A schematic drawing of the system used for the measurements is provided in figure 1.



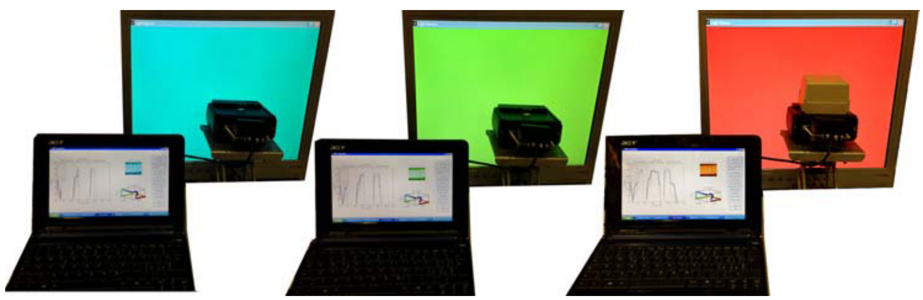


Fig. 1. (a) Schematic drawing of the arrangement used for the measurements (b) actual aspect of the experimental setup with different illuminating colors.

The sensing membranes are prepared dispersing in tetrahydrofuran solvent a plasticized polyvinylchloride (PVC), with the following composition: PVC 33%wt, Dioctyl sebacate (DOS) 66%wt, chromophore 1%wt. When present, the lipophilic salt was in concentration 1%wt. The membranes composing the array are listed in Table 1.

Table 1. List of sensing membranes in the array.

#	Sensing dye	Acronym
1	Bromocresol Purple	BCP
2	Manganese-Tetraphenylporphyrin	MnTPP
3	Zinc-Tetraphenylporphyrin	ZnTPP
4	Phenol Red + tridodecylmethylammonium chloride	PR + TDMAC
5	Bromocresol Purple + tridodecylmethylammonium chloride	BCP + TDMAC
6	Manganese-Tetraphenylporphyrin + Bromocresol purple	MnTPP + BCP
7	Manganese-Tetraphenylporphyrin + tridodecylmethylammonium chloride	MnTPP + TDMAC
8	Manganese-Tetraphenylporphyrin + potassium tetrakis (4-chlorophenyl)borate	MnTPP + TpClPBK

The sensing layer was immersed in a buffer solution at pH 5.5, composed of *2*-(N-*morpholino*)ethanesulfonic acid (MES) 0,01 M. Measures were performed in buffer in order to avoid any influence in the response due to a variation of pH. Increasing concentrations of analytes are obtained through subsequent injections of mother solutions at higher concentration. The sensing layer is illuminated with a rainbow of color sequence that ranges from blue to red color.

3. Results and discussion

Data are extracted from the video stream calculating the average intensity of primary colors (red, green and blue) in selected regions of interest, for each illuminating color window. The three contributions in red, green and blue filters are concatenated to obtain a single vector for each indicator and for each measure, as depicted in Fig. 2a for the representative example of ZnTPP. In this case, the increase of creatinine concentration results in a decrease of the transmitted light. Figure 2b shows the response curve of the whole array to urea. The response is calculated as the sum of the red, green and blue components and it is normalized subtracting the value acquired in the buffer reference solution.

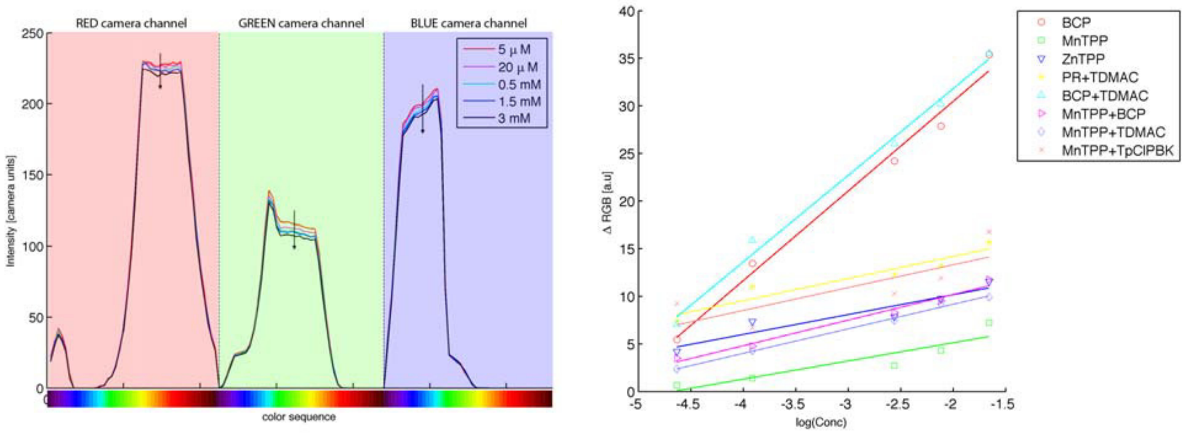


Fig. 2 (a) Response of ZnTPP (membrane #3) to increasing concentration of creatinine under the illuminating color sequence. (b) Response curve of the whole array to urea.

Among the advantages of using such optical platform, there is the possibility of reading out simultaneously the color changes underwent by a large number of indicators. In this way, we can exploit the basic concepts of the electronic nose, combining the array of sensitive spots with a tool of pattern recognition for multivariate data. Then, through an explorative data analysis method, such as Principal Components Analysis, we are able to obtain a representation of the space of measurements that allow for evaluating the capability of the array to recognize different compounds. The scores plot in Fig. 3 shows the clusters formed in data, and evidences that it is possible to distinguish different compounds both organic and inorganic.

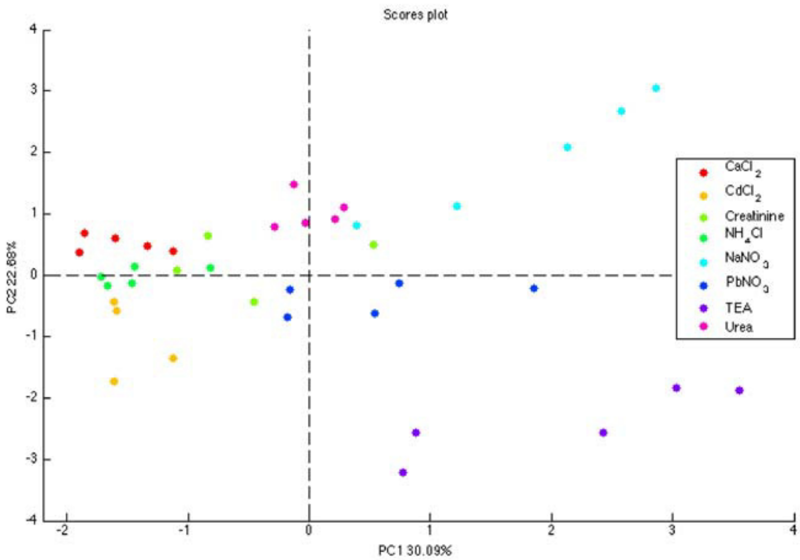


Fig. 3 Scores plot of all data. The analyzed compounds are inorganic compounds: $CaCl_2$, $CdCl_2$, NH_4Cl, $NaNO_3$, $PbNO_3$. Organic compounds: urea, creatinine, and triethylamine (TEA).

4. Conclusions

The colorimetric array consisting of porphyrins, pH indicators and hybrid material composed on their mixtures together with lipophilic salts, offers the possibility to detect dangerous species in water as well as organic compounds of interest for clinical diagnosis. The sensor array can be easily read out with a setup consisting of a computer screen and a camera, providing a method for online monitoring of chemical content in water solution.

4. Acknowledgment

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