OPTICAL SENSORS CROSS-SENSITIVITY AMENDMENT: THE CASE STUDY OF HEAVY METALS CSPT DETECTION

L. Lvova[1,2], P. Galloni[1], B. Floris[1], C. Di Natale[3], I. Lundström[4], V. Lippolis[5], A. Garau[5] and R. Paolesse[1].
[1]Department of Chemical Science and Technologies, University "Tor Vergata", Rome, ITALY
[2]Faculty of Biology and Soil Science, St. Petersburg State University, St. Petersburg, RUSSIA
[3]Department of Electronic Engineering, University "Tor Vergata", Rome, ITALY
[4]IFM, Linköping University, SWEDEN
[5]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Monserrato, ITALY

ABSTRACT

5,10,15,20-Tetraferrocenyl porphyrin (**PFc$_4$**) and coumarin-based thia-aza macrocycle ligand (**L3**) were studied for the development of cross-sensitive optical chemical sensors aimed to the determination of transition metal ions. The ligands oppositely vary their fluorimetric response: **PFc$_4$** fluorescence is quenched upon the several transition metal ions concentration growth, while the fluorescence of **L3** increases upon mercury ions exposure. By the simultaneous incorporation of both ligands in the same membrane, a series of cross-sensitive materials were obtained and tested for transition metal ions detection by CSPT method.

KEYWORDS

Porphyrin-ferrocene ligand; thia-aza coumarin-substituted heterocycle ligand; CSPT cross-sensitive materials; transition metals detection.

INTRODUCTION

The application of optical sensors has recently spread in many fields, such as environmental analysis, industrial control, and routine laboratory testing [1]. Being non invasive, easy to handle, and possessing a notable selectivity, optical chemical sensors have been previously exploited for the analysis of several hazardous compounds in aquatic environments, and in particular for the transition metal ions detection [2,3]. For this purpose several optically active receptors, such as heteroatomic macrocycles [2], in particular porphyrins [3], and other types of mixed donor-type compounds have been tested. The selectivity of optical sensors can be varied by the rational design of the chromoionophore, the accurate definition of the sensing matrix composition and the measurement set-up conditions. Nevertheless, many of the reported sensors still suffer of side interferences, especially in the complex multi-component samples. The multisensor approach, which simultaneously implements a big number of cross-sensitive sensors, may overcome the problem of insufficient sensors selectivity and the amendment of optical sensors cross-sensitivity becomes an important issue.

Recently we reported novel optical sensors based on the mixed aza-thioether macrocycles bearing coumarin pendant arm, [4] and tetraferrocenylporphyrin **PFc$_4$** [5] chromophores for the selective fluorimetric detection of Hg(II) and Pb(II) respectively; the former increases the fluorescence with the analyte concentration growth, while **PFc$_4$** fluorescence quenches under exposure to analyte, Fig. 1. The possibility to use the Computer Screen Photo-Assisted Technique (CSPT) for the fluorimetric signal detection of the developed optodes, [6] applying a computer monitor screen as polychromatic light source and a webcam as optical response detector, have been also demonstrated.

In this contribution we propose the simple, fast and effective method to tune the cross-sensitivity of optical sensors for multisensory CSPT analysis of heavy metals in complex liquid samples.

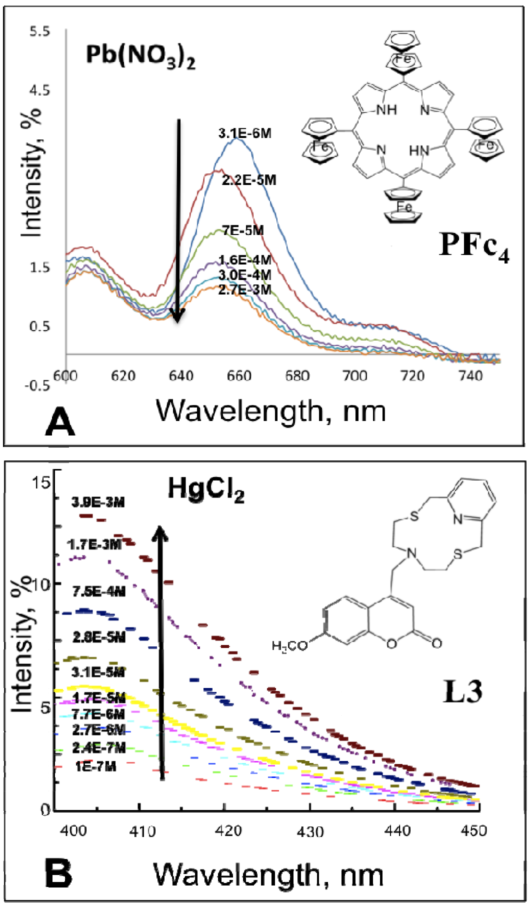

Figure 1: The chemical structures and fluorimetric response of (A) ***PFc$_4$*** *and* ***(B) L3*** *chromophores.*

EXPERIMENTAL

Reagents and membrane preparation

High molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS) and o-nitrophenyl octyl ether (oNPOE) plasticizers, potassium tetrakis-(4-chlorophenyl)borate (TpClPBK) anionic additive, 2-(*N*-morpholino)ethanesulfonic acid (MES) buffering agent and tetrahydrofuran (THF) solvent were purchased from Fluka. THF was freshly distilled prior to use. The **PFc$_4$** and **L3** ligands were prepared according to the previously reported respective synthetic procedures [7,8]. Distilled water was used for aqueous solutions preparation. All the other chemicals were of analytical grade and used without further purification.

In total five PVC-based solvent polymeric membranes, Mb1-Mb5, were prepared. Membranes Mb 1 and Mb 5 were obtained by incorporation of respectively 1 and 3 wt% of **PFc$_4$** and **L3** ligands in PVC matrix plasticized with DOS or oNPOE, and containing 5 wt% of TpClPBK cation exchanger. All components (total weight of 100 mg) were dissolved in 1 ml of THF. The membranes were deposited onto transparent glass slides and the solvent was permitted to evaporate over the night under room temperature. The membranes were then conditioned in 0.1 M MES (pH 5.5) buffer for 10 min before the first measure.

Optical CSPT measurements and data treatment

For CSPT measurements a glass slide, coated with five spots of Mb1-Mb5 polymeric films, was placed in a transparent cuvette and backside illuminated with the polychromatic light provided by TFT-LCD (Samsung) computer monitor screen, Fig. 2. The outcoming optical signal was captured with a digital web-cam (Logitech Quickcam® for Notebook, 352*288 pixels resolution). The H_2TFcP-based films optical intensity variation upon the exposure to the growing concentrations of target metal ions and illumination by the sequence of 50 colors, was registered and transformed in analytically useful signal by in-house written MATLAB (v.7.9, 2010b, The MathWorks, Inc., Natick, USA) codes. The measurement cell was properly shielded from ambient illumination.

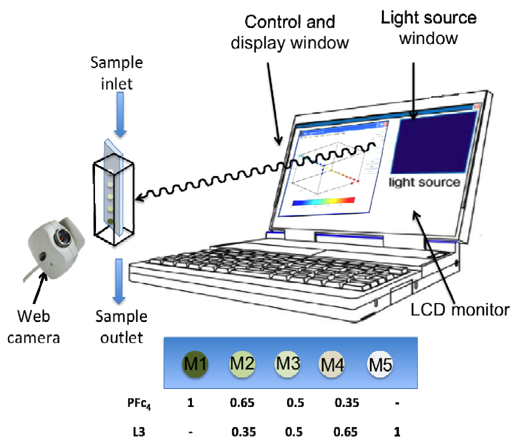

Figure 2: The CSPT measurement set-up.

The CSPT response was evaluated in the individual solutions of Na^+, Cd^{2+}, Hg^{2+} and Pb^{2+}- inorganic salts in the range from 5×10^{-7} M to 7.5×10^{-3} M at 0.1M MES (pH = 5.5) buffer background at ambient temperature (+22 °C). The freshly prepared films were soaked in MES buffer for at least 24 hours prior the testing.

The optical sensor response signature was extracted from the webcam video-registrations and plotted in accordance to the concentration change of the added cations, Fig. 3. The mean CSPT membrane response was then calculated as the mean value of the optical intensity in the Red/Green/Blue regions, Fig. 4. Principal component analysis (PCA) was applied for the CSPT-optical response interpretation. The multivariate data treatment was performed with Unscrambler software (v. 9.1, 2004, CAMO PROCESS AS, Norway).

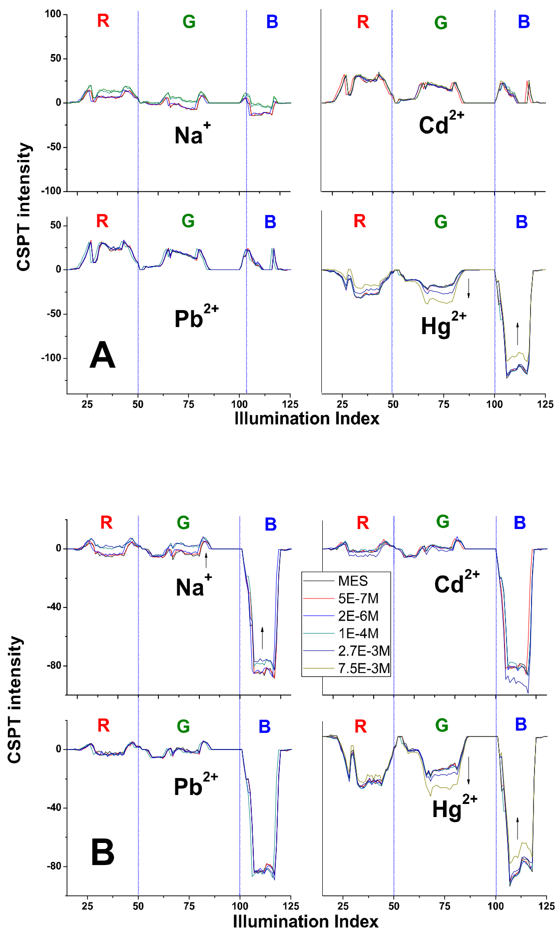

Figure 3: The CSPT response of membranes towards several metal ions: (A) Mb 5 based on L3; (B) Mb 3 containing 1:1 ratio of L3 and PFc$_4$.

RESULTS AND DISCUSSION

The method consists in the systematic variation of the composition of optodes sensing material by mixing the two membrane cocktails (Mb 1 and Mb 5), based on singular selective chromoionophore, in different ratios: 2:1, 1:1 and 1:2 in volume, see insert on Fig. 2. The amount of 1 and 3 wt % of **PFc$_4$** and **L3** were incorporated in membranes Mb 1 and Mb 5 respectively and were determined by the ligand solubility in the membrane phase. We have initially supposed a neutral cationic carrier working mechanism for both **PFc$_4$** and **L3** ligands. The 5 wt % of TpClPB- lipophilic anionic sites were also incorporated in the single-ligand membranes to facilitate the analyte transport into the membrane phase, to tune the ion-exchange properties and to decrease the membrane resistances.

As it is shown on Fig. 3, the different CSPT fingerprints towards various metal ions were registered for membranes Mb 5 and Mb 3 based on singular **L3** ligand or **L3:PFc$_4$** in 1:1 molar ratio correspondingly. As expected, **L3** based Mb 5 exhibited the high response to mercury ions in all the three red, green and especially blue region, Fig. 3a. At the same time, the Mb 3 still demonstrated enhanced Hg^{2+}-ions response, but the influence of other tested ions indicated the growing degree of Mb 3 cross-sensitivity. On the Fig. 4 the mean CSPT response of the Mb 1-Mb 5 towards all the tested metal ions it presented. It is possible to observe that **PFc$_4$** based Mb 1 exhibited the highest response to lead ions, while the improvement in Hg (II) response was obtained for Mb 2, containing both **L3** and **PFc$_4$** ionophores in 1:2 ratio.

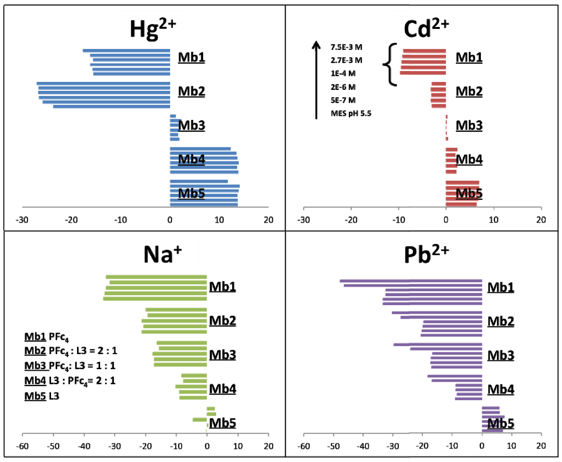

Figure 4: Mean CSPT response of cross-sensitive optodes towards different metal ions.

The application of optical sensor array composed of Mb 1-5 has permitted to clearly discriminate all tested metal ion species and to observe their concentration gradients, Fig. 5.

The further work on the application of cross-sensitive optical sensors arrays for the analysis of real matrices, such as surface and potable waters and soil extracts, are now in progress in our laboratories.

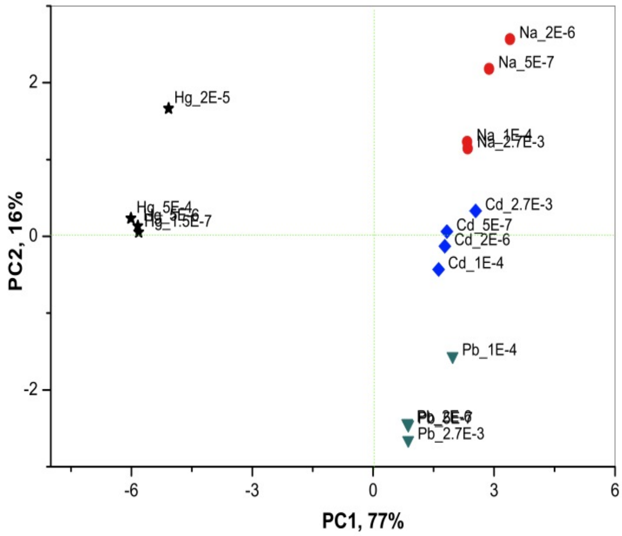

*Figure 5: PCA analysis of metal ions with cross-sensitive optodes array based on chromoionophores **L3** and **PFc$_4$**.*

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