OPTICAL CHARACTERIZATION OF A NEW INDICATOR DYE COVALENTLY BOUND ON CONTROLLED PORE GLASSES, POTENTIALLY SUITABLE AS OPTICAL TRANSUDER FOR Hg(II)

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Abstract: The current paper describes a novel absorption-based optode for mercury (II) detection. The dye 2-(5-amino-3,4-dicyano-2H-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (L', C₃N₃-C₄N(CN)₂-NH₂), which is a specific indicator for Hg(II) undergoing a colour change from violet to blue on the formation of the corresponding monochelated [HgL] complex, was covalently bound on a suitable matrix and its optical characterization as optode was performed in the presence of mercury acetate [Hg(AcO)₂] aqueous solutions.

Keywords: optical fibre sensors, mercury, absorption, optode

INTRODUCTION

Continuous monitoring of heavy metal ions, especially the most hazardous ones (Hg, Cd, Cu, Zn, Pb), is considered to be extremely necessary for the in-situ evaluation of the water quality and, in general, simple and low-cost sensing systems for their determination in water would be highly desirable. However, some difficulties exist in order to develop devices
capable of meeting this need: in aqueous solution, foreign species can interfere with the sensor response and, also, the metal to be determined may exist in several forms, which generally respond differently to the sensor. As a matter of fact, the analytical procedures for determining the total content of a particular metal in a water sample, are quite complicated and a sample pretreatment is normally required before the final determination.

In turn, the development of optical fibre sensors could allow the generation of systems capable of a continuous monitoring of metals in water. During the past recent years we have been investigating the sensor properties of L' with this aim in mind, in particular for sensing Hg(II) in water. Some optical fibre sensors for Hg(II) are described that are based on fluorescence quenching [1,2] or on absorption [3]. On the other hand, selectivity or stability of the developed optodes do not seem capable of satisfying all the requirements for continuous in situ monitoring.

Our previous attempts were devoted to incorporated L' either physically in sol-gel hybrid-silica matrices [4,5] or electrostatically on anion exchangers [6]. The results were not completely satisfactory, since both the physical and the electrostatic entrapment was not reliable in terms of stability, as a consequence of the continuous leakage of the entrapped chromophore.

The present work is related to the optical characterization of an optode for the Hg(II) detection, realised by means of the covalent immobilization of L' on controlled pore glasses.
MATERIALS AND METHODS

As can be seen in Fig. 1, the first step was the conversion of L’ into its trimethoxysilyl-propyl-amino-derivative anion (TPAL’, C₆N₃-C₄N(CN)₂-NH-CH₂CH₂CH₂Si(OCH₃)₃⁻) from the reaction between the tetraphenyl-

\[
\text{NC} \quad \text{NC} \quad \text{NC} \quad \text{NC} \\
\text{N} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{CN} \quad \text{CN} \quad \text{CN} \quad \text{CN}
\]

\[
\text{L'} \quad \text{Hg(II)} \quad \text{H₂O} \rightarrow \quad \text{Hg(L)}
\]

\[
\text{H} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{CH}
\]

\[
\text{TPD} \quad \text{C₆H₆N} \\
\text{N} \quad \text{N} \quad \text{N}
\]

\[
\text{DMF, RT, 72 h} \quad \rightarrow \quad \text{C}_6\text{H}_{12} \text{H}_3
\]

\[
\text{NC} \quad \text{NC} \quad \text{NC} \quad \text{NC} \\
\text{N} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{CN} \quad \text{CN} \quad \text{CN} \quad \text{CN}
\]

\[
\text{TPAL'} \quad \text{CPG} \quad \text{Hg(II)} \quad \text{H₂O} \rightarrow \quad \text{blue-doped-CPG}
\]

\[
\text{H} \quad \text{C} \quad \text{H} \quad \text{CH} \quad \text{CH} \quad \text{CH}
\]

\[
\text{TPD} \quad \text{C₆H₆N} \\
\text{N} \quad \text{N} \quad \text{N}
\]

\[
\text{violet-doped-CPG}
\]

![Figure 1](image-url)  
**Figure 1** Scheme of the sequence of the reactions followed to bind covalently L’ to CPGs. The capability of the bound chromophore to complex Hg²⁺ (as the free ligand do) is also shown.
arsonium salt of L' and the trimethoxysilyl-propyl-iodide (TPI, I-\(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3\)) in the presence of 2,6-lutidine (C\(_7\)H\(_9\)N). 2,6-Lutidine, which is a poor nucleophile but a strong base, acts as iodidric acid acceptor without undergoing the alkylation by the iodide:

\[
\text{AsPh}_4\cdot\text{L}' + \text{TPI} + \text{C}_7\text{H}_9\text{N} \rightarrow \text{AsPh}_4\cdot\text{TLPA}' + \text{C}_7\text{H}_9\text{N}\cdot\text{HI}
\]

As\(\text{Ph}_4\cdot\text{L}'\) (0.5 g, 0.81 mmol) [7], 3-iodopropyltrimethoxysilane (ABCR, 1.4 g, 4.8 mmol) and 2,6-lutidine (Fluka, 0.3 ml or 0.277 g, 2.6 mmol) were dissolved in dimethyl-formamidine (dehydrated over 5A molecular sieves and freshly distilled at 30 °C under 0.2 mmHg pressure, 15 ml). After 72 h standing in a stoppered flask at room temperature, the solution was evaporated to dryness in air. The dark violet residue, the tetraphenylarsonium salt of TPAL', was dissolved in dichloromethane (20 ml).

Controlled pore glasses (Fluka, CPG-10-350, 0.2 g) were poured in the As\(\text{Ph}_4\cdot\text{TPAL}'\) dichloromethane solution coming out from the previous step and left there under stirring in a rotavapour apparatus for 72 hours at room temperature. After filtration on a G2 glass frit, treated CPGs were thoroughly washed with acetone and water in order to remove the adsorbed and not covalently bound As\(\text{Ph}_4\cdot\text{TPAL}'\), and finally dried in air. Violet coloured As\(\text{Ph}_4\cdot\text{TPAL}'\)-doped CPGs were obtained.

Optical characterization of the As\(\text{Ph}_4\cdot\text{TPAL}'\)-doped CPGs was performed with a configuration previously described: a layer of CPGs was immobilized on the flat surface of a plastic reflector (a copolymer of polyethylene and polypropylene) by heating the plastic material up to its melting point. The reflector was then positioned in front of the common end of a bifurcated bundle of plastic optical fibres by means of a thin
stainless steel wire (see Fig. 2) [8]. The two branches of the optical fibre bundle were connected to a halogen lamp and to a spectrophotometer.

![Sketch of the optode with AsPh₄·TPAL' covalently bound on CPGs immobilized on the plastic reflector.](image)

**Figure 2** Sketch of the optode with AsPh₄·TPAL' covalently bound on CPGs immobilized on the plastic reflector.

Due to the mild conditions of the current silylation, CPGs were doped also after their immobilization on the flat surface of a plastic reflector. This procedure had the advantages of avoiding the exposure of AsPh₄·TPAL'-doped CPGs to a temperature which could cause an undesirable modification of their optical properties. Moreover only the portion of CPGs which was really exposed to the external environment was chemically modified, while there was no chemical reaction on the portion embedded inside the plastic reflector.

**SPECTROPHOTOMETRIC CHARACTERIZATION**

The optical characterization of the probe in Fig. 2 was performed with the optical fibre bundle connected to an Ocean Optics Spectrophotometer (model S2000); a halogen lamp was used as optical source.
First the stability of the reflectors in pure water was checked: the probe was dipped in water and absorption spectra were recorded for three days; a stable situation was reached after two hours, and the occurred change could be ascribed to the modification of the local electric field following the change of the external environment from neutral (air) to polar (water). After three days, the probe was dipped in aqueous solution of Hg(AcO)$_2$ at different concentrations.

Fig. 3 shows the absorption spectra recorded in water and at the three different concentrations of Hg(AcO)$_2$.

The absorbance as a function of time in correspondence of the peak wavelength of immobilized AsPh$_4$·TPAL' ($\lambda$=588 nm) and of the complex ($\lambda$=669 nm) is shown in Fig. 4.
The difference $A$ of the absorbances at the two wavelengths is also shown. A decrease and a slight shift of the absorption peak of the complex is observed with time mainly for the highest concentration ($5 \times 10^{-4}$ M), while the absorption peak of the AsPh$_4$·TPAL$^-$ species is quite stable. This behaviour is yet under study, and could be ascribed to the amount of molecules available for the formation of the complex: for high concentrations of the metal, no ligand molecules are available and the formation of different mercury complexes, characterized by slightly different optical properties, could take place.

Fig. 5 shows the relationship between the absorbances at the different wavelengths and the concentration: the working range of the optode is below $5 \times 10^{-5}$ M and for higher concentrations the saturation takes place. As can be seen, the sensitivity is promising and concentrations below $5 \times 10^{-6}$ M should be easily detected.
CONCLUSIONS

L’ was first converted into its trimethoxysilyl-propyl-amino-derivative and, then, in situ covalently bound to CPGs as tetraphenylarsonium salt. TPAL’ has not been isolated so far, and experiments are being carried out to this end. However, we are quite confident about the above given formulation on analogy with the results of the analogous reaction with I-CH₃, as alkylating agent, from which AsPh₄-C₄N₃-C₄N(CN)₂-NH-CH₃ was isolated (yield 20%) and structurally characterized [9]. In this regard it is to be noted that the $\lambda_{\text{max}}$ of TPAL’ on CPGs (588 nm, see text) is significantly different from that of unsubstituted L’ on the same phase (555 nm) [7]. The subsequent covalent immobilization of TPAL’ on CPGs appears extraordinarily easy in comparison to the well-known silylation procedure of CPGs [8], so that, when neat AsPh₄·TPAL’ is available, additional experiments will be needed to make clear this point. Then, it will be also
possible to determine another important parameter of the system, that is the total amount of TPAL' loaded on the support.

Optical characterization of the optode is still in progress in order to identify its limit of detection for Hg(II) and to investigate the effect of other metallic ions and/or metal-coordinating anions, which might compete with L', as interfering agents.

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