



# Highly selective sensing of mercury (II) by development and characterization of a PVC-based optical sensor

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## ABSTRACT

A novel optical sensor that is highly selective to  $\text{Hg}^{2+}$  ions is described. This is based on the use of 4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1,4,7]trioxononin-9-yl)pyrylium perchlorate as an ionic carrier in a plasticized poly(vinyl chloride) membrane. The sensing membrane is capable of determining mercury(II) with a high selectivity over a wide dynamic range between  $2.95 \times 10^{-10}$  and  $3.20 \times 10^{-3}$  M at pH 5.0 with a lower detection limit of  $1.01 \times 10^{-10}$  M. Validation of the assay method reveals excellent performance characteristics, including long life span, good selectivity for  $\text{Hg}^{2+}$  ions over a wide variety of other metal ions, long-term response stability, and high reproducibility. Applications for direct determination of mercury in samples including dental amalgam, shaft water, and fountain give results with good correlation with data obtained using cold vapor atomic absorption spectrometry.

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## 1. Introduction

The design of sensitive and discriminating optical sensors remains as an emerging frontier in analytical chemistry and has gained scientific interest, mainly due to the need for fast, easy and economical monitoring of our environmental samples especially for heavy metal ions in real time. Generally, optodes include a sensing membrane that selectively reacts with the analyte, a light source, a wavelength selection device, and a detector. The spectral change in absorption (or emission) caused by either the analyte itself, or the analyte reacting with a specific indicator, gives a more or less direct measure of the analyte concentration. No further samplings, addition of reagents or dilutions are normally required [1–5]. In addition, the determination of heavy metals in the aquatic environment is of tremendous interest due to their hazardous effects on the ecosystem and the human health depending on their dose and toxicity.

Mercury is one of the heavy metals which are highly toxic. Thus, determination of trace amounts of mercury in environmental samples is of great importance nowadays due to its high toxicity, accumulative and persistent character in the environment and living organisms. Increases in mercury concentration in waters and plants have resulted from industrial and domestic waste discharge, refineries and disposal of mining washing. In this connection, chemical sensors based on optical signal measurement are those of the advanced techniques in analytical chemistry that they have been

accepted as advantageous because they can be miniaturized and manufactured in low costs [6–8].

Several methods exist to determine the Hg(II) concentration. They range from polarography to atomic absorption spectrometry (AAS), inductively coupled plasma (ICP) spectroscopy [9], molecular absorption spectrometry [10], anodic stripping voltammetry [11], neutron activation analysis [12] and atomic fluorescence spectrometry [13]. In spite of their exact and fast measurement capabilities, recent analytical interest has focused on developing optical sensors. They have the advantages of size, cost-effectiveness, simplicity, no necessity of the reference solution, and fieldwork applicability [14–18].

In this work we introduce a novel photometric sensor, based on a recently synthesized ligand, for selective determination of trace amounts of mercury in various samples. The proposed optical sensor shows a significant absorbance signal change on exposure to an aqueous solution containing mercury(II) ion, which exhibits the theoretically expected absorbance response to mercury(II) ion concentration. The selectivity, response time, reproducibility, reversibility, and lifetime of the optode membrane are discussed.

## 2. Experimental

### 2.1. Materials and reagents

All reagents (all from Merck) were of analytical reagent grade and used as purchased without further purification, except for vacuum drying. The selected sensing material, 4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1,4,7]trioxononin-9-yl)pyrylium perchlorate (LX, Fig. 1), was prepared as described elsewhere [19].

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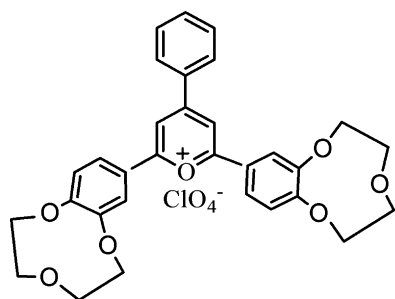


Fig. 1. The structural formula of the sensing material, LX.

For membrane preparation, high molecular weight PVC, plasticizers di-isodecyl phthalate (DDP), tri(methylhexyl) phthalate (TMP), bis(2-ethylhexyl) azelate (BEA), dioctyl sebacate (DOS), teris (2-ethylhexylbutyl) phosphate (TEP), bis (2-ethylhexyl) phosphate (BEP), ethylhexyl phthalate (EHP), and freshly distilled tetrahydrofuran (THF) were used. Tetraethylammonium perchlorate (TEAP) was used as an additive (in the membranes) and as the ionic strength stabilizer in the spectrophotometric solution studies. The metal cations tested were of their nitrate salt. Doubly distilled and deionized water was used throughout.

## 2.2. Instrumentation

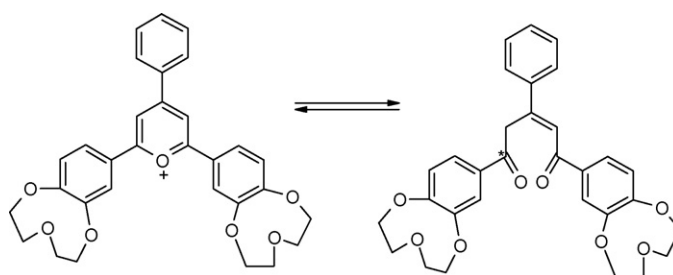
Spectroscopic measurements were made using a Shimadzu UV-76 1650 PC UV-vis spectrophotometer with 1.0-cm quartz cells. A Jenway 3020 (UK) pH meter was used to measure of pH. A cold vapor atomic absorption spectrometry system (CV-FAAS) including an AA 670 Shimadzu atomic absorption spectrometer with an air/acetylene flame was used for measurement of mercury contents of the samples.

## 2.3. Optical sensing membrane preparation

A typical membrane cocktail consisted of appropriate amounts of active components, 1 mg LX, 2 mg TEAP, 40 mg PVC and 100 mg of DDP was prepared (see Table 1). These compounds were dissolved in 2.0 ml of fresh distilled THF to make a clear and homogenous solution. An aliquot of 0.2 ml of this solution was applied to the surface of a 15 mm × 25 mm thin glass plate which was mounted on a platform under a THF-saturated atmosphere [20]. In this way, a membrane of approximately 4 μm thick [21] was coated onto the plate and allowed to stand in ambient air for 1 h before use.

## 2.4. General procedure

A very thin and homogeneous membrane on the plate was mounted in the diameter direction of a measuring cell. The volume



Scheme 1.

capacity of the cell was ca. 4 ml. A stock solution of  $1.0 \times 10^{-2}$  M  $\text{Hg}^{2+}$  was prepared by dissolving exactly weighed amounts (with an accuracy of 0.00001 g) of mercury(II) nitrate,  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , diluted with distilled water and standardizing with the EDTA solution [22]. Lower concentrations of solutions were obtained by serial dilution of the stock solution. Standard solutions containing the metal cation was added sequentially into the system by a micropipette (with 2-μl step) and the absorbance data were recorded at  $\lambda_{\text{max}} = 580$  nm. The limiting absorbencies  $A_0$  and  $A_c$  were determined with the optode membrane in contact with ( $1.0 \times 10^{-2}$  M) and without  $\text{Hg}^{2+}$ . By plotting the calibration curve of the absorbance signal values versus the logarithmic concentration of mercury ion (pHg), the unknown mercury(II) concentration can be read. All measurements were carried out at the room temperature.

## 3. Results and discussion

### 3.1. Spectrophotometric study of the solution

To explore the properties of LX as an optically sensing material for the metal cation, various metal ions tested in a preliminary experiment. It was found that the addition of proper amounts of  $\text{Hg}^{2+}$  to an acetonitrile solution of LX results in a fast change in the color of the solution from pale orange to red, while the presence of other alkaline and transition-metal ions showed no observable color change in the ligand solution. This is most possibly indicative of selective complex formation of the ligand with  $\text{Hg}^{2+}$  ions in the acetonitrile solution.

Pyrylium salt (LX) could undergo ring opening when dissolves in the solution (Scheme 1). A similar behavior for ring-opening and ring closure of different pyrylium compounds has already been reported in literature [23]. It is known that the re-cyclization occurs by electrophilic attack of the C\* carbon to the lone pair of the other ketonic oxygen of the resulted dione. Ring closure in the presence of metal ions is most likely due to the Lewis acid character of the metals that, when coordinated to the crown-oxygen atoms, might enhance the electrophilic character of the C\* carbon [24]. The

Table 1  
Optimization of membrane ingredients.

No.	Ionophore (L)	PVC	Plasticizer (100 mg)	Additive (TEAP)	Response time (min)	Linear range (M)
Composition (mg)						
1	1	40	BEA	2	4	$6.87 \times 10^{-8}$ – $1.25 \times 10^{-5}$
2	1	40	TMP	2	5	$8.36 \times 10^{-8}$ – $4.02 \times 10^{-5}$
3	1	40	BEP	2	4	$9.05 \times 10^{-8}$ – $3.61 \times 10^{-5}$
4	1	40	DOS	2	4	$8.87 \times 10^{-8}$ – $1.25 \times 10^{-4}$
5	1	40	TEP	2	3	$3.36 \times 10^{-8}$ – $4.52 \times 10^{-4}$
6	1	40	EHP	2	3	$1.05 \times 10^{-8}$ – $3.11 \times 10^{-4}$
7	1	30	DDP	2	3	$4.21 \times 10^{-9}$ – $7.10 \times 10^{-4}$
8	1	40	DDP	1	2	$6.99 \times 10^{-10}$ – $1.03 \times 10^{-3}$
9	1	50	DDP	2	3	$8.03 \times 10^{-10}$ – $7.80 \times 10^{-5}$
10	1	40	DDP	2	<2	$2.95 \times 10^{-10}$ – $3.20 \times 10^{-3}$
11	2	40	DDP	1	2	$5.57 \times 10^{-9}$ – $1.29 \times 10^{-4}$
12	2	40	DDP	4	2	$6.37 \times 10^{-10}$ – $0.92 \times 10^{-4}$

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