



## Membrane optode for mercury(II) determination in aqueous samples

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### ABSTRACT

A color changeable optode for Hg(II) was prepared by the immobilization of a dye 4-(2-pyridylazo)resorcinol (PAR) and a liquid ion-exchanger trioctylmethylammonium chloride (Aliquat-336) in the tri-(2-ethylhexyl) phosphate plasticized cellulose triacetate matrix. Hg(II) and  $\text{CH}_3\text{Hg}^+$  from aqueous samples could be quantitatively preconcentrated in this transparent optode producing a distinct color change ( $\lambda_{\text{max}} = 520 \text{ nm}$ ) within 5 min equilibration time in bicarbonate aqueous medium or 30 min in natural water. Whereas optode sample without Aliquat-336 did not change its color corresponding to Hg-PAR complex on equilibrium with the same aqueous solution containing Hg(II) ions. The uptake of Hg(II) was found to be pH dependant with a maximum (>90%) at a pH 7.5. The uptake of ions like Cu(II), Fe(II), Zn(II) and Pb(II) was negligible in the optode where as the uptake of Cd(II) and Zn(II) ions was 10–15% at pH 7.5. The optode developed in the present work was studied for its analytical application for Hg(II) in the aqueous samples by spectrophotometry, radiotracer ( $^{203}\text{Hg}$ ), Energy Dispersive X-ray Fluorescence (EDXRF) analyses and Instrumental Neutron Activation Analysis (INAA). The minimum amount of Hg(II) required to produce detectable response by spectrophotometry, INAA and EDXRF were found to be 5.5, 1 and 12  $\mu\text{g}$ , respectively. This optode showed a linear increase in the absorbance at  $\lambda_{\text{max}} = 520 \text{ nm}$  over a concentration range of 0.22–1.32  $\mu\text{g}/\text{mL}$  of Hg(II) ions in aqueous solution for 5 min. The preconcentration of Hg(II) from large volume of aqueous solution was used to extend the lower limit of concentration range that can be quantified by the spectrophotometry of optode. It was observed that preconcentration of 11  $\mu\text{g}$  Hg(II) in 100 mL (0.11  $\mu\text{g}/\text{mL}$ ) in aqueous samples gives a distinct color change and absorbance above  $3\sigma$  of the blank absorbance. The optode developed in the present work was found to be reusable.

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### 1. Introduction

Optical chemical sensors (optodes) are considered to be better suited for monitoring of toxic ions/species [1–4]. Optodes are easy to prepare, selective for preconcentration of target analyte in the sensing matrix, and there is no need for separate reference devices. These optodes are based on the preconcentration of the analyte on a solid substrate that produces change in the optical property of the solid substrate which is proportional to the analyte concentration. The measurement of the change in the optical property (absorption, reflectance, fluorescence, scintillation, refractive index etc.) of the solid phase can be used for the detection and quantification of the target analyte [5,6]. The presence of extractant provides an increase in the selectivity and sensitivity of the optodes as compared to that obtained by solution spectrophotometry using same chromophore [7–9]. Most of the optodes reported in the literature for Hg(II) involve the use of optical fiber based optodes [10–12] or membrane based optodes [13–20]. Optical fiber optodes are based

on the immobilization of indicators in the resins or beads, which are attached to the optical fiber tip for measuring the optical response produce by the optode [10–12].

The membrane based optodes are more suitable for the preconcentration and subsequent visual colorimetric detection of Hg(II). The choice of matrix for the membrane optode is governed by the parameters such as permeability for the analyte, mechanical stability and suitability for immobilization of the chromophore and extractant. Generally, sol-gel glasses [21,22] or polymer matrices [1,2] are used for the preparation of the optodes. Poly(vinyl chloride) (PVC) has been used for the preparation of membrane optodes for Hg(II) due to its relatively low cost, good mechanical properties and amenability to plasticization. However, PVC based membranes are known to take up water from aqueous phase and become opaque [23]. In our previous work, the cellulose triacetate (CTA) has been used as a matrix forming polymer in the preparation of the optodes as they do not absorb water significantly and have good optical properties [8,9]. The different schemes used for the preparation of membrane optodes for Hg(II) are: (i) porphyrin-doped sol-gel films [13], (ii) plasticized PVC containing a lipophilic borate salt as an extractant for Hg(II) and the fluorescent oxacarbocyanine dye for its detection [14],

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(iii) 1-(2-pyridylazo)-2-naphthol (PAN) immobilized in PVC [15], (iv) fluorescence quenching of  $\text{Hg}^{2+}$ -selective ionophore 5,10,15,20-tetraphenylporphyrin immobilized in PVC [16], (v) irreversible plasticized PVC optode incorporating the neutral ionophore along with lipophilic salt [18], (vi) dithizone immobilized on a triacetylcellulose film [17], (vii) 4-(2-pyridylazo)resorcinol (PAR) covalently attached to triacetylcellulose film [19] and (viii) trityl-picolinamide and a chromophore immobilized in the plasticized PVC [20]. The optode should be simple to prepare and capable of producing visual response in the form of distinct color change for  $\text{Hg}(\text{II})$  ions within a short period of equilibration time. Monolayer functionalized silica with 5,10,15,20-tetraphenylporphinetetrasulfonic acid (TPPS) has been reported for the determination of  $\text{Hg}(\text{II})$  based on color change of TPPS from orange to green as a result of the formation of a charge-transfer complex with  $\text{Hg}^{2+}$  [24]. This optical sensor has all the required characteristics to use it as a sensor for  $\text{Hg}(\text{II})$ , but beads/resins do not provide a reproducible geometry for quantitative measurements.

In the present work, an optode for  $\text{Hg}(\text{II})$  has been developed by the immobilization of a dye 4-(2-pyridylazo)resorcinol and a liquid ion-exchanger trioctylmethylammonium chloride (Aliquat-336) in the tri-(2-ethylhexyl) phosphate plasticized cellulose triacetate matrix. PAR is a highly sensitive and non-selective reagent applicable for many heavy metal ions such as  $\text{Cd}(\text{II})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Pb}(\text{II})$  and  $\text{Zn}(\text{II})$  [25]. PAR also forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , but PAR is 2000 times more sensitive for the heavy metal ions than  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [25]. In the present case, the PAR immobilized in the optode without Aliquat-336 did not interact with metal ions. The Aliquat-336 facilitates the transfer of  $\text{Hg}(\text{II})$  in the optode, which preconcentrates  $\text{Hg}(\text{II})$  in it as PAR– $\text{Hg}$  complex. The uptake of  $\text{Hg}(\text{II})$  in the optode has been studied using  $^{203}\text{Hg}$  radiotracer tagged  $\text{Hg}(\text{II})$  in bicarbonate aqueous medium. The effect of experimental parameters such as pH,  $\text{NaHCO}_3$  concentration, interference of cations and anions on the determination of  $\text{Hg}(\text{II})$ , preconcentration from large aqueous volume and reusability have been studied. The optimized composition of the optode and chemical conditions of aqueous samples were used for the determination of  $\text{Hg}(\text{II})$  and  $\text{CH}_3\text{Hg}^+$  present in the aqueous samples. Finally, the loaded optode samples have been subjected to Instrumental Neutron Activation (INAA) and Energy Dispersive X-ray Fluorescence (EDXRF) analyses to arrive at the reliable values of  $\text{Hg}(\text{II})$ , and to improve upon the colorimetry determination of  $\text{Hg}(\text{II})$ .

## 2. Experimental

### 2.1. Materials and apparatus

Analytical reagent grade mercuric chloride, cadmium nitrate, ferrous sulphate, lead nitrate, zinc acetate, copper chloride and dichloromethane were obtained from Merck (Mumbai, India). Deionized water (18 M $\Omega$ /cm) was used throughout the present studies. Cellulose triacetate (molecular weight 72,000–74,000, acetyl value = 43.2%) and Aliquat-336 from Sigma–Aldrich (Steinheim, Switzerland), 4-(2-pyridylazo)resorcinol from Fisher Scientific (Hong Kong) and tri-(2-ethylhexyl)phosphate (TEHP) from Koch-Light Laboratories (Coinbrook Bucks, England) and methylmercury(II) chloride from Sigma–Aldrich were used as obtained. Radiotracers  $^{203}\text{Hg}$ ,  $^{115\text{m}}\text{Cd}$ , and  $^{65}\text{Zn}$  (with the carriers) were obtained from the Board of Radiation and Isotope Technology (Mumbai, India). For neutron activation analysis samples were irradiated in the APSARA reactor in BARC, Mumbai, India. The radioactivity was measured by using either an HPGe detector or a well-type NaI (TI)  $\gamma$ -ray detector connected to a multi-channel analyzer. All the samples and standards containing radiotracers were counted in an identical sample to detector geometry. A micro-

processor based pH meter model PHAN from Lab India (Mumbai, India) was used for pH measurements. The thickness of the membrane samples was measured using a digital micrometer (Mitutoyo, Japan) with an accuracy of  $\pm 0.001$  mm. The absorbance measurements were carried by mounting the optode samples inside a quartz cell (3 cm  $\times$  1 cm  $\times$  1 cm) and recording the spectra using UV–vis spectrophotometer model V 530 from JASCO (Tokyo, Japan). Blank measurements were carried out for each set of the samples.

### 2.2. Preparation of optode

CTA (0.1 g) was dissolved in 10 mL of dichloromethane. A separate solution containing PAR (0.001 g), Aliquat-336 (0.05 g) and TEHP (0.1 g) was prepared in 5 mL of dichloromethane. Both the solutions were mixed and ultrasonicated for 2 min to form a homogenous casting solution. The casting solution was spread on a Petri dish (internal diameter of 9 cm) kept on a leveled surface. The lid of Petri dish was closed in such a way that it allowed slow evaporation of  $\text{CH}_2\text{Cl}_2$  from the casting solution. After evaporation of the dichloromethane from casting solution for 2 days, the transparent optode was peeled off from the Petri dish. The optode was self-supporting, having good mechanical strength for its application in the stirred aqueous solution. Therefore, transparent support was not required. The optode thus prepared was thoroughly washed with water to remove soluble component, if any. The thickness of the optode membrane was found to be  $40 \pm 5$   $\mu\text{m}$ . The area of the optode samples was kept as 2 cm  $\times$  1 cm throughout the experiments except for EDXRF where 2 cm  $\times$  2 cm size samples were taken.

### 2.3. Radiotracers uptake in the optode

In order to study the effect of pH on the uptake, a known radioactivity of the radiotracer ( $^{65}\text{Zn}$ ,  $^{115\text{m}}\text{Cd}$ , or  $^{203}\text{Hg}$ ) was spiked into tap water samples and solutions having different pH values ranging from pH 1 to 9. The optode samples were equilibrated with 25 mL of these solutions for a period of 24 h without stirring. The uptake of radiotracer in the optode sample was monitored by  $\gamma$ -counting of samples (50–100  $\mu\text{L}$ ) of solution taken before and after equilibration with the optode. The uptake (%) of the radiotracer in the optode was obtained from following equation:

$$\text{Uptake (\%)} = \frac{(A_{\text{before}} - A_{\text{after}})}{A_{\text{before}}} \times 100$$

where  $A_{\text{before}}$  and  $A_{\text{after}}$  are the radioactivity in counts/s of  $^{65}\text{Zn}$ ,  $^{115\text{m}}\text{Cd}$ , or  $^{203}\text{Hg}$  in the samples taken from the feed solution before and after equilibrating the optode sample, respectively.

The uptake of  $\text{Hg}(\text{II})$  in the optode samples and interference studies were also carried out by Instrumental Neutron Activation Analysis. For this study, optode samples were equilibrated with solutions having varying amounts of  $\text{Hg}(\text{II})$  and  $\text{Cd}(\text{II})$ . After equilibration, the optode samples were sealed in polythene and irradiated at the E8 position of APSARA reactor for a period of 2 h. The radioactivities of  $^{203}\text{Hg}$  ( $t_{1/2} = 46.6\text{d}$ ) and  $^{113}\text{Cd}$  ( $t_{1/2} = 43\text{d}$ ) produced in the optode samples during neutron activation were measured using  $\gamma$ -ray spectrometry for monitoring the uptake in the optode as a function of the concentration of these cations in the equilibrating solutions.

The EDXRF measurements were carried out using an EX 3600-M spectrometer, Jordan valley AR Ltd. (Migdal Haemek, Israel). This EDXRF spectrometer has a 50W Rh-anode X-ray tube, an assembly of 6 filters (Cu, Fe, Mo, Rh, Sn and Ti), a Ge secondary target and a Si(Li) detector with a 12.5  $\mu\text{m}$  thick beryllium window (energy range of 1–40 keV, resolution 139 eV at 5.9 keV of Mn  $K_{\alpha}$ ). The optode samples (2 cm  $\times$  2 cm) were placed on the base of the

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