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 CH_3Hg^+ from aqueous samples could be quantitatively preconcentrated in this transparent optode producing a distinct color change (λ_{max} = 520 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}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 μg, respectively. This optode showed a linear increase in the absorbance at λ_{max} = 520 nm over a concentration range of 0.22–1.32 μg/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 μg Hg(II) in 100 mL (0.11 μg/mL) in aqueous samples gives a distinct color change and absorbance above 3σ 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 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 triacetyl-cellulose 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 Hg(II) ions within a short period of equilibration time. Monolayer functionalized silica with 5,10,15,20-tetraphenylphinetetrasulfonic acid (TPPS) has been reported for the determination of Hg(II) based on color change of TPPS from orange to green as a result of the formation of a charge-transfer complex with Hg^{2+} [24]. This optical sensor has all the required characteristics to use it as a sensor for Hg(II), but beads/resins do not provide a reproducible geometry for quantitative measurements.

In the present work, an optode for Hg(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 Cd(II), Cu(II), Pb(II) and Zn(II) [25]. PAR also forms complexes with Ca^{2+} and Mg^{2+}, but PAR is 2000 times more sensitive for the heavy metal ions than Ca^{2+} and 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 Hg(II) in the optode, which preconcentrates Hg(II) in it as PAR–Hg complex. The uptake of Hg(II) in the optode has been studied using ^{203}Hg radiotracer tagged Hg(II) in bicarbonate aqueous medium. The effect of experimental parameters such as pH, $NaHCO_3$ concentration, interference of cations and anions on the determination of Hg(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 Hg(II) and CH_3Hg^+ 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 Hg(II), and to improve upon the colorimetry determination of Hg(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 MΩ/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}Hg, ^{115m}Cd, and ^{65}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 (Tl) γ-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 (Mitutoy, Japan) with an accuracy of ±0.001 mm. The absorbance measurements were carried by mounting the optode samples inside a quartz cell (3 cm × 1 cm × 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 CH_2Cl_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 ± 5 μm. The area of the optode samples was kept as 2 cm × 1 cm throughout the experiments except for EDXRF where 2 cm × 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}Zn, ^{115m}Cd, or ^{203}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 γ-counting of samples (50–100 μL) 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_{before} and A_{after} are the radioactivity in counts/s of ^{65}Zn, ^{115m}Cd, or ^{203}Hg in the samples taken from the feed solution before and after equilibrating the optode sample, respectively.

The uptake of Hg(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 Hg(II) and Cd(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}Hg ($t_{1/2}$ = 46.6d) and ^{113}Cd ($t_{1/2}$ = 43d) produced in the optode samples during neutron activation were measured using γ-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, Jordon valley AR Ltd. (Migdal Haemek, Israel). This EDXRF spectrometer has a 50 W 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 μm thick beryllium window (energy range of 1–40 keV, resolution 139 eV at 5.9 keV of Mn K_α). The optode samples (2 cm × 2 cm) were placed on the base of the

Table 1
Uptake of radiotracers (sub-ppm conc.) in the optode samples from well-stirred 25 mL aqueous samples.

Aqueous samples	Uptake of Hg(II) (%)	Uptake of Cd(II) (%)	Equilibration time for optimum uptake
Distilled water (pH 6.4)	75 ± 3	10 ± 3	24 h
Tap water (pH 7.4–7.6)	89 ± 1	12 ± 2	30 min
Bicarbonate aqueous solution (pH 7.5)	89 ± 1	11 ± 3	5 min

Teflon cup assembly in EDXRF spectrometer. The cross-sectional area available for X-ray sample was of 8 mm diameter. Both L_α and L_β X-rays of Hg (9.987 and 11.823 keV) were used for the calibration and estimation of Hg content in the optode samples. The integrated peak area was calculated using the NEXT software provided with this instrument.

2.4. Spectrophotometry

The intensity of Hg(II)–PAR complex formed in the optode sample as a function of Hg(II) concentration in the equilibrating solution was obtained by spectrophotometric measurements of the optode samples. The pH of the equilibrating solutions (25 mL) was maintained in the pH range of 7.4–7.8. Known amounts of Hg(II) (0–110 μg) and NaHCO$_3$ (600 μg) were added to the equilibrating solution. The absorbance of the Hg(II)-loaded optode samples was recorded at $\lambda_{max} = 520$ nm. For studying the kinetics, the optode sample was placed in a well-stirred solution having a known concentration of Hg(II) in the bicarbonate medium (or tap water) at pH 7.4. After equilibrating for a predetermined time, the optode sample was taken out of the equilibrating solution and absorbance at 520 nm was recorded. The time of equilibration of the optode sample was continued till a constant absorbance value was obtained.

The desorption of Hg(II) was studied by equilibrating the optode sample in well-stirred 10 mL aqueous solution of disodium salt of EDTA (0.02 M) for a predetermined time. The desorption of Hg(II) from the optode was monitored from the measured absorbance of the optode sample at 520 nm. The preconcentration efficiency of the optode sample was studied by equilibrating it in well-stirred 10–100 mL tap water spiked with 0.11 μg/mL Hg(II). The uptake of methylmercury (CH$_3$Hg$^+$) was studied by adding 2 mL of CH$_3$Hg$^+$ solution (2 μg/mL) in the 10 mL aqueous solution having bicarbonate medium at pH 7.4. The uptake of CH$_3$Hg$^+$ in the optode was monitored by recording the absorbance of the optode sample equilibrated with well-stirred CH$_3$Hg$^+$ solution for 30 min.

2.5. Interference studies

The interference of cations like Cd(II), Cu(II), Fe(II), Pb(II) and Zn(II) on the uptake of Hg(II) in the optode was studied by equilibrating the optode samples with solutions containing fixed amount of Hg(II) tagged with ^{203}Hg radiotracer and varying amounts of interfering cations in bicarbonate medium at pH 7.4. The uptake of Hg(II) was measured from the difference in radioactivity of ^{203}Hg in solutions before and after equilibrations of the optode samples as described in Section 2.3. The interference of Zn(II), Cd(II) and Pb(II) was also studied by the spectrophotometry as these ions are known to form colored complex with PAR in the aqueous medium. A fixed amount of Hg(II) and the varying amounts of interfering cations were added in the equilibrating solution having a known concentration of NaHCO$_3$ at pH 7.4.

2.6. Application to real samples

The protocol used for the quantifying the Hg(II)/CH$_3$Hg$^+$ in the real samples was based on the comparison of the absorbance of the optode at 520 nm with the calibration curve. The optode sample of 2 cm × 1 cm area was equilibrated with 10–100 mL of well-stirred

ground water/tap water samples for 30 min. The pH of the aqueous sample was adjusted to 7.5 by dil. NaOH before equilibration with the optode. In the case of 5 min equilibration, 24 μg/mL of NaHCO$_3$ was added in the aqueous sample. The optode sample was washed thoroughly with the deionized water, and its absorbance at 520 nm was monitored with respect to air or blank optode sample. The net absorbance of the equilibrated optode sample at 520 nm was correlated to the concentration of Hg(II) or CH$_3$Hg$^+$ from the calibration curve.

3. Results and discussion

4-(2-Pyridylazo)resorcinol forms a colored complex with divalent cations like Hg(II), Zn(II) and Cd(II) in the pH range of 5–9 [12,26,27]. PAR immobilized on the surface of triacetylcellulose membrane was found to complex with Hg(II) ions in acetate buffer [19]. In the present work, PAR has been immobilized in a cellulose triacetate plasticized with tri-(2-ethylhexyl) phosphate. On equilibration of this optode sample with solutions containing Hg(II) ions in the pH range of 1–8, the color of the optode did not change significantly. Radioactivity measurements of these equilibrated optode samples did not show the presence of ^{203}Hg corroborating that Hg(II) was not sorbed in the optode having only PAR. This indicated that the PAR immobilized in TEHP plasticized matrix of CTA did not interact with Hg(II) ions present in the equilibrating solution. This is contrary to the optode for mercury(II) reported by using indicator 1-(2-pyridylazo)-2-naphthol, which did not require an extractant or transfer reagent in the optode [15]. This may be attributed to the difference in the complexes formed by PAR and PAN with Hg(II). PAN forms neutral complex with Hg(II), while PAR forms anionic complex with Hg(II) as shown in Fig. 1 [28]. Aliquat-336 in the optode was found to facilitate the transfer of Hg(II) from aqueous medium to optode matrix, and its preconcentration as PAR–Hg(II) complex in the optode. The optimized amount of PAR in the optode was fixed to get a better optical property. The TEHP was found to form a uniform optode with better kinetics as compared to other plasticizer like NPOE and DOP. The proportions of CTA, TEHP and Aliquat-336 in the optode were optimized in terms of better uptake, kinetics, mechanical strength and uniformity. The optimized composition of the optode was found to be: CTA = 39.8 wt.%, TEHP = 39.8 wt.%, Aliquat-336 = 20.0 wt.%, and PAR = 0.4 wt.%.

The uptake of Hg(II) by this optode membrane from the aqueous solution was studied by using ^{203}Hg radiotracer which indicated quantitative uptake of Hg(II) (>80%) at pH > 6. The sorption of radio-
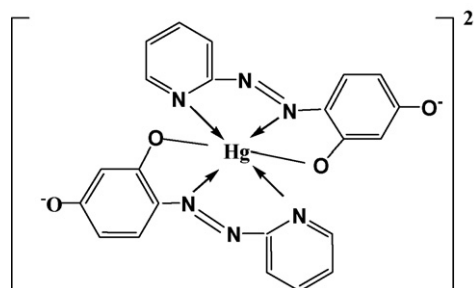

Fig. 1. Chemical structure of Hg(II)–PAR complex.
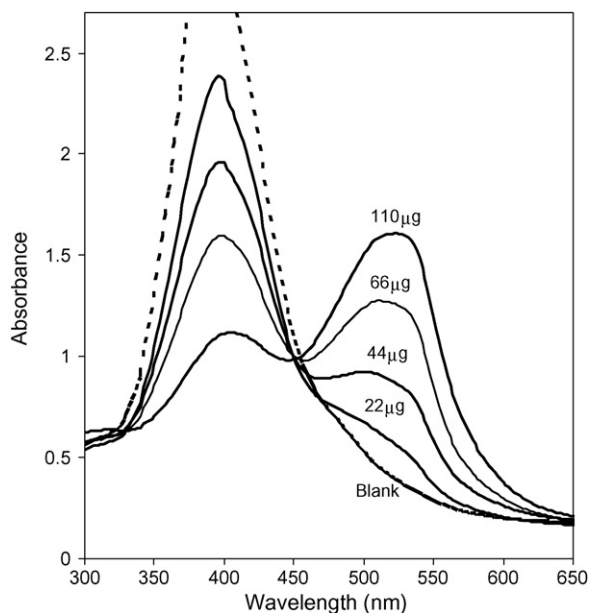
Fig. 2. UV–vis spectra of optode samples equilibrated with tap water spiked with different amounts of Hg(II) ions.

tracers of Cd(II) and Zn(II) ions in the optode was found to be considerably lower (10–15%) at pH higher than 6. The uptake of radiotracers of Hg(II) and Cd(II) in the optode samples from different water samples are given in Table 1. It is seen from this table that uptake of Hg(II) from distilled water was quite slow. The kinetics of Hg(II) sorption was considerably increased from tap water (30 min) as well as aqueous solution containing bicarbonate ions (5 min). This is due to the fact that Hg(II) may exist as hydrated Hg^{2+} species or $HgOH^+$ in aqueous medium in pH range of 5–8. The sorption of these Hg(II) species in the optode would be hindered due to the presence of quaternary ammonium salt in the optode matrix. Hg(II) forms an anion or neutral complex with carbonate [29] which may easily be sorbed in the optode matrix. The optode developed in the present work would be suitable for tap water and ground water because these contain carbonate/bicarbonate ions. In order to further study the effects of carbonate/bicarbonate ions, the variation in the absorbance of the optode at wavelength 520 nm corresponding to Hg(II)–PAR complex was studied by equilibrating the optode samples for 5 min in the solution having varying amounts of $NaHCO_3$ and a fixed amount of Hg(II) (2.64 μg/mL) at pH 7.5. The uptake of Hg(II) in the optode sample was enhanced with increase in the amount of $NaHCO_3$ up to 24 μg/mL of $NaHCO_3$ in the equilibrating solution, and thereafter it remains constant.

Based on the acid constants of PAR, the PAR would exist in aqueous sample as H_3L^+, H_2L, HL^{-1}, and L^{2-} species at pH < 3, 3 < pH < 6, 6 < pH < 12.5, and pH > 12.5, respectively [30]. At pH 7.5, it is likely that PAR would be present as HL^{-1} in the optode. There is a possibility that HL^{-1} may form the ion-pair with Aliquat-336 in the optode. The uptake of Hg(II) in the optode can be represented by the reaction:

$$2HL^{-1} + Hg(II) \leftrightarrow HgL_2^{2-} + 2H^+$$
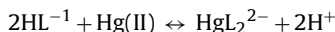
in which H^+ is formed and thus HCO_3^+ would also act as a buffer. The anionic complex HgL_2^{2-}, shown in Fig. 1, might be retained in the optode matrix due to its electrostatic binding with anion-exchanger Aliquat-336.

UV–vis absorbance spectra of blank optode and optode samples loaded with varying amounts of Hg(II) are shown in Fig. 2. It is seen from this figure that the absorbance maximum (λ_{max}) at 396 nm in the blank optode corresponds to uncomplexed PAR

[27]. On complexation with Hg(II), there was a large bathochromic shift in the absorbance of the optode samples from 396 nm (blank) to 520 nm with an isobestic point at 448 nm. The absorbance at λ_{max} = 520 nm increased proportionally with increase in the amount of Hg(II) sorbed in the optode. This indicated that the optode response is directly proportional to the concentration of Hg(II) ions sorbed in the optode from the equilibrating solution. The applicability of the optode for organomercury was studied by equilibrating the optode sample with tap water spiked with CH_3Hg^+. UV–vis absorption spectrum of the equilibrated optode sample was recorded, and shown in Fig. 3. It is evident from this figure that the optode described in the present work also respond to CH_3Hg^+. The absorbance at 520 nm of the optode equilibrated with CH_3Hg^+ can be used to quantify CH_3Hg^+ in the aqueous sample. This clearly indicates that the developed optode is sensitive to both Hg(II) ions and CH_3Hg^+ and therefore cannot individually estimate these species if present in the sample.

The response time of the optode towards Hg(II) was found to be dependent on the thickness of the optode sample. The equilibration time required for the optode sample (2 cm × 1 cm) in well-stirred solution containing Hg(II) and bicarbonate ions to attain maximum absorbance at λ_{max} = 520 nm of Hg(II)–PAR complex was found to reduce considerably from 30 min to 5 min on reducing the thickness of optode from 80 μm to 40 μm. A further reduction in the thickness was found to affect the mechanical strength of self-supporting optode. The optimum equilibration time required for quantitative uptake of Hg(II) in the optode sample (40 μm thickness) from tap water/ground water and aqueous medium with 24 μg/mL of bicarbonate were found to be 30 min and 5 min, respectively. The kinetics of Hg(II) sorption was not found to vary with the Hg(II) concentration ranging from 0.55 to 3.3 μg/mL in well-stirred aqueous sample (see Fig. 4).

The linearity range of the optode for Hg(II) was studied by the spectrophotometry, INAA and EDXRF. The advantages of using membrane optode samples for INA and EDXRF analyses of Hg(II) is that it contains mainly low Z elements like H, C, and O that do not produce significant amount of background. Since INAA and EDXRF is element specific, the Hg(II) sorbed in the optode matrix can be unambiguously quantified. Thus, these techniques can eliminate the possible interference in spectrophotometry. Since the optode developed in the present work can be used for the preconcentration of Hg(II) from aqueous medium, the detection limit and concentration range for which optode can be used for quantitative determination of Hg(II) are dependent upon the volume of the equilibrating solution, amount of Hg(II) required in the optode matrix to produce detectable analytical response and Hg(II) sorption capacity of the optode samples. The radiotracer studies indicated
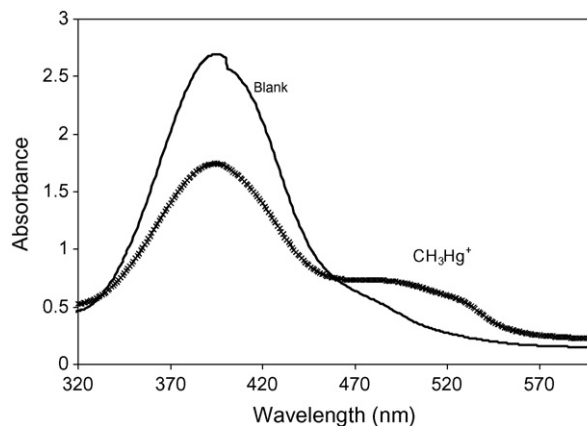

Fig. 3. Comparison of UV–vis spectra of blank optode and optode equilibrated with aqueous sample spiked with 2 mL of 2 ppm methyl mercury solution.
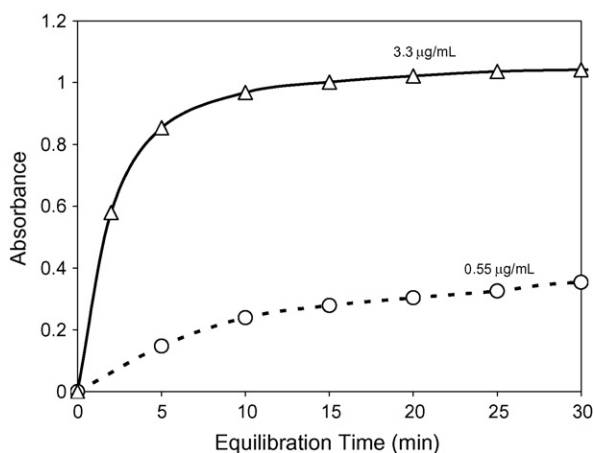
Fig. 4. Variation of absorbance of optode at 520 nm as a function of its equilibration time in well-stirred 10 mL of tap water spiked with a known concentration of Hg(II).

that the Hg(II) sorption capacity of the $2 cm \times 1 cm$ optode sample was 88 μg. 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 μg, respectively. Detection limit of Hg(II) by INAA can be further enhanced by increasing neutron irradiation and radioactivity counting durations and using a high efficiency γ-detector. In order to study linear response range, tap water samples of 25 mL were spiked with known amounts of Hg(II) ions and equilibrated with optode sample with constant stirring for 30 min. The absorbance of the equilibrated optode samples at 520 nm showed a linear response over a range of 0.22–1.32 μg/mL of Hg(II) in the aqueous samples. Similar response was obtained in 5 min equilibration time in presence of bicarbonate. The reproducibility of absorbance of optode samples equilibrated with a fixed quantity of Hg(II) was found to be within 1–2%. Contrary to spectrophotometry, the EDXRF and neutron activation analyses indicated that the linearity range in the optode sample (40 μm thickness, $2 cm \times 2 cm$ area) was up to 3.52 μg/mL. As shown in Fig. 2, the upper limit of linear range of optode by spectrophotometry is dependent on the concentration of PAR that preconcentrates Hg(II) as a colored PAR–Hg(II) complex. The upper limit of the analytical range for Hg(II) by spectrophotomety of optode can be extended up to

3.52 μg/mL by linearizing with log function as reported in the literature [31]. The lowest concentration of Hg(II) that can be quantified by spectrophotometry of the optode is dependent upon the volume of the aqueous sample. It was observed that 11 μg in 100 mL (0.11 μg/mL) aqueous samples (tap water) gives a distinct color change and absorbance above 3σ of the blank absorbance in 30 min equilibration. This seems to suggest that detection limit in present case can be extended by taking large volume of sample to preconcentrate the Hg(II) in the optode above 5.5 μg to produce detectable response.

The selectivity of the optode was tested for the determination of Hg(II) in the presence of other interfering cations namely Cu(II), Fe(II), Zn(II), Pb(II) and Cd(II). The optode samples were equilibrated with solutions containing Hg and Cd/Pb in different proportions. Pb(II) did not form a colored complex with PAR in the optode sample up to a concentration of 3.85 μg/mL which was three times higher than the concentration of Hg(II) ions in the equilibrating solution. Cd(II) was found to give a distinct color change ($\lambda_{max} = 520 nm$) in the optode when present more than 1.76 μg/mL in the equilibrating solution. This is expected as radiotracer studies indicated that Cd(II) sorption in the optode was of the order of 10–15%. The possibility of discriminating Cd(II) sorbed in the optode sample was studied by INAA. In these experiments, the amounts of Hg(II) was varied by keeping a constant amount of Cd(II) (40 μg) in the 25 mL equilibrating solution. The radioactivity produced by the neutron activation of Hg(II) (^{203}Hg) sorbed in the optode samples was found to vary linearly as a function of Hg(II) amount in the equilibrating solution. This indicated that the interference of Cd(II) can be accounted for by subjecting the optode samples to INAA. As such, other metal ions were not found to produce the color change in the optode samples under the chemical conditions used in the present work. In order to evaluate any possible interference of Cu(II), Fe(II), Zn(II) and Pb(II) ions, the Hg(II) uptake studies were carried out using ^{203}Hg radiotracer in the presence of these ions and the results are summarized in Table 2. It is evident from this study that the uptake of Hg(II) in the optode samples was unaffected (>85%) by the presence of Cu(II), Fe(II), Zn(II) and Pb(II) ions whose concentration was 10 times more than that of Hg(II).

The reusability of the optode was studied by repeating three cycles of Hg(II) sorption and desorption from the optode sample. For Hg(II) sorption, the optode sample was equilibrated with well-stirred 10 mL tap water spiked with 2.64 μg/mL of Hg(II) at pH
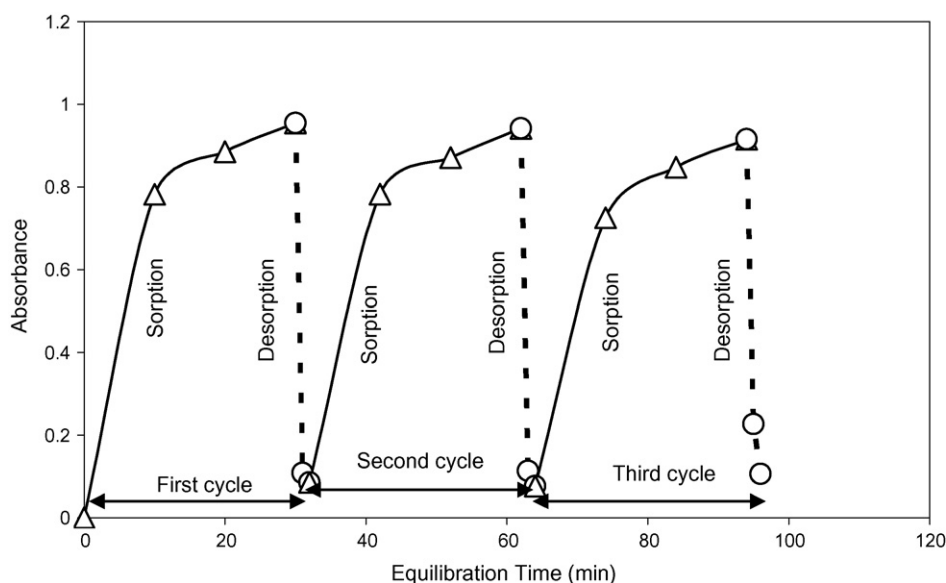

Fig. 5. Sorption and desorption cycles of the optode in 10 mL aqueous solution containing 2.64 μg/mL of Hg(II) in tap water and 0.02 mol L^{-1} disodium salt of EDTA, respectively.

Table 2
Uptake of Hg(II) in presence of interfering cations in the equilibrating solution determined by the radiotracer method.

Interfering cation [X(II)]	Amount of Hg(II) ($10^{-8} \times$ mol)	Amount of X(II) ($10^{-6} \times$ mol)	[X(II)]/[Hg(II)]	Hg(II) uptake (%)
–	5	–	–	90 ± 3
Cu(II)	5	2.7	50	87 ± 2
Fe(II)	5	0.5	10	88 ± 5
Zn(II)	5	0.5	10	85 ± 3
Pb(II)	5	0.5	10	84 ± 3

7.5. The desorption of Hg(II) from the optode was carried out in 0.02 mol L^{-1} aqueous solution of disodium salt of EDTA. The sorption and desorption of Hg(II) from the optode were studied by monitoring the absorbance at 520 nm. The profiles of the three repeated cycles of Hg(II) sorption–desorption are shown in Fig. 5. It is seen from Fig. 5 that the time span of sorption profile was 30 min while Hg(II) could be desorbed quantitatively from the optode within 2–5 min equilibration in well-stirred 10 mL aqueous solution of EDTA. This indicated that the optode described in the present work is reusable.

Finally, the optode was used for the analysis of surface water spiked with different amounts of Hg(II). The concentrations of Hg(II) in some of the samples in 25 mL volume were above the upper limit of analytical range of spectrophotometry of the optode (1.32 µg/mL). Therefore, two sets of experiments were carried out using samples as received and diluted by 10 times. The pH of aqueous samples was adjusted to 7.5 and 24 ppm of bicarbonate was added, and optode samples were equilibrated with stirring for 5 min. The average concentrations of Hg(II) in three different surface water samples were found to be 2.41, 1.54 and 0.19 µg/mL with relative standard deviation of 2–5%.

4. Conclusions

The color changeable optode for the detection of Hg(II) ions in aqueous samples was developed by the immobilization of a dye 4-(2-pyridylazo)resorcinol with a liquid ion-exchanger Aliquat-336 in the tri-(2-ethylhexyl) phosphate plasticized cellulose triacetate matrix. This optode was found to have linear response within 5 min equilibration in well-stirred bicarbonate medium and 30 min equilibration under similar conditions in tap water/ground water. The Hg(II) or CH_3Hg^+ sorbed in the optode matrix could be determined by the visual colorimetry or spectrophotometry but cannot discriminate if both the species coexist in the sample. The optode reported in the present work was found to be reusable after desorbing Hg(II) from the optode by equilibrating it for 2–5 min in 0.02 mol L^{-1} EDTA disodium salt solution. The optode samples were subjected to INAA or EDXRF to account for possible interference from Cd(II) and Zn(II), which were found to sorb 10–15% in the optode under the experimental conditions used in the present work. Interference from the cations like Cu(II), Fe(II), Zn(II) and Pb(II) was not found to be significant either in the uptake of Hg(II) in the optode sample or subsequent color formation in the optode. It was observed that 11 µg in 100 mL (0.11 µg/mL) aqueous samples (tap water) gives a distinct color change and absorbance above 3σ of the blank absorbance in 30 min equilibration.

Acknowledgments

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