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Development of a mercury ion-selective optical sensor based on fluorescence quenching of 5,10,15,20-tetraphenylporphyrin

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Abstract

A selective optical chemical sensor for mercury ion based on a lipophilized sensing material (5,10,15,20-tetraphenylporphyrin, H2tpp) dissolved in a plasticized poly(vinyl chloride) (PVC) membrane has been developed. H2tpp immobilized in the PVC membrane acts not only as a selective host molecule for Hg^{2+}, but also as a fluorescing transducer. The sensing mechanism involves the extraction of Hg^{2+} from aqueous sample solution to organic membrane phase and the formation of a metalloporphyrin complex between H2tpp and Hg^{2+}, which results in the fluorescence quenching of H2tpp. The optode membrane containing H2tpp reversibly responds to Hg^{2+} and shows extremely high selectivity to Li^+, Na^+, K^+, Mg^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Ag^+ and Pb^{2+}. The detection limit for Hg^{2+} is 4.0×10^{-8} mol/l at pH 8.0. The response characteristics of the sensor including dynamic range, reversibility, reproducibility, response time and lifetime are discussed in detail. This sensor has been used for the determination of mercury ion in water samples containing potential interferents with satisfactory recovery.

Keywords: Optical sensor; PVC membrane; Fluorescence quenching; H2tpp; Hg^{2+}

1. Introduction

The rapid analysis of trace heavy-metal cations is of tremendous interest in environmental and biomedical application. The toxicity of mercury in environment has been established. As for other metal cations species, the techniques used for mercury determination involve analytical steps. The most widely used techniques for quantification of Hg^{2+} are based on cold vapor atomic absorption spectrometry [1] and cold vapor atomic fluorescence spectrometry [2]. Other published methods include neutron activation analysis [3], anodic stripping voltammetry [4], X-ray fluorescence spectrometry [5] and inductivity coupled plasma mass spectrometry [6]. The use of ion-selective electrode, based on plasticized polymer membrane containing neutral carrier is most common for cation detection. However, detection of mercury by electrochemical analysis has found scarce application and is rarely found in the routine analysis of environmental or biological sample [7]. Optical chemical sensor (optode) is one of the advanced techniques in analytical chemistry, and it is receiving ever-increasing attention by researchers for the determination of toxicologically relevant ions [8–10]. In recent years, the optical chemical sensors for Hg^{2+} employing different chemical transducers and optical principles have been developed. Czolk and co-workers

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[11–13] used water-soluble porphyrin derivatives immobilized on Nafion or sol–gel films, while Lerchi [14] and Sanchez-Pedreño et al. [15] used methylene bis(diisobutyl dithiocarbamate) and 1-(2-pyriddylazo)-2-naphthol, respectively, dissolved in plasticized PVC membrane, Savvin et al. [16] used *H*-phenylazo-3-aminorhodanine adsorbed on polyacrylonitrile fiber with finely dispersed ion exchangers, or dithizone immobilized on cellulose-based materials as support [17] and Kuswandi and Narayanaswary [18] used 1-(2-thiazolyazo)-2-naphthol in Nafion. Most of these investigations were based on the use a neutral carrier as the selective ionophore for Hg^{2+}, and a lipophilized pH indicator dye as the transduction element. Generally, some of the sensors suffer from lack of selectivity to Hg^{2+} over other soft heavy-metals. Search for new sensing materials that can respond reversibly, selectively and sensitively to the analyte is the key step in such sensor design.

Because of high fluorescence quantum yield ($\Phi = 0.13$) and large Stokes shift ($\Delta\lambda > 200$ nm) [19], porphyrins have been used as fluorescing reagents for the determination of metal cations [20,21]. Furthermore, a number of studies regarding the relationship between the optical characteristics and the structure of these compounds have been published [22,23]. In our laboratory, we have embarked on an investigation of the water-insoluble porphyrin compounds in optical sensor design utilizing their excellent optical properties and high lipophilicity [24,25]. In the present work, 5,10,15,20-tetraphenylporphyrin(H2tpp) was utilized for the selective detection of Hg^{2+}. This approach combines the capability of H2tpp for selective Hg^{2+} recognition with the fluorescence response upon metal cation complex. H2tpp as a macrocylic compound, exhibits strong fluorescence in visible region owing to the conjugated double bond system and its high mobility of its π-electron. After being immobilized in a plasticized PVC membrane, H2tpp can selectively extract Hg^{2+} from aqueous sample solution into organic membrane phase and form a metalloporphyrin compound, which results in a decrease of H2tpp fluorescence.

To explore the properties of H2tpp as an optically sensing material for the metal cation, the principle of operation, measuring range, response time, stability, reproducibility, reversibility and the effect of the experimental variables were investigated.

2. Experimental

2.1. Materials and apparatus

The selected sensing material, H2tpp, was prepared according to Adler method and the product was verified by IR and NMR [26]. For membrane preparation, high molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS) and tetrahydrofuran (THF) were used. A stock solution of 4.52×10^{-3} mol/l Hg^{2+} was prepared by dissolving mercury(II) nitrate, $Hg(NO_3)_2{\cdot}H_2O$ (Fluka A.G.) in 0.2 mol/l nitric acid and diluted with distilled water. Lower concentrations of Hg^{2+} solutions were obtained by serial dilution of the stock solution in Tris–HCl buffer of pH 8.0 (ionic strength $I = 10^{-3}$ mol/l). Except when specified, all solutions were prepared with distilled water, all other chemicals were of analytical reagent grade.

All fluorescence measurements were performed on a spectrofluorimeter from Photon Technology International (London, Ontario, Canada), consisting of a lamp power supply (Model LPS-220), a xenon lamp (Model A1010) and a photomutiplier detection system (Model 710). Fluorescence emission intensities were recorded at 650 nm with an excitation wavelength of 419 nm. The excitation and emission bandwidth slits were all set at about 3 nm. The fluorescence emission spectra of H2tpp were smoothed with the standard software of the spectrofluorimeter.

2.2. Membrane preparation

A membrane cocktail was prepared by dissolving 50 mg of PVC, 100 mg of DOS and 1.54 mg (2.5 μmol) of H2tpp in 2.0 ml of freshly distilled THF. An aliquot of 0.2 ml of this solution was applied to the surface of a circular 35 mm diameter quartz plate which was mounted on a rotating (rotating frequency 600 rpm) aluminum alloy rod under a THF-saturated atmosphere [27]. After a spinning time of only 5 s, a membrane was obtained onto the quartz plate. From the volume applied, the thickness of dry membrane was estimated to be approximately 4 μm. For comparative studies, membranes incorporating different components were prepared (see Table 1). The resulting membranes were placed in ambient air for drying 2 h before being used.

Table 1
Composition of optode membrane[a]

Entry	H2tpp
M1	0.62 mg (1.00 μmol)
M2	1.54 mg (2.50 μmol)
M3	2.48 mg (4.00 μmol)
M4	3.70 mg (6.00 μmol)

[a] Each membrane contains 50 mg of PVC and 100 mg of DOS. Compositions of given amount were soaked up by microsyringes, mixed with 50 mg of PVC and 100 mg of DOS, then diluted to 2 ml with fresh THF.

2.3. Procedure

An ideal membrane on the plate was mounted in a specially designed laboratory-made flow-through measuring cell and conditioned in buffer solution (pH 8.0) for 15 min. The volume capacity of the cell was ca. 3.4 ml. The cell was introduced into the spectrofluorimeter in an appropriate position to guarantee the detection of the intensity of the fluorescence emission without interference from the excitation source [28]. Standard solution containing the metal cation buffer at pH 8.0 was passed sequentially through the system and the steady-state fluorescence spectra stored. The detection limit (LOD) of the sensor membrane was determined by alternately exposing the sensor layer by five times to plain buffer and low concentrations of Hg^{2+} and calculating the Hg^{2+} concentrations corresponding to signal changes that are six times the standard deviation of the plain buffer signals. After each measurement, the membrane was rinsed with 0.1% 3-mercaptopropionic acid and then the buffer solution until the original fluorescence intensity of the optode membrane was resumed.

3. Results and discussion

3.1. Principle of operation

The optode membrane described here belongs to the class of ionic-exchange system described previously [29]. The extraction of Hg^{2+} from the aqueous sample solution into membrane phase and its complexation by the lipophilized fluorescing indicator H2tpp proceed with the loss of two protons from the nitrogen atoms (Fig. 1). This ionic-exchange process is determined by the electroneutrality in the organic membrane phase. Fig. 2 shows the fluorescence emission spectra of the optode membrane M2, as obtained after equilibration with Tris–HCl solutions (pH 8.0) containing different concentrations of Hg^{2+}. The fluorescence spectra were recorded at $\lambda_{ex} = 419$ nm and $\lambda_{em} = 630$–690 nm. The values of the fluorescence intensities of the optode membrane decrease considerably as the concentrations of Hg^{2+} increase. The fluorescence response of the optode membrane incorporating H2tpp to different metal ions is summarized in Table 2. Only Hg^{2+} shows strong fluorescence quenching of the sensing membrane. This illustrates that the optode membrane can be used for the assay of Hg^{2+} in aqueous sample solutions.

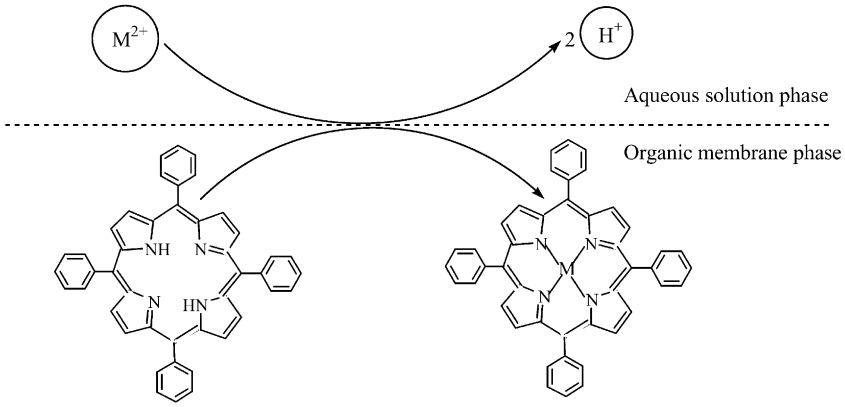

Fig. 1. The scheme of the chemical reaction of H2tpp with mercury ion.

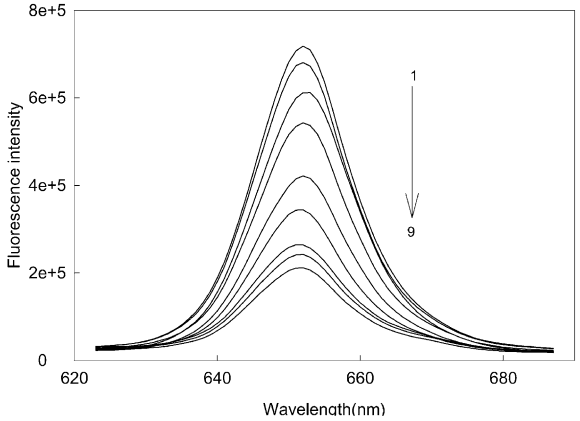

Fig. 2. Fluorescence emission of the sensing membrane M2 in the absence and presence of different concentrations of Hg^{2+}: (1) 0; (2) 4.52×10^{-8}; (3) 2.26×10^{-7}; (4) 4.52×10^{-7}; (5) 1.81×10^{-6}; (6) 4.52×10^{-6}; (7) 1.81×10^{-5}; (8) 4.52×10^{-5}; (9) 4.52×10^{-4} mol/l ($\lambda_{ex} = 419$ nm, pH 8.0).

The over-all equilibrium between the organic membrane phase (org) and the aqueous sample solution phase (aq) is described:

$$HgL(org) + 2H^+(aq) \overset{K_{exch}}{\rightleftharpoons} H_2L(org) + Hg^{2+}(aq) \quad (1)$$

where H_2L and HgL denote the ligand H2tpp and its metal–ligand complex, respectively. The corresponding equilibrium constant K_{exch} depends on the complex formation constant and the distribution coefficients of Hg^{2+} and H^+ ions between the aqueous sample solution phase and the organic membrane phase. If an 1:1 Hg^{2+}–ligand complex is formed in the optode membrane phase [20], substituting the activities of the species in the membrane phase by the concentrations and with the introduction of α (the ratio of the free ligand [L] relative to the total amount of ligand L_T present in the membrane phase), the response of the optode membrane can be given by

$$a_{Hg} = (a_H)^2 K_{exch} \frac{1-\alpha}{\alpha} \quad (2)$$

where a_{Hg} and a_H denote the activities of Hg^{2+} and H^+ ions, respectively. By providing a nearly constant ionic strength, the activity coefficient of Hg^{2+} can be assumed constant, and hence the activity of Hg^{2+} can be represented by the concentration. If K_{exch} and H^+ are assumed to be constant over the whole dynamic range, and if all constant values are summarized in K', the Eq. (3) can be derived from Eq. (2):

$$[Hg^{2+}] = K' \frac{1-\alpha}{\alpha} \quad (3)$$

The measured fluorescence intensity values F are directly related to α:

$$\alpha = \frac{F - F_1}{F_0 - F_1} \quad (4)$$

where F_1 and F_0 are the limiting fluorescence values for $\alpha = 1$ (in the absence of Hg^{2+}) and $\alpha = 0$ (fully complexed H2tpp).

The relationship between α and $[Hg^{2+}]$ as expressed by Eq. (3) is the basis of quantitative determination of Hg^{2+} concentration in aqueous sample solution by using this optode membrane.

Table 2
Fluorescence response of H2tpp optode membrane to different metal cations

Sample	Concentration (mol/l)	Fluorescence intensity
Reagent blank	0	$(7.23 \pm 0.37)^a \times 10^5$
Na^+	0.1	$(7.14 \pm 0.33) \times 10^5$
K^+	0.1	$(7.20 \pm 0.54) \times 10^5$
Mg^{2+}	0.1	$(7.12 \pm 0.26) \times 10^5$
Ca^{2+}	0.1	$(7.27 \pm 0.34) \times 10^5$
Ba^{2+}	0.1	$(7.68 \pm 0.41) \times 10^5$
Al^{3+}	0.1	$(7.17 \pm 0.13) \times 10^5$
Zn^{2+}	5.0×10^{-6}	$(7.42 \pm 0.44) \times 10^5$
Fe^{2+}	5.0×10^{-6}	$(6.82 \pm 0.35) \times 10^5$
Fe^{3+}	5.0×10^{-6}	$(6.77 \pm 0.38) \times 10^5$
Cu^{2+}	5.0×10^{-6}	$(6.81 \pm 0.46) \times 10^5$
Ag^+	5.0×10^{-6}	$(7.54 \pm 0.22) \times 10^5$
Hg^{2+}	4.52×10^{-6}	$(3.43 \pm 0.24) \times 10^5$
Pb^{2+}	5.0×10^{-6}	$(6.52 \pm 0.31) \times 10^5$
Cd^{2+}	5.0×10^{-6}	$(6.85 \pm 0.41) \times 10^5$

[a] Average value ± standard deviation of three determinations.

3.2. Response behavior

In Fig. 3, the relative fluorescence value, α, is given as a function of the logarithm of Hg^{2+} concentration at pH 8.0. The curve fitting for the experimental data points was calculated from Eq. (3) with $\log K' = -4.74$. The good correlation of the measured data with the theoretical predication confirms the validity of the assumption made in Eq. (3). The curve can serve as the calibration curve for the determination

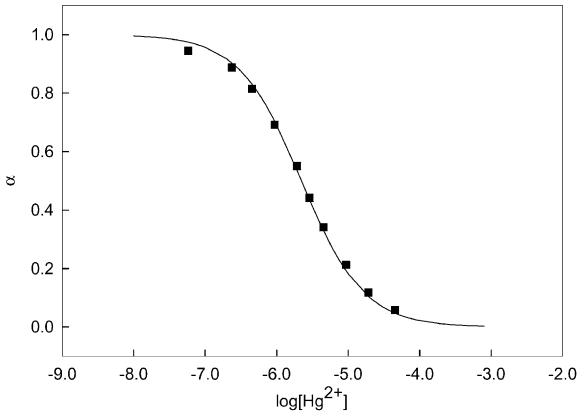

Fig. 3. Relative fluorescence response value (α) of M2 at $\lambda_{ex/em} = 419/650$ nm as a function of logarithm of Hg^{2+} concentration at pH 8.0. The curve fitting the experimental points was calculated from Eq. (3).

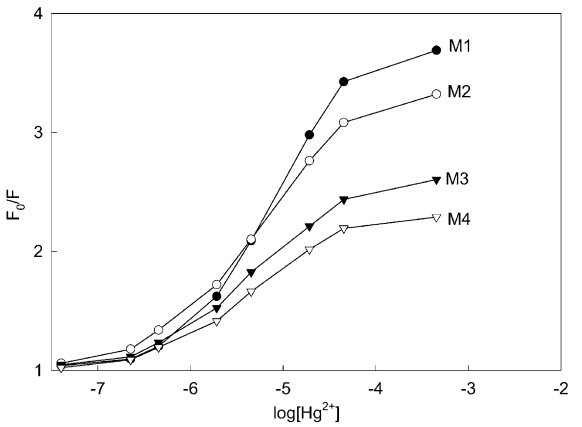

Fig. 4. Fluorescence response of different composition membranes on exposure to Hg^{2+} solution at pH 8.0 measured at an excitation wavelength of 419 nm and an emission wavelength of 650 nm.

of Hg^{2+}concentration. It is clear that a sufficient response to Hg^{2+} is obtained from 2.26×10^{-7} to 4.52×10^{-5} mol/l. The detection limit is 4.0×10^{-8} mol/l. In order to avoid depletion of the analyte close the optode membrane, which would result in a large concentration gradient in the sample solution, a sufficient amount analyte must be ensured. For this reason, the steady-state was reached significantly faster for a total Hg^{2+} concentration of less than 1.0×10^{-5} mol/l, when the sample solution was pumped through the measuring cell. At low Hg^{2+} concentrations a reduction of the total amount of the indicator dye would of course also lead to shorter response times, but unfortunately at the expense of sensitivity.

3.3. Optimization of membrane composition

The optode membrane response to the analyte may be changed by variation of the compositions of the membrane cocktail. This can be seen in the variation of sensor characteristics (working range and response slope) due to the different concentration of H2tpp. In Fig. 4, the fluorescence quenching efficiencies (F_0/F) for four membranes (M1, M2, M3 and M4, see Table 1) at $\lambda_{ex/em} = 419/650$ nm, are plotted as functions of the logarithm of Hg^{2+} concentration at pH 8.0, where F_0 and F are the fluorescence intensities of the optode membrane in the absence and presence of Hg^{2+}. Obviously, optode membrane M2 emerged as the best in terms of the working range and sensitivity for the determination of low concentration of mercury ion.

It has been reported that the addition of a salt with a highly lipophilc anion (such as potassium tetra(4-chlorophenyl)borate, KTpClPB) in the membrane phase may ensure a sufficiently high amount of cations in the organic phase [30]. In the present investigation, unfortunately, we found that the H2tpp fluorescence was quenched by KTpClPB. In the presence of Hg^{2+}, the fluorescence intensity of the optode membrane restored owing to the decomposition of the borate anion by the metal ion [31], then decreased again.

Changing the type of the plasticizer is another way to alter sensor characteristics. Appropriately, plasticizers must be selected so as to obtain a transparent and flexible membrane, which has the maximum response to the analyte. Sensing membranes made of different plasticizers were prepared, membrane containing bis(2-ethylhexyl)seacate (DOS) gives the maximum sensitivity to the Hg^{2+}. The optimum ratio of DOS and PVC was 2:1 (w/w).

3.4. Effect of acidity

The blank fluorescence intensity of the sensing membrane itself was found to be dependent on the acidity of the soaking solution due to the existing of

nitrogen atoms in H2tpp molecule. At high acidity, H^+ may be extracted into membrane phase and complex with the nitrogen atoms forming the protonated complex [32]:

$$\mathrm{H2tpp} + \mathrm{H}^+ \rightleftharpoons \mathrm{H3tpp}^+ \quad (5)$$

$$\mathrm{H3tpp}^+ + \mathrm{H}^+ \rightleftharpoons \mathrm{H4tpp}^{2+} \quad (6)$$

Thus, the π-electron conjugated double bound system of H2tpp would be destroyed, and the values of the fluorescence intensities decrease. On the other hand, the coordination interaction between the protonated porphyrin and metal cation is very weak, and hence the fluorescence quenching efficiency (F_0/F) would of course also decrease. Fig. 5 shows the dependence of the fluorescence intensities of the sensing membrane M2 in the absence and presence of 4.52×10^{-6} mol/l Hg^{2+}, at a series of different pH values. It is obvious that, in the absence of Hg^{2+} (curve 1), the fluorescence intensities (F_0) of the optode membrane is significantly pH-dependent. F_0 increase up to pH 10.3, then decrease slightly at higher pH values. Curve 2 shows the fluorescence intensities of the sensing membrane in buffer containing 4.52×10^{-6} mol/l Hg^{2+}. Curve 2 has a similar shape to curve 1, although the fluorescence intensities (F) were smaller. Taking the sensitivity (F_0/F) and the absolute values of the fluorescence signals into account, a pH 8.0 Tris–HCl buffer solution was used.

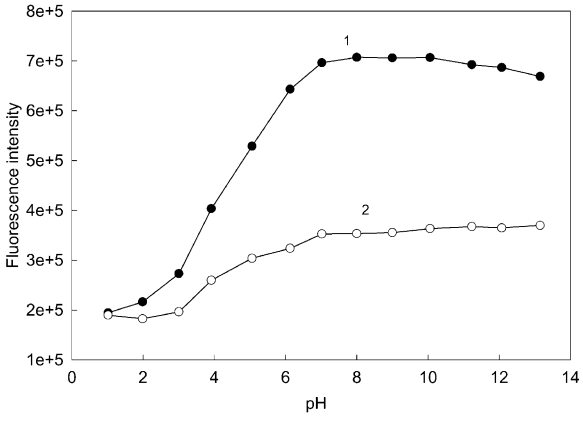

Fig. 5. Effect of pH on the fluorescence intensity of the optode membrane M2 in the absence (curve 1) or presence of 4.52×10^{-6} mol/l Hg^{2+} (curve 2) at an excitation and emission wavelength of 419 and 650 nm, respectively.

3.5. Reproducibility and reversibility

It would be desirable for an optical sensor to have good reproducibility and reversibility. The reproducibility and reversibility of the sensing membrane was evaluated by repeatedly switching the membrane into three standard solutions. Fig. 6 shows the fluorescence intensity response at $\lambda_{ex/em} = 419/650$ nm versus time recording for the sensing membrane M2 when it was exposed to repeated concentration step changes among 2.26×10^{-7}, 4.52×10^{-7} and 1.81×10^{-6} mol/l Hg^{2+} in Tris–HCl buffer solution. The relative standard deviations were found to be 3.1% (2.26×10^{-7} mol/l Hg^{2+}, $n = 4$), 1.8% (4.52×10^{-7} mol/l Hg^{2+}, $n = 4$) and 4.6% (1.81×10^{-6} mol/l Hg^{2+}, $n = 4$), respectively. The results indicate that the sensor has good reproducibility and reversibility.

3.6. Response time

The response time ($t_{95\%}$) of the sensor depends on the thickness of the sensing membrane and the concentration of analyte. When the thickness of the membrane reaches the order of millimeters, there is no obvious response to be observed, thus, it is necessary to prepare a very thin, homogenous and reproducible PVC-based membrane. At membrane thickness of

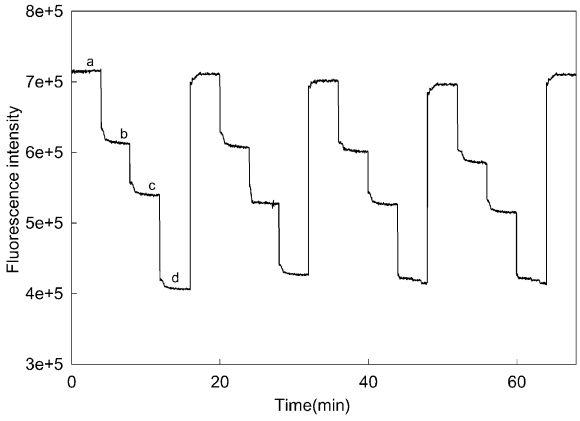

Fig. 6. Reproducibility and reversibility of the response of the optode membrane M2 on exposure to Hg^{2+} solution at pH 8.0: a, blank solution; b, 2.26×10^{-7} mol/l Hg^{2+}; c, 4.52×10^{-7} mol/l Hg^{2+}; d, 1.81×10^{-6} mol/l Hg^{2+}. Fluorescence intensity measurement at an excitation and emission wavelength of 419 and 650 nm, respectively.

$4 \pm 0.2\,\mu m$, the $t_{95\%}$ values are found within 4 min. When the response of the same membrane to the different step changes in Hg^{2+} concentration are measured, there is about 20% difference in the response time, the time required to reach equilibrium increases with increasing of Hg^{2+} concentration. The time limiting step is not the diffusion within the organic phase, but the convective mass extraction from the bulk of the aqueous solution that goes on until the required absolute amount of measuring ion is reached.

3.7. Short-term stability and life time

The stability of the sensor was tested by using 4.52×10^{-6} mol/l Hg^{2+} solution. The fluorescence response of the membrane M2 at $\lambda_{ex/em} = 419/650$ nm in contact with 4.52×10^{-6} mol/l Hg^{2+} was recorded over a period of 10 h with an interval of 30 min. The mean fluorescence intensity value and standard deviation was found to be $33.77 \times 10^5 \pm 2.46 \times 10^5$ ($n = 21$). This shows the optode membrane has good short-term stability. Additionally, the fluorescence intensity of the optode membrane at $\lambda_{ex/em} = 419/650$ nm dropped by about 10% during the determination of sample solution of 3 weeks. The decrease of the fluorescence intensity of the membrane might be due to leaching and the photodecomposition of the membrane components when it was excited by stronger incident lights. Apparently, the life time of the optode membrane is acceptable for continuous analytical applications.

3.8. Selectivity

In order to assess the possible analytical application of the sensing method, the effects of some alkali, alkaline-earth and heavy-metal ions as well as some anions on the sensing of Hg^{2+} were examined. The data were obtained with a fixed concentration of Hg^{2+} (4.52×10^{-6} mol/l) and different foreign interferents. No significant interferences were observed if a less than ±5% relative error was tolerated. The results of these tests on potential interferences are summarized in Table 3. Some ions existing in environmental water

Table 3
Effect of different interferents on the fluorescence signals of the optode membrane[a]

Interferent	Concentration (mol/l)	Fluorescence change value, $\Delta F = (F_1 - F_2)$[b]	Relative signal change value (%) $(\Delta F/F_1) \times 100$
Li^+	1.00	5.4×10^3	1.58
Na^+	1.00	7.0×10^3	2.02
K^+	1.00	4.6×10^3	1.37
NH_4^+	1.00	-9.2×10^3	−2.73
Ca^{2+}	1.00	7.9×10^3	2.33
Mg^{2+}	0.50	2.5×10^3	0.75
Al^{3+}	0.50	-1.03×10^4	−3.05
Ba^{2+}	0.50	5.5×10^3	1.61
Zn^{2+}	1.0×10^{-5}	-1.45×10^4	−4.28
Fe^{2+}	2.0×10^{-5}	1.13×10^4	3.31
Fe^{3+}	2.0×10^{-4}	1.03×10^4	3.02
Cu^{2+}	5.0×10^{-5}	3.16×10^3	0.93
Ag^+	2.0×10^{-5}	-1.14×10^4	−3.37
Pb^{2+}	1.0×10^{-5}	1.02×10^4	3.01
Cl^-	1.00	5.4×10^3	1.66
NO_3^-	1.00	-1.01×10^4	−3.01
NO_2^-	0.05	-4.1×10^3	−1.23
SO_4^{2-}	0.50	2.9×10^3	0.83
I^-	0.10	4.8×10^3	1.46
PO_4^{3-}	0.1	8.7×10^3	2.54

[a] Each sample solution containing a fixed Hg^{2+} concentration of 4.52×10^{-6} mol/l.

[b] F_1 and F_2 are the fluorescence intensities of the sensing membrane M2 in the presence of 4.52×10^{-6} mol/l Hg^{2+} without and with interferents, respectively.

Table 4
Results of Hg^{2+} determination in three synthetic samples

Sample	Composition of sample ($\times 10^{-6}$ mol/l)	Determination ($\times 10^{-6}$ mol/l)[a]	Recovery (%)
1	KCl 50, NaCl 500, NH_4Cl 500, $CaCl_2$ 500, $MgCl_2$ 400, $AlCl_3$ 400, $BaCl_2$ 200, $ZnCl_2$ 80, $FeCl_2$ 100, $FeCl_3$ 100, $CuSO_4$ 50, $AgNO_3$ 20, $Cd(NO_3)_2$ 50, $Pb(NO_3)_2$ 10, $Hg(NO_3)_2$ 2.0	2.04	102
2	KCl 500, NaCl 500, NH_4Cl 500, $CaCl_2$ 800, $MgCl_2$ 500, $AlCl_3$ 400, $BaCl_2$ 500, $ZnCl_2$ 80, $FeCl_2$ 150, $FeCl_3$ 200, $CuSO_4$ 100, $AgNO_3$ 50, $Cd(NO_3)_2$ 80, $Pb(NO_3)_2$ 50, $Hg(NO_3)_2$ 8.0	8.70	108.7
3	KCl 1000, NaCl 800, NH_4Cl 500, $CaCl_2$ 500, $MgCl_2$ 800, $AlCl_3$ 800, $BaCl_2$ 800, $ZnCl_2$ 400, $FeCl_2$ 500, $FeCl_3$ 500, $CuSO_4$ 400, $AgNO_3$ 300, $Cd(NO_3)_2$ 200, $Pb(NO_3)_2$ 200, $Hg(NO_3)_2$ 20.0	19.68	98.4

[a] Average value of three determinations.

such as Li^+, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, NO_3^-, NO_2^-, Cl^-, SO_4^{2-} and I^- show no interference for the detection of 4.52×10^{-6} mol/l Hg^{2+}. Heavy-metal cations such as Pb^{2+} and Ag^+ that can be complexed with porphyrin, at concentration levels one order of magnitude higher than the concentration of Hg^{2+} in sample solution, exhibit fluorescence signal changes of the optode membrane of less than 5%. The sensor exhibits a fairly high selectivity for Hg^{2+}, rendering its application to the analysis real sample feasible.

3.9. Preliminary application

The application of the proposed method was evaluated for determination of Hg^{2+} in tap water samples. In our experiment, all the water samples were spiked with Hg^{2+} at different concentration levels which were prepared on the basis of possible metal ions presenting in the environmental water and then analyzed with the method proposed. The results are given in Table 4, the recovery was 98.4–108.7%.

Acknowledgements

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