Electrochemical analysis to construct specific sensor, selective for mercury (II) ions

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Abstract: *The present work deals with preparation and characterization of mercury selective membrane-sensor based on prometryn compound as ionophore. This sensor exhibited good response to mercury (II) ion over the concentration range $10^{-5}-10^{-2}$ M with Nernstian slope 27.7±0.l mV/decade at pH 3 with response time less than 20 sec. and the lower limit of detection 6×10^{-6} M. The response characteristics of this sensor are studied. The comparison between the proposed sensor and the other sensors which are reported in the literature is noted.*

Keywords: *Selective membrane sensor – Ion electrode - Ionophore - Prometryn – Mercury.*

I. INTRODUCTION

Hg-compounds are toxic but they play an important role in agriculture as fungicides. Thus, there is great need to determine its concentration in the environment.

In recent years, particular concern has been devoted to the presence of mercury species in natural waters, which is recognized as an area of major environmental concentration. The most dangerous form is methyl mercury, a potent neurotoxicant, which concentrates in the blood and permanently effects on the brain and central nervous system [1].

Many mercury compounds are widely used in agriculture and caused severe reductions of bird populations but used in pharmaceutical drugs. The resulting possible health hazards of these compounds and their degradation products have increased the interest in developing simple and sensitive methods for the determination of mercury at trace levels [2].

Polyvinylchloride(PVC)membrane electrode selective to Hg (II) ions was prepared by using bis-[((4nitrophenyl) azosalicylaldehyde)] (BNAS) as a suitable neutral carrier. The sensor exhibits a Nernstian response for mercury ions over a wide concentration range (5.0×10^{-2}-7.0×10^{-7} M) with a slope of 30±1 mV/decade. It has a response time of 10s and can be used for at least 3 months without any measurable divergence in potential [3].

A mercury ion-selective electrode (ISE) was prepared with a polymeric membrane based on a calixarene derivative containing a thiazole azo group as the ionophore. Several lSEs were conditioned and tested for the selection of common metal ions. The ISE gave two kinds of response slope for Hg^{+2} one, which has twice the Nernstian response for Hg^{+2} is obtained at pH 6.5 with a slope of 61.l mV/decade in the concentration range of 7.5×10^{-6}- 5×10^{-2} M which has a typical Nernstian response for Hg^{+2} is obtained at pH 4 with a slope of 28.7 mV/decade in the concentration range of 5×10^{-6}-10^{-2} M. The ISEs exhibit stable detection reproducibility and high selectivity towards alkali, alkaline earth and transition metal ions except Ag^+ Fig.(2), [4].

Polystyrene-based membrane of 2,3,4,9,l0,11-dipyridine-3,l0-diaza-1, 5, 8,12-tetrathiacyclotetradeca-2,9-diene with sodium tetraphenylborate (STP) and dibutyl phthalate (DBP) as anion excluder and plasticizing agent was prepared and investigated as Hg (lI)- selective electrode [5].

A PVC electrode based on p-tert-butyl calix crown with imine units as an ionophore showed a good potentiometric response for Hg (II) ions over a wide concentration range of 5×10^{-5}- 1×10^{-1} M with a near Nernstian slope of 27.3 mV/decade. The detection limit of the electrode was 2.24×10^{-5} M and over the pH range of 1.3-4 [6].

A new PVC membrane electrode for Hg (II) ion based on a recently synthesized mercapto compound of 2-benzoylamino -3- (4-chloro-phenyl)-thioacrylic acid S-(2-mercapto-4-methyl-phenyl) ester was reported. The electrode exhibits a Nernstian response for Hg^{+2} ions over a wide concentration range (2×10^{-7}- 3×10^{-2}M) with a slope of 29 (±l). The limit of detection is 5×10^{-8} M. The proposed sensor revealed good selectivities over a wide variety of other cations. This electrode could be used in over pH range of 1-4 [7].

A new PVC membrane Hg(II)-ISE with the complex of iodomercurate with diphenylhydramine as electroactive material was prepared. The Nernst response of the electrode to Hg (II) in the range of $1x10^{-2}$-1.6×10^{-5} M with a slope of 29 mV/decade was found and the detection limit was found to be $lx\ 10^{-5}$ M [8].

PVC based membranes of a double armed crown ether, N,N'-dibenzyl l, 4, 10,l3-tetraoxa-7,16-diaza cyclooctadecane (I) as ionophore with sodium tetra phenyl borate (NaTPB) as anion excluder and with many plasticizing solvent mediators were prepared and used for Hg(II) ion determination [9].

A selective liquid membrane electrode to Hg (II) was developed with 1-Furoyl-3-cyclohexylthiourea as neutral mobile carrier. The PVC membrane was deposited dropwise directly into a composite graphite-epoxy support. The sensor exhibits a twice Nernstian responses for both pH. The slope at pH = 7 was 59.15 ± 1.38 mV/decade and slope at pH=4 was 29.66 mV/decade. The ISE lifetime is l0 weeks, with a response time of 27s. The ISE showed a good selectivity for Hg [10].

A new ion-selective PVC membrane electrode based on salicylaldehyde thiosemicarbazone as an ionophore sensor for Hg (II) ions. The electrode shows excellent potentiometric response characteristics and displays a linear log $[Hg^{+2}]$ versus EMF response over a wide concentration range of 1.778×10^{-6}-$1x\ 10^{-1}$ M with Nernstian slope of 29 mV/decade with the detection limit of $1x10^{-6}$ M. The response time of the electrode is <30s and the membrane electrode operates well in the pH range of 1-3. The lifetime of the sensor is 2 months [11].

A novel Hg ion selective electrode was constructed to have strongly coordinating macrocyclic ligand binding site covalently attached to polythiophene film using l-l,4,l0-trioxa-7,l3-diazacyclo-pentadecane-1 thiophenylmetha (TDCD) thiophenylmethane) as a specific chelator. Reversible cyclic voltammetric waves show that both Hg (I) and Hg (II) are stabilized by the ligand. Monomethyl Hg and vapor phase elemental Hg are also electrochemicaly determined [12].

The electrode for Hg (II) is based on a macrocyclic ligand, i.e., Kryptofix-222. The monomeric and polymeric approaches were examined [13].

A compound Hg chalcogenide glass ion-selective electrode (ISE) was characterized using SEM, x-ray diffraction, and XPS, and the compositional data were used in the fabrication, continuous flow analytical (CPA) is suitable for rapid determination of ultra trace levels of Hg in saline media when used in conjunction with an extrapolation method that predicts the steady-state potential of the Hg ISE by the initial data following a stepwise change in Hg^{+2} activity, The CFA technique yields a near-Nernstian response of 28 mV/decade change in Hg^{+2} activity in Hg buffers in the range 10^{-18}-10^{-12} M Hg^{+2} [14].

A new liquid membrane, Hg (II) ion-selective electrode (ISE) based on 1,3-diphenylthiourea as a neutral carrier was developed. In tests of 1,3-diphenyl-thiourea in six different plasticizers, tris(2-ethylhexyl) phosphate (TEHP) showed the best performance and was selected for the membrane. Several ISEs were conditioned and tested for the selection of seven metal ions, from which Hg^{2+}. The best Nernstian response was obtained for Hg^{+2} with an extrapolated slope of 58.6 ± 0.8 mV/decade in the concentration range $6x10^{-6}$-$5x10^{-4}$ M, the presence of the complex $Hg(OH)^{+}$ ion explains the slope of the response curve. The ISE showed stable detection reproducibility during 6 week, with a practical detection limit of 10^{-6} M and a high selectivity for the several ions from which Hg^{+2} ion. A second linear response curve for Hg^{+2} was obtained at pH4 with a slope of 30.8 mV/decade in the concentration range $2x10^{-6}$-$2.1x10^{-4}$ M [15].

Best perfonnance was observed with the membrane l0, 200 and 200 mg of TPT, DOP (dioctylphthalate) and PVC respectively the membrane electrode works well over a wide concentration range $1.1x10^{-5}$- $1x\ 10^{-1}$ M of Hg^{+2} with a slope of 28.6 mV/decade of concentration of Hg^{+2}. The useful pH range for the electrode is 2.3-4.2 with a response time of 30s. The selectivity coefficients values are of the order of 0.01 for mono-bi- and trivalent cations which indicate good selectivity for Hg^{+2} ions over a large number of cations, the electrode has a life time of 3 months [16].

Hg-compounds are toxic and thus there is great need to determine its concentration in the environment. Thereby, the present work deals with preparation and characterization of mercury selective membrane-sensor based on prometryn compound as ionophore.

II. MATERIALS AND METHODS

II.1. Equipments:

All potentiometric measurements were made at $25\pm1^{\circ}$C with an Orion digital pH/mV meter using prometryn (N^2, N^4 di-isopropyl-6-methylthio-l,3,5- triazine-2.4 diamine membrane), as in the figure in conjunction with an Orion double junction Ag/AgCl reference electrode (Model 90-2) filled with 10% W/W KNO_3 in the outer compartment, all Orion combination pH electrode was used for pH adjustment.

II.2. Chemicals and Reagents:

Prometryn-ionophore was obtained from national organization for Agriculture Research analytical reagent grade chemicals, and distilled water were used for preparing all aqueous solutions.

High molecular weight poly(vinylchloride carboxylated) (PVC-COOH, nitrophenyl octylether (NPOE), Dibutyl sebacate (DBS), Dioetyl phthalate (DOP) and (THF) tetrahydrofuran were obtained from fluka. Stock solutions (10^{-1} M) of different metal salts (chloride, sulfate, nitrate) were prepared from reagent grade chemical.

II.2.1. Membrane preparation and sensor construction:

PVC based Hg(II) membrane sensor was prepared. A portion of prometryn ionophore, dibutyl sebacate (DBS) and PVC-COOH mixed in a glass petridish. This mixture was dissolved with tetrahydrofuran. The solvent was allowed to evaporate and the resulting transparent membrane was obtained. Membranes discs fixed to a piece of PVC tube using THF solvent. The sensor was subsequently conditioned overnight in solution of $HgSO_4$. The potential of this working electrode was measured against a constant potential provided by an external reference electrode.

II.3. Effect of pH and response time:

Buffer potassium hydrogen phthalate was prepared by dissolving potassium hydrogen phthalate in distilled water adjust to pH=3 by hydrochloric acid and diluted as a buffer. Response time can calculated for each concentration.

II.4. Effect of internal solution:

The three different concentrations of internal solution 10^{-2}, 10^{-3} and 10^{-4} M filled the sensor body was examined. The performances of the sensor was tested by measuring EMF of 10^{-3} M of the primary ion solution and plotted against logarithm of concentration.

II.5. Effect of plasticizer:

Prometryn
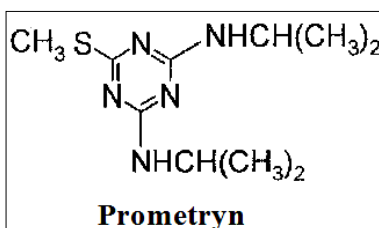
Mercury PVC membrane sensors incorporating ionophore (N^2,N^4-di- isopropyl-6 methylthio-1,3,5 triazine- 2,4 diamine) was prepared using diocty-phthalate (DOP),2-nitrophenyl octylether (NPOE) and dibutyl sebacate (DBS) with ionophore, PVC-COOH. The slope, linear range, lower limit of detection of each membrane were determined.

II.6. Determination of selectivity coefficients of mercury PVC-COOH membrane sensor:

Selectivity coefficients of the sensor were determined using the separate solution method [17] and calculated from the following equation where:

E_{Hg}: is the potential measured in 10^{-3}M. $HgSO_4$ solution.

E_M: is the potential measured in 10^{-3}M solution of the interfering cation.

S: slope of the electrode calibration plot.

III. RESULTS AND DISCUSSION

III.1. Performance characteristic of Hg^{++} sensor:

Prometryn showed sensitivity to mercury similar to silver when soaking in mercuric sulphate 24h .This behavior depends on prometryn which contain sulphur and nitrogen atoms that serve as donor atoms for complexation. The metal ions of soft acid character (i.e.,Hg^{2+}, Ag^{+}) reveal the most sensitive response to interaction with sulfur atoms. It generates stable potentials when placed in contact with Hg^{2+} [18]. The emf response of the membrane at varying concentrations of Hg^{+2} ion indicates a linear range from $lx10^{-5}$-$1x10^{-2}$ M. The slopes of the calibration curves were 27.7 mV/decade of Hg^{+2} concentration. The limit of detection as determined from the intersection of the two extrapolated segments of the calibration graph (Fig. 4). Table (3) illustrated most important characteristics of the membrane sensor.

III.2. Effect of pH and response time

The influence of the pH of the test solution on the potential response of the sensor was tested at 10^{-3}M Hg^{+2} concentration. potentials were found to stay constant at pH range 2-3 but more than pH3 gradual drift was observed. Fig.(1). The observed drift at higher pH values appear due to hydrolysis of mercury sulfate and formation of some hydroxy complexes of Hg^{+2} ion in solution. Thus, the working pH equals 3 [19]. The static response time of the membrane sensor obtained was >25s and potentials stayed constant for more than 3 minutes.

III.3. Effect of internal solution

The proposed sensor was also examined at different concentrations of inner reference solutions 10^{-2}, 10^{-3} and 10^{-4} M which does not cause any significant difference in the corresponding potential response, except for an expected Nernstian slope. Fig. (2). It was found that 10^{-2} M concentration of the internal solution is quite appropriate for smooth functioning of the electrode system Table (1).

$$-\log K^{pot}_{Hg,,M} = [E_M - E_{Hg}/S] - \log a^{(Z_{HgM}/Z_M)} + \log a_{Hg}$$

III.4. Effect of plasticizer on the response of Hg selective electrode:

In general, the sensitivity and selectivity of an ion-selective electrode is strongly influenced by the nature and amount of the plasticizer.

The effect of the Hg^{+2} selective electrode was investigated by using three kinds of plasticizers DBS, NPOE and DOP. The potential responses of the ion are shown in Fig. (3). The electrodes plasticized with (NPOE) and (DBS) showed somewhat better linear dynamic range and sensitivity Table (2).

III.5 Determination of selectivity coefficients 3

The most important characteristic of a membrane sensor is its relative response for the primary cation over other cations present in the solution, which is expressed in terms of potentiometric selectivity coefficients K$^{pot}_{HgM}$, which were evaluated graphically by the separate solution method. Fig.(5) shows that these metal ions have negligible disturbance of the functioning of Hg^{+2} membrane sensor except silver ion. The resulting values of the selectivity coefficients are summarized in Table (4).
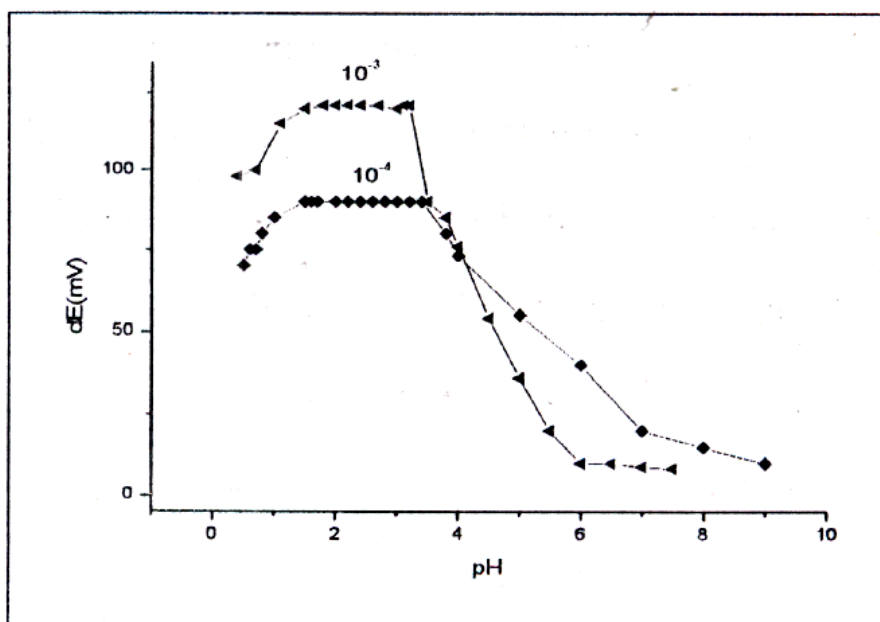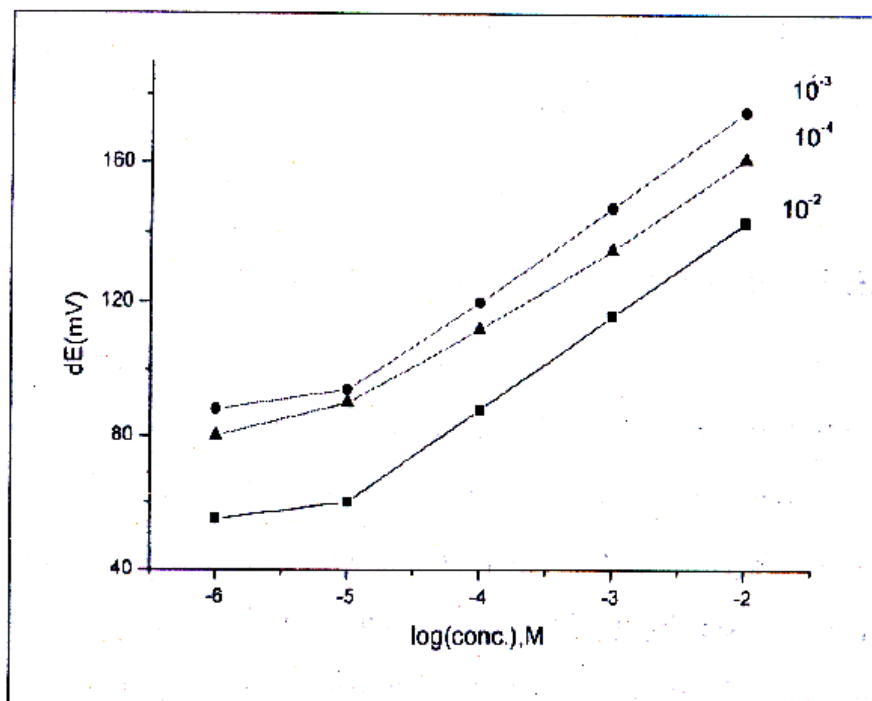
Fig. 1. Effect of pH on Hg^{++} sensor

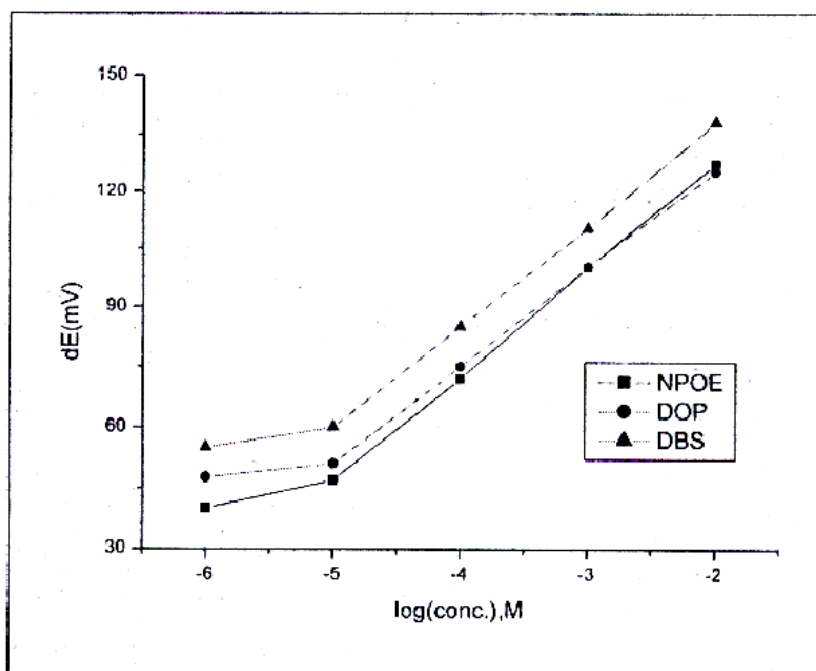**Fig. 2.** Effect of concentration of internal solution

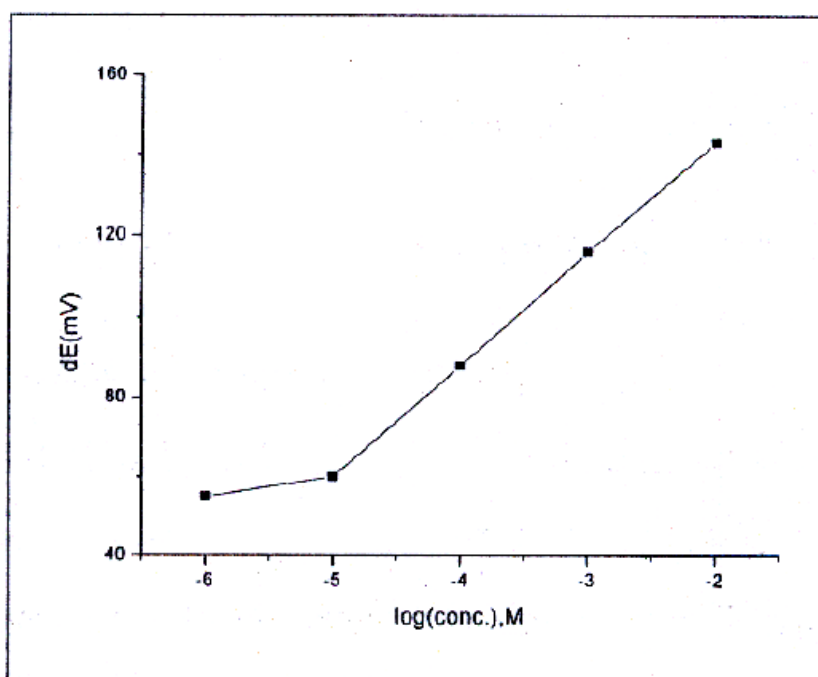**Fig. 3.** Effect of solvent mediator

Fig. 4 . Calibration curve of Hg^{++} based on Prometryn sensor
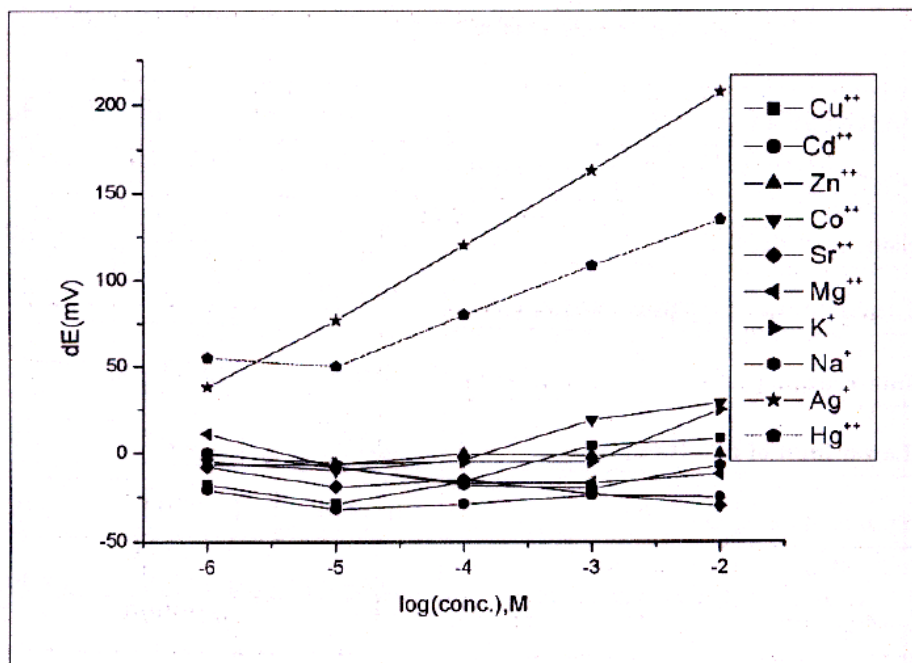
Fig. 5. Selectivity of Hg^{++} sensor

Table 1. The effect of internal solution on the (PM)-Hg sensor

PARAMETER	Concentration	Int. Soln. 10^{-2} M	Int. Soln. 10^{-3} M	Int. Soln. 10^{-4} M
Slope,(mV/decade)		27.7	26.8	23.6
Linear concentration range, (M)		$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$	$10^{-5} - 10^{-2}$
Intercept,(mV)		498.7	527.3	507.1
Lower limit of detection,(M)		6×10^{-6}	6.2×10^{-6}	3.7×10^{-6}
Standard deviation		0.3873	1.70294	1.44914
Correlation coefficient,(r)		0.99996	0.99919	0.99925

Table .2 . Effect of plasticizer on Hg^{++} sensor

PARAMETER	NPOE	DOP	DBS
Slope, (mV/decade)	26.8	24.7	25.9
Linear concentration range, (M)	10^{-5} - 10^{-2}	10^{-5} - 10^{-2}	10^{-5} - 10^{-2}
Intercept, (mV)	180.3	174	188.9
Lower limit of detection, (M)	5.6×10^{-6}	6.8×10^{-6}	6.6×10^{-6}
Standard deviation	0.94	0.38	1.16
Correlation coefficient, (r)	0.99975	0.99995	0.9996

Table 3. Performance characteristics of Hg^{++} sensor based on (PM)

PARAMETER	(PM)-Hg sensor results
Slope, (mV/decade)	27.7 ± 0.1
Linear concentration range, (M)	10^{-5} - 10^{-2}
Intercept, (mV)	498.7
Working pH range	3
Lower limit of detection, (M)	6×10^{-6}
Response time, (s)	20
Life span, (week)	3 weeks
Standard deviation	0.3873
Correlation coefficient, (r)	0.99996

Table 4. Selectivity coefficients of Hg^{++} sensor

Interferent	$K_{Hg,M}^{pot}$
Cu^{+2}	0.17×10^{-3}
Cd^{+2}	0.017×10^{-3}
Zn^{+2}	0.11×10^{-3}
Co^{+2}	0.6×10^{-3}
Sr^{+2}	0.01×10^{-3}
Mg^{+2}	0.03×10^{-3}
K^{+}	0.08×10^{-3}
Na^{+}	0.02×10^{-3}
Ag^{+}	0.09×10^{3}

Table .5 Comparison between different Ionophores used in determination of mercury

Ionophores	The working range	Nernstian slope	Detection limit	Reference
* P-tert-Bu calix crown with imine units	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M	27.3 mV/decade	2.24×10^{-5} M	(Mahajan et al., 2004)
* 2-benzoylamino-3-(4- chlorophenyl) – thioacrylic acids – (2- mercapto – 4- methyl – pheny 1) ester	$2.0 \times 10^{-7} – 3.0 \times 10^{-2}$ M	29 mV/decade	5.0×10^{-5} M	(Begheri et al., 2003)
* Iodomercurate with diphenyl amine	$1.0 \times 10^{-2} - 1.6 \times 10^{-5}$ M	29 mV/decade	1.0×10^{-5} M	(Li et al., 2003)
* Salicyladehyde thiosemicarbazono	$1.778 \times 10^{-6} - 1.0 \times 10^{-1}$ M	29 mV/decade	1.0×10^{-6} M	(Mahajan et al., 2003)
* 1,3 – diphenylthiourea	$6.0 \times 10^{-6} – 5.0 \times 10^{-4}$ M	58.6 ± 0.8 mV/decade	10^{-6} M	(Perez et al., 2000)
* bis-benzoin-semiethylene – diamine (BB-SEA)	$5 \times 10^{-7} – 5 \times 10^{-4}$ M	58 mV/decade	NR	(Song et al., 1997)
* N^{2}, N^{4} – di – isopropyl – 6 – methyl thio - 1,3,5 - triazine – 2,4 diamine	$1 \times 10^{-5} - 1 \times 10^{-2}$ M	27.7 ± 0.1 mV/decade	6×10^{-6} M	This work

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