



Highly selective potentiometric determination of mercury(II) ions using 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based membrane electrodes

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ABSTRACT

The electrode characteristics and selectivities of PVC-based mercury(II) selective coated graphite electrode (CGE) and polymeric membrane electrode (PME) incorporating the recently synthesized 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide are reported here. The electrodes exhibit Nernstian slope for mercury(II) ions over wide concentration ranges, i.e. 1.0×10^{-1} M to 1.0×10^{-6} M (with CGE) and 1.0×10^{-1} M to 1.0×10^{-5} M (with PME). The lower detection limits shown by CGE and PME are 8.91×10^{-7} M and 6.30×10^{-6} M, respectively, in the pH range of 1.0–4.0. From the comparative study of these electrodes, CGE has been found to be better than PME in terms of lower detection limit and better selectivity for mercury(II) ions with comparatively less interference from silver(I) ions. The proposed electrodes can be successfully used as an indicator electrode for potentiometric titration of mercury with potassium dichromate. The electrodes have been successfully applied for estimation of mercury content in synthetic water samples, insecticide (parad tablet) and dental amalgam.

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1. Introduction

Mercury and its compounds are extremely toxic and widespread in the environment. Mercury can cause both chronic and acute poisoning. Studies have shown that the health problems such as tremors, impaired cognitive skills and sleep disturbance are prominent in workers with chronic exposure to mercury even at low concentrations. Occupational exposure has also been found to be resulting into broad-ranging functional disturbances, including erethism, irritability, excitability, excessive shyness and insomnia. Besides these effects from occupational and occasional exposures, mercury is also known to enter the food chain. Fish and other aquatic organisms used as seafoods concentrate mercury in their bodies particularly in muscle tissues from where it moves on to the higher levels of food chain, ultimately resulting into the phenomenon of biomagnification. The first occurrence of widespread mercury poisoning in humans, now called Minamata disease, was reported in Minamata, Japan. However, mercury exposure is still an occupational hazard for people in many industries. So the rapid analysis of trace mercury ions is attended in many usual inspects [1].

Ion-selective electrodes (ISEs) based on polymeric membrane with ion-carriers are now established analytical tools in the fields of environmental, medicinal and agricultural analysis. Since late 1960s, many ion-carriers with high selectivity for specific ions have been applied to measure different ionic species in various environmental samples, as this method offer many advantages, such as speed, ease of preparation, better selectivity, wide linear concentration range and low cost [2,3]. Many organic and inorganic compounds have been tested as mercury-selective ionophores for producing ISEs, including crown ethers, amides, oxamides, metalloporphyrines, Schiff bases, etc. [4–12]. The interference of silver(I) ions in the performance of mercury(II) ion-selective electrodes is reported to be a major problem except few reports in literature where ligands have highly selective binding tendency towards mercury(II) ions [13–16]. This interference can be attributed to the similarity in size and other characteristics of both the ions along with ion flux effects which initially were not considered to be relevant [17–22]. Several attempts have been made by various research groups [23–27] to achieve spectacular improvements in lower detection limit and better selectivity with the conventional electrodes. More recently, ISEs with solid internal contact, i.e. without an inner solution, have been reported to produce better values of lower detection limits and selectivity values than conventional electrodes with optimized inner solutions [28–30]. In the present work, an attempt has been

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Table 1
Composition and response characteristics of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) ion-selective polymeric membrane electrodes (PMEs).

S. no	PVC (mg)	Plasticizer (mg)	NaTPB (mg)	Ionophore (mg)	Linear range (M)	Detection limit (M)	Slope (mV/decade)
PME-1	100.0	201.0 ^a	1.9	6.2	1.0×10^{-1} to 1.0×10^{-5}	6.30×10^{-6}	29.35
PME-2	100.9	200.4 ^a	–	6.3	1.0×10^{-1} to 5.0×10^{-5}	4.31×10^{-5}	36.94
PME-3	99.0	199.4 ^a	0.8	6.4	1.0×10^{-1} to 1.0×10^{-5}	5.00×10^{-5}	26.92
PME-4	99.1	202.5 ^a	1.9	4.9	1.0×10^{-1} to 5.0×10^{-5}	5.00×10^{-5}	23.56
PME-5	99.1	202.5 ^a	1.9	8.4	5.0×10^{-2} to 1.0×10^{-4}	7.08×10^{-5}	16.10
PME-6	100.0	202.0 ^b	1.9	5.9	1.0×10^{-2} to 5.0×10^{-5}	5.00×10^{-5}	61.03
PME-7	100.0	202.1 ^c	2.0	5.8	1.0×10^{-2} to 5.0×10^{-5}	1.78×10^{-5}	51.55
PME-8	101.3	201.5 ^d	1.8	5.9	5.0×10^{-2} to 1.0×10^{-4}	6.31×10^{-5}	19.28
PME-9	99.6	199.0 ^e	1.8	5.8	1.0×10^{-2} to 5.0×10^{-5}	3.98×10^{-5}	52.62

^a DOS.

^b TBP.

^c DBP.

^d DOP.

^e DOA.

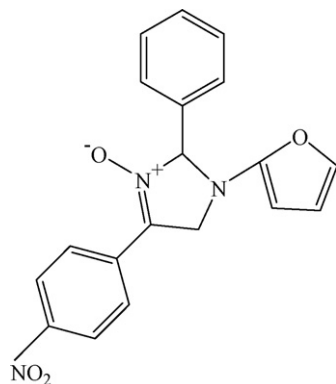


Fig. 1. Structure of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide.

made to improve the sensitivity and selectivity of mercury(II) ion-selective electrodes towards various secondary ions particularly silver(I) ions with the use of coated graphite electrode (CGE).

Earlier, our group had successfully employed a variety of calixarenes and thiosemicarbazone derivatives as ionophores to develop PVC membrane based mercury(II) ion-selective electrodes [31–33]. In continuation to that work, we have investigated the use of recently synthesized 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as carrier for mercury(II) ions in PVC membrane electrode (PME) and coated graphite electrode.

The resulting ion-selective electrodes were characterized in terms of slope, linear range, lower detection limit, selectivity and response time. From the comparative studies of these electrodes, CGE has been found to be better than PME in terms of lower detection limit and better selectivity for mercury(II) ions with less interference from silver(I) ions. In addition, the performance of proposed 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) sensors have been compared with those already reported in literature.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of analytical reagent grade. 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide was synthesised as reported in literature [34] (Fig. 1). The plasticizers such as bis(2-ethylhexyl)sebacate (DOS), bis(2-

ethylhexyl)phthalate (DOP), bis(2-ethylhexyl)adipate (DOA), dibutylphosphate (DBP) and tributylphosphate (TBP) and high molecular weight poly(vinylchloride) (PVC) were used as received from Fluka (Buchs SG, Schweiz). Spectroscopic grade graphite rods and sodium tetraphenyl borate (NaTPB) were obtained from Aldrich (St. Louis, MO, USA). Mercuric nitrate and other metal ion nitrates received from Merck (Darmstadt, Germany) were used without any further purification. Doubly distilled deionised water was used throughout. Samples for analytical application, i.e. Parad tablet (Zandu Pharmaceutical Works Ltd., South Mumbai, India) and Dental amalgam capsules of Non-Gamma 2 amalgam (Dental Products of India, The Bombay Burmah Trading Corporation Ltd., Mumbai, India) were purchased from local market.

2.2. Preparation of PVC membrane based mercury(II) ion-selective electrodes

The membrane was prepared by dissolving PVC, plasticizer, additive NaTPB and varying amounts of ionophore in about 5.0 mL of tetrahydrofuran (THF) (composition of membranes given in Table 1). The mixture was shaken vigorously and the clear solution was poured in a Petri dish (50.0 mm in diameter). The solvent was allowed to evaporate at room temperature. The resulting membrane of 0.4 mm thickness was cut to the size, attached to the PVC tube with the help of PVC glue and conditioned with mercury(II) nitrate solution for 24 h till it gave reproducible and stable potential. The electrochemical cell assembly used for the study was as follows:



2.3. Preparation of coated graphite based mercury(II) ion-selective electrodes

To prepare the coated graphite electrodes, spectroscopic grade graphite rods 10.0 mm in length and 3.0 mm in diameter were used. A shielded copper wire was glued to one end of the graphite rod and the electrode was sealed at the end of a glass tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurry on a polishing cloth, sonicated in distilled water and dried in air. Membrane solution was prepared by thoroughly dissolving ionophore, powdered PVC, plasticizer and additive NaTPB in 3.0 mL THF (composition given in Table 2). The resulting clear solution was evaporated slowly at room temperature until an oily concentrated mixture was obtained. The polished graphite electrode was then coated with the prepared membrane solution and the solvent was allowed to evaporate at room temperature. A membrane was formed on the graphite surface and the

Table 2

Composition and response characteristics of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) ion-selective coated graphite electrodes (CGEs).

S. no	PVC (mg)	Plasticizer (mg)	NaTPB (mg)	Ionophore (mg)	Linear range (M)	Detection limit (M)	Slope (mV/decade)
CGE-1	20.0	40.0 ^a	1.5	4.0	1.0×10^{-1} to 1.0×10^{-6}	8.91×10^{-7}	32.60
CGE-2	20.0	40.2 ^a	–	4.0	1.0×10^{-1} to 5.0×10^{-5}	1.58×10^{-5}	39.92
CGE-3	20.0	40.1 ^a	0.7	4.1	1.0×10^{-1} to 1.0×10^{-5}	7.94×10^{-6}	37.52
CGE-4	20.0	40.0 ^a	1.5	2.5	1.0×10^{-1} to 1.0×10^{-5}	7.08×10^{-6}	24.58
CGE-5	20.0	40.0 ^a	1.5	6.1	1.0×10^{-1} to 1.0×10^{-5}	9.55×10^{-6}	27.64
CGE-6	20.2	40.2 ^b	1.4	4.2	1.0×10^{-1} to 5.0×10^{-5}	1.0×10^{-5}	64.26
CGE-7	20.1	40.1 ^c	1.5	4.1	1.0×10^{-1} to 1.0×10^{-4}	8.91×10^{-5}	34.69
CGE-8	20.2	39.8 ^d	1.5	4.6	1.0×10^{-1} to 1.0×10^{-4}	6.31×10^{-5}	22.14
CGE-9	20.2	40.1 ^e	1.4	4.2	1.0×10^{-1} to 5.0×10^{-5}	3.98×10^{-5}	37.54

^a DOS.^b TBP.^c DBP.^d DOP.^e DOA.

electrode was allowed to stabilize overnight. The electrode was finally conditioned by soaking in a 5.0×10^{-3} M mercuric nitrate solution for 48 h. The potentiometric measurements were carried out using the following electrochemical cell assembly:

Graphite surface | PVC membrane | Test solution | 3.0 M KCl | Ag–AgCl

All the measurements of the electrode potentials were made with an EQUIPTRONICS model EQ-602 potentiometer. The pH measurements were made using an Elico LI-MODEL-120 pH meter. Silver/silver chloride electrodes with 3.0 M KCl as salt bridge were used as internal and external reference electrodes in PVC membrane electrodes whereas no internal reference electrode was used in case of CGE.

3. Results and Discussion

3.1. Response characteristics

In the preliminary experiments, different PVC-based ion-selective membrane sensors using 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier were prepared for various metal ions using 100.0 mg PVC, 200.0 mg DOS, 2.0 mg NaTPB and 6.0 mg ionophore. The membranes so prepared were conditioned in 1.0×10^{-2} M solutions of different metal ions for 24 h. Their potential responses were observed and plotted over a wide concentration range (1.0×10^{-1} M to 1.0×10^{-8} M) of respective metal ions (Fig. 2). Results indicated that except mercury, sensors based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide exhibited little or no response towards other metal ions studied. Mercury(II) ions were found to give better response as compared to all the other metal ions tested. On optimization, sensor (PME-1) containing 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as ionophore exhibited Nernstian slope of 29.35 ± 1 mV per decade over a wide concentration range of mercury(II) ions (1.0×10^{-1} M to 1.0×10^{-5} M) with lower detection limit of 6.30×10^{-6} M (Table 1).

Presence of lipophilic negatively charged additives is known to improve the response characteristics of ion-selective electrodes by reducing its ohmic resistance and increasing the extraction capability of ionophore. Effect of sodium tetraphenyl borate as an additive on the response characteristics of mercury(II) ion-selective electrodes incorporating 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier was studied by using varying amounts of NaTPB for membrane preparation (Table 1). Out of different membranes electrodes so prepared (PMEs:1,2,3), the electrode PME-1 containing 1.9 mg NaTPB exhibited better slope of 29.35 mV per decade and lower detection limit of 6.30×10^{-6} M

within a wide concentration range (1.0×10^{-1} M to 1.0×10^{-5} M) of mercury(II) ions.

Similarly, the effect of ionophore content on response characteristics of mercury(II) ion-selective electrode incorporating 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier was also studied by incorporating varying amounts of ion-carrier in membrane preparation (Table 1). From the different membranes sensors so prepared (PMEs:1,4,5), the membrane sensor PME-1 containing 6.2 mg of ionophore exhibited Nernstian slope (29.35 mV per decade) over wide concentration range (1.0×10^{-1} M to 1.0×10^{-5} M) of mercury(II) ions with lower detection limit of 6.30×10^{-6} M.

Plasticizers are known to influence the membrane response by changing its dielectric constant, affecting the ligand state and ionic mobility. The effect of nature of plasticizer on potential response of mercury(II) ion-selective electrode incorporating 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier was studied by preparing membrane sensors (PMEs:1,6,7,8,9) containing different plasticizers such as DOS, DOP, DOA, DBP, TBP and the results so obtained are summarized in Table 1. The electrodes prepared by incorporating TBP, DBP and DOA (PMEs:6,7,9) exhibited super-Nernstian slope while one with DOP (PME-8) exhibited sub-Nernstian response. The potential response of membrane sensor (PME-1) incorporating DOS as a plasticizer was found to be better in terms of slope (29.35 ± 1 mV per decade) and linear concentration range (1.0×10^{-1} M to 1.0×10^{-5} M).

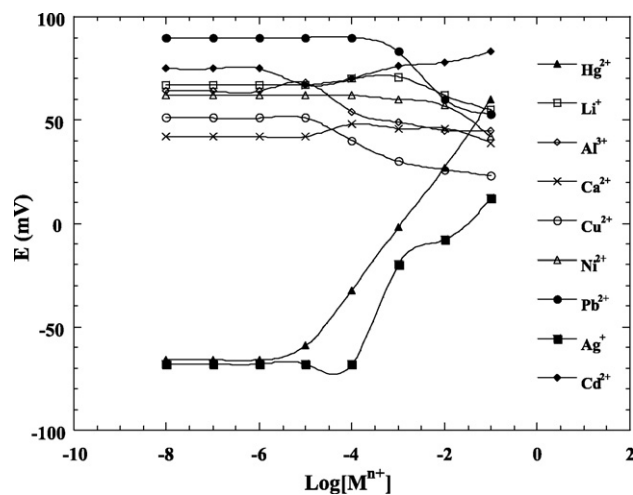


Fig. 2. Potentiometric response of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based polymeric membrane electrodes (PMEs) for various metal ions.

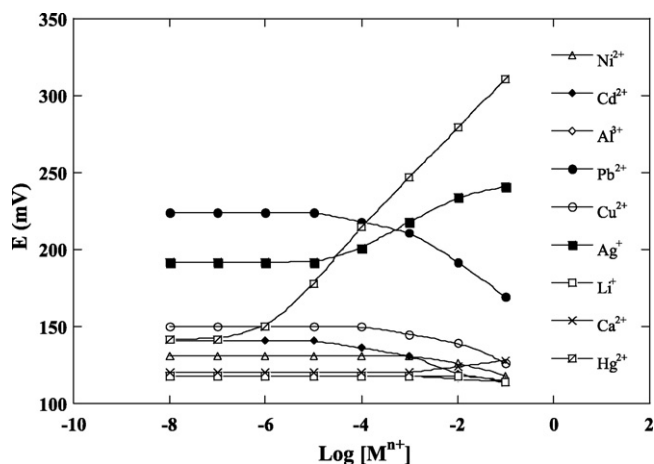


Fig. 3. Potentiometric response of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based coated graphite electrodes (CGEs) for various metal ions.

Recently, it has been reported that the replacement of inner solution of PME by solid substance like graphite rod (CGE) inhibits the leakage from internal solution into the test solution and therefore improves the characteristic properties of the electrode along with its selectivity towards different secondary ions [35]. It was, therefore, decided to prepare the coated graphite electrode for mercury(II) ion based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier. In preliminary experiments, coated graphite electrodes were prepared incorporating 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier and their response was investigated for a variety of metal ions. From the results so obtained, it was observed that the coated graphite electrode based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier exhibit best response for mercury(II) ions compared to other metal ions tested (Fig. 3). Coated graphite mercury(II) sensor, CGE-1, exhibited a near-Nernstian slope of 32.60 mV per decade over a wide concentration range of 1.0×10^{-1} M to 1.0×10^{-6} M for mercury(II) ions with lower detection limit of 8.91×10^{-7} M (Table 2). Composition of the mercury(II) ion-selective coated graphite electrode was further optimized in the similar manner as in case of PMEs and the electrode characteristics so obtained are summarised in Table 2. It is clear from the Table 2 that CGE-1 consisting of membrane composition 20.0 mg PVC, 40.0 mg DOS, 1.5 mg NaTPB and 4.0 mg 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier provides best response. Therefore, the selectivity and other parameters of the CGE-1 have been investigated in detail and are discussed in the following sections.

From the data summarised in Tables 1 and 2, a comparison between mercury(II) ion-selective coated graphite electrode CGE-1 and polymeric membrane electrode PME-1 reveals that the coated graphite electrode CGE-1 based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide exhibits better electrode characteristics (Fig. 4) than the corresponding polymeric membrane electrode PME-1 in terms of wide concentration range (1.0×10^{-1} M to 1.0×10^{-6} M) and lower detection limit (8.91×10^{-7} M).

3.2. Effect of pH

The pH dependence of PVC membrane (PME-1) and coated graphite (CGE-1) sensors based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide was examined at 1.0×10^{-3} M concentration of mercury(II) ions (Fig. 5). The pH of the solution was

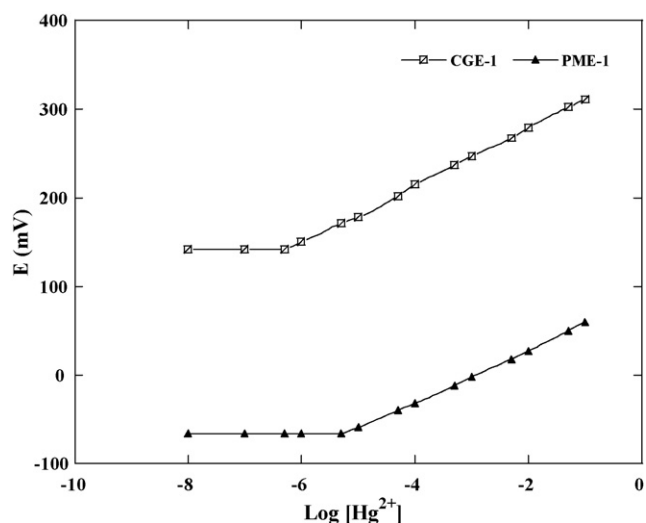


Fig. 4. Potential response curves of various 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) ion-selective electrodes (PME-1 and CGE-1).

varied by small addition of nitric acid or hexamine and potential was measured. The potential for both sensors was found to remain constant in the pH range 1.0–4.0, which was considered as a functional pH range. Beyond pH 4.0, the potential was found to decrease sharply due to the formation of $\text{Hg}(\text{OH})^+$ ion. No pH adjustments were required because pH of pure solutions of mercuric nitrate lies within the functional pH range of the sensors.

3.3. Response time and lifetime of mercury(II) ion sensors

Response time is another important characteristic of an ion-selective electrode. The measurements of potential versus time were carried out with the mercuric nitrate solutions from lower (1.0×10^{-5} M) to higher (1.0×10^{-1} M) concentrations (Fig. 6). The response time of sensors was found to be less than 20 s at various concentrations of the test solution. The reproducible and stable potentials with the standard deviation of ± 1.0 mV at various concentrations of mercuric nitrate solutions were recorded.

In terms of lifetime of the sensors, the stable and reproducible signals were obtained for three months after which the sensors showed deviation from normal behavior.

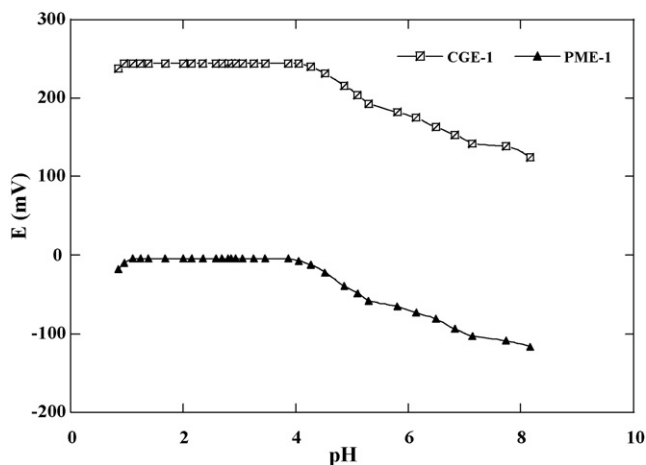


Fig. 5. Effect of pH on potential response of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) ion-selective electrodes (PME-1 and CGE-1).

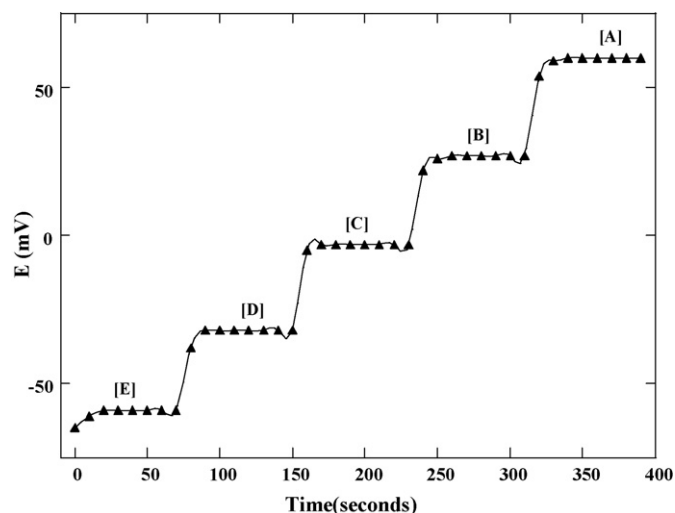


Fig. 6. Response time obtained with electrode PME-1 based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide. [A] 1.0×10^{-1} M Hg^{2+} [B] 1.0×10^{-2} M Hg^{2+} [C] 1.0×10^{-3} M Hg^{2+} [D] 1.0×10^{-4} M Hg^{2+} [E] 1.0×10^{-5} M Hg^{2+} .

3.4. Selectivity

The selectivity, an important characteristic of a sensor, is measured in terms of the potentiometric selectivity coefficients ($\log K_{A,B}^{\text{Pot}}$). It measures the response of the sensor towards the primary ion (A) in the presence of secondary ions (B) present in the test solution. The selectivity coefficients have been determined using fixed interference method (FIM) based on the semi empirical Nikolsky–Eisenman equation. In this method, the concentration of primary ion, mercury(II) ion, is varied whereas the concentration of secondary ion is kept constant in test solution, which is 1.0×10^{-2} M in the present case. The potentiometric selectivity data of PME-based sensor (PME-1) and Coated graphite-based sensor (CGE-1) for various secondary ions are given in selectivity diagram (Fig. 7). It is clear from the selectivity diagram that the $\log K_{\text{Hg}^{2+},B}^{\text{Pot}}$ values are of the order of ~ -3 for alkaline earth (Mg^{2+} , Ca^{2+}) and some heavy metal ions (Zn^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , etc.), which indicate that these divalent metal ions do not cause much interference in the normal functioning of mercury(II) ion sensors when present at a high concentration of 1.0×10^{-2} M in the test solution. The $\log K_{\text{Hg}^{2+},B}^{\text{Pot}}$ values of the monovalent ions (Na^+ , K^+ , NH_4^+) were found to be comparatively higher than those of the divalent ions. They also do not disturb the normal functioning of the sensors and the sensors possess high mercury(II) selectivity and respond weakly to these secondary ions. The higher value for monovalent ions in comparison to values for divalent ions can be attributed to basic limitation involved in equation being used for calculating selectivity coefficients as discussed in Ref. [31].

On comparing the selectivity data of PME-1 and CGE-1, it has been found that the $\log K_{\text{Hg}^{2+},B}^{\text{Pot}}$ values for most of the secondary ions are less in case of CGE-1. The better selectivity is more pronounced in case of the major interferent silver(I). The $\log K_{\text{Hg}^{2+},\text{Ag}^+}^{\text{Pot}}$ values for PME and CGE are +3.4 and -0.1 , respectively, which shows the increase in selectivity of CGE manifold in comparison to PME. This increase in selectivity in case of CGE is attributed to the ion flux mechanism. In case of PME sensors, the mercury(II) ions solution is used as an internal reference solution and there is a probability of leaching of ions across the PVC membrane that results in change in concentration of ions near the membrane surface. This change in concentration results in inferior values of detection limit and selectivity coefficients for PME in comparison to that of CGE. In case of CGE sensor, the internal solution has been replaced by solid graphite

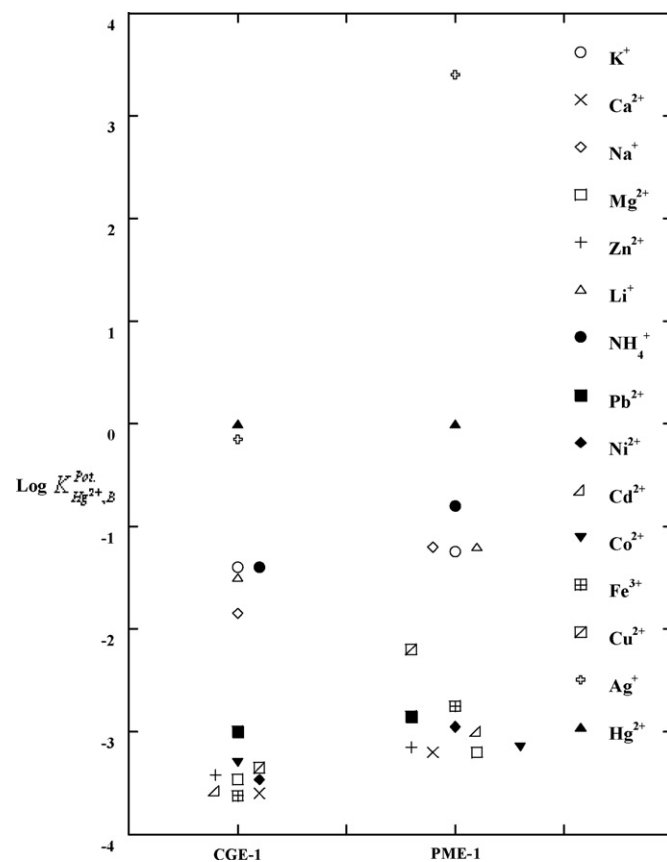


Fig. 7. Selectivity diagram of 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) ion-selective electrodes (PME-1 and CGE-1).

rod, so, the phenomenon of diffusion of ions across the PVC membrane has been eliminated. This replacement of internal reference mercury(II) ion solution by graphite rod resulted in the enhanced selectivity of mercury sensor towards silver and other ions. This enhancement in selectivity is very helpful in solving the major problem of silver interference in mercury(II) ion-selective electrodes that was greatly affecting the scope for detection of mercury(II) ions by ion-selective electrodes.

3.5. Comparison with literature

From the comparative study of proposed mercury(II) ion-selective electrodes and those which are already reported in literature, the proposed electrode based on 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide, especially the coated graphite electrode CGE-1, has been found to be better in terms of its wide concentration range, lower detection limit and improved selectivity with respect to the various secondary ions, especially the silver(I), which has been reported to be major interferent in many of the reports (Table 3). In the ion-selective electrodes reported in literature for the detection of mercury(II) ion, other major problem was poor selectivity of sensors towards secondary ions such as Fe^{3+} and Cd^{2+} , etc., which is almost eliminated in CGE-1 proposed in the present work.

3.6. Analytical applications

The practical significance of the sensors was tested by using them as indicator electrodes for estimation of mercury content in synthetic water samples (Table 4). In addition, the proposed sensors were also used to estimate mercury content in various mercury

Table 3
Comparison of proposed 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based mercury(II) ion-selective electrodes with mercury(II) ion-selective electrodes already reported in literature.

Ionophore	Linear range (M)	Detection limit (M)	Slope (mV per decade)	Log $K_{Hg^{2+}, Ag^+}^{Pot.}$	Log $K_{Hg^{2+}, Fe^{3+}}^{Pot.}$
CGE-1 (present work)	1.0×10^{-1} to 1.0×10^{-6}	8.9×10^{-7}	32.60	-0.10	-3.62
PME-1 (present work)	1.0×10^{-1} to 1.0×10^{-5}	6.3×10^{-6}	29.40	3.40	-2.75
Antimony(III) arsenate [36]	1.0×10^{-2} to 5.0×10^{-5}	5.0×10^{-5}	28.00	1.25	-0.39
N-(O,O-diisopropylthiophosphoryl)thiobenzamide [37]	1.0×10^{-2} to 5.0×10^{-5}	$>10^{-5}$	29.00	-0.02	-3.41
Tetraethenyl-1,10-dioxo-4,7,13,16 tetraazacyclooctadecane(TTOTC)[38]	1.0×10^{-3} to 3.2×10^{-6}	1.6×10^{-6}	28.40	0.39	-5.00
Diaza-18-crown-6 [39]	1.0×10^{-3} to 1.0×10^{-5}	-	28.40	2.60	-
[5,11,17,23,29,35-Hexa(1-thiazole)azo] 37,38,39,40,41,42-hexahydroxycalyx[6] arene [15]	1.0×10^{-2} to 5.0×10^{-6}	4.0×10^{-6}	28.70	0.70	4.00
MB1M [40]	1.0×10^{-1} to 1.0×10^{-5}	7.0×10^{-6}	28.50	0.56	-1.54

Table 4
Estimation of mercury(II) content in synthetic water samples, parad tablet and dental amalgam.

Sample	Mercury(II) content (M) estimated in different samples		
	Volumetric method	CGE-1	% compatibility
Water sample 1	4.98×10^{-3}	4.94×10^{-3}	99.0
Water sample 2	6.23×10^{-3}	6.08×10^{-3}	97.6
Water sample 3	2.44×10^{-2}	2.41×10^{-2}	98.6
Water sample 4	3.14×10^{-2}	3.10×10^{-2}	98.7
Parad Tablet	4.01×10^{-3}	4.08×10^{-3}	99.0
Dental Amalgam	2.70×10^{-2}	2.76×10^{-2}	98.9

containing samples like insecticide (Parad Tablet) and dental amalgam. One gram of each sample material (Parad tablet and Dental amalgam) to be tested was dissolved in the minimum amount of concentrated nitric acid upon mild heating. Sample solutions thus prepared were further diluted to 100.0 mL using double distilled water. These solutions were then employed for the determination of mercury content using mercury(II) ion-selective electrode (CGE-1). In case of synthetic water samples, 100.0 mL of sample solution was taken for estimation of mercury content. The mercury content in these samples was also estimated by the traditional volumetric method using potassium iodide as titrant. Results of both the methods were compared and have been found to be fairly in agreement with each other (Table 4). Results indicate that the proposed sensors can be efficiently used for estimation of mercury content in natural and environmental samples. Along with this, proposed sensors have also been successfully used for potentiometric titration of mercury(II) ion solution with potassium dichromate solution

(Fig. 8). Before the end point, the potential shows usual logarithmic change with the volume of titrant added, while the potential response after the end point remains almost constant, due to the low concentration of free mercury(II) ions in solution.

4. Conclusion

Mercury(II)-selective membrane sensors prepared by incorporating 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide as an ion-carrier exhibit Nernstian slope for mercury(II) ions with lower detection limit up to 8.91×10^{-7} M. The sensors were found to work well in the pH range of ~ 1.0 – 4.0 with response time of less than 20 s. The selectivity coefficient values obtained by using coated graphite electrode CGE-1 showed better sensitivity and selectivity in comparison to those obtained in case of PVC membrane electrode PME-1. The sensors were successfully applied as indicator electrodes in potentiometric titration of mercury(II) ion solution with potassium dichromate solution. The sensors have also been applied to estimate mercury(II) content in the synthetic water samples, parad tablet and dental amalgam.

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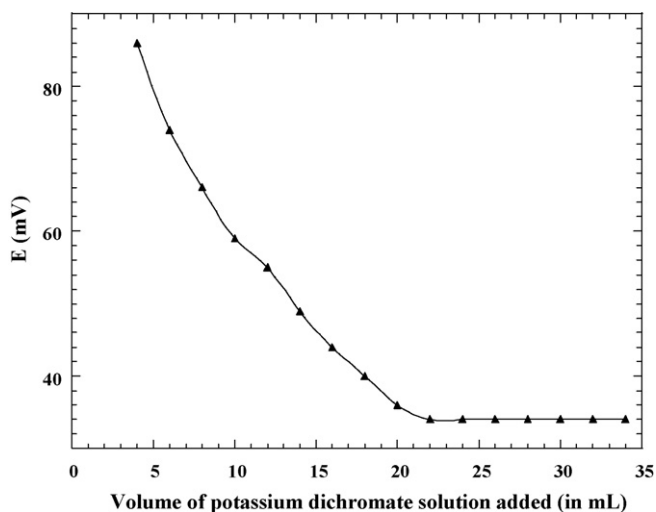


Fig. 8. Titration curve for titration of 1.0×10^{-3} M mercury(II) ion solution with 1.0×10^{-3} M $K_2Cr_2O_7$ solution using the electrode PME-1 as an indicator electrode.

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