A mercury(II) selective sensor based on N,N′-bis(salicylaldehyde)-phenylenediamine as neutral carrier for potentiometric analysis in water samples

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ABSTRACT

Mercuric ions in water samples were determined by a new modified carbon paste electrode based on N,N′-bis(salicylaldehyde)-phenylenediamine (salophen) as a chemical modifier. The construction, performance, and applications of mercury carbon paste electrode are described. The electrode displays a linear $\log[Hg^{2+}]$ versus EMF response over a wide concentration range of 3.2×10^{-7} to 3.2×10^{-4} with Nernstian slope of 58.8 ± 0.3 mV/decade with limit of detection 1.5×10^{-7} over the pH range 3.8–7.8; the presence of the complex $Hg(OH)^+$ ion explains the slope of the response curve. The proposed sensor shows a reasonable discrimination ability towards Hg(II) in comparison to some alkali, alkaline earth transition and heavy metal ions. The modified electrode was applied as indicator electrode in potentiometric titration and successfully used to determine mercury(II) in water samples with satisfactory results.

1. Introduction

Mercury is generally found at very low concentration in the environment. Mercuric ion can be absorbed readily by humans and other organisms. It may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defeats. Elemental mercury and short-chain alkyl mercurials are known to be responsible for causing damage to the sensory parts of the central nervous system [1].

Due to its serious hazardous effect on human health and toxicity in the environment, it is important to control its levels in natural waterways and potable water [2]. Therefore, it is necessary to determine Hg(II) at lower levels in our environment. Various analytical techniques have been used for determination of mercury at low concentrations, but the most commonly used ones are the cold vapour technique coupled with atomic absorption (CV-AAS), atomic fluorescence (CVAFS), inductively coupled plasma emission (CV-ICP-AES) spectrophotometry and inductively coupled plasma mass spectrometry (ICP-MS) [3].

These detection methods are attractive for mercury speciation because of their excellent detection limits and selectivity. However, their relatively high instrumental and/or running costs as well as complicated instrument setup make it difficult to employ these hyphenated techniques for routine speciation analysis.

Potentiometric sensors offer several advantages such as speed, low cost, ease of preparation, simple instrumentation, relatively fast responses, very low detections limit, wide dynamic ranges and reasonable selectivity [4,5].

A number of ISEs based on conventional polymeric membrane, and coated wire electrodes [1,6–14] utilizing various neutral ionophores were made for determination of mercury ion.

Conventional polymeric membrane ion-selective electrodes (ISEs) have high detection limit due to leaching of primary ions from the inner filling solution. Such fluxes can be reduced if primary ions in the inner filling solution are buffered with certain ligands, making their concentration effectively constant. However, for each individual experiment one must find an appropriate composition of the inner filling solution, which can be tedious and inconvenient task [15].

Today, the response of ISEs in the presence of ion fluxes is well understood, and their effects can be strongly reduced but cannot be entirely eliminated [16].

One of the important methods to avoid these fluxes is using membrane electrodes with solid inner contact. However, such systems suffer from poor potential stability and erratic emf changes [17,18].

Considering these notes, most of the above mentioned sensors [1,6–14] lack the sensitivity and selectivity required for determination of low concentrations of mercury ion. In addition mercury(II) ions cause irreversible damage to the PVC membrane and produce erratic responses after each calibration [19]. Therefore, development of a suitable Hg(II) selective electrode has become a priority

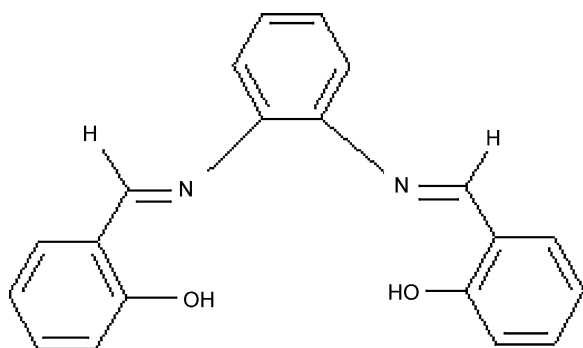*E-mail address:* hazemona1@yahoo.co.uk.

Fig. 1. Structure of N,N'-bis(salicylaldehyde)-phenylenediamine (salophen).

for the analytical chemist. Using potentiometric carbon paste electrodes, one may overcome most of the problems encountered by polymeric membrane (PVC) and coated wire electrodes (CWE).

Potentiometric carbon paste electrodes (CPEs) offer very attractive properties for the electrochemical investigation of inorganic and organic species over polymeric membrane and coated wire electrodes. These are ease of preparation and use, renewal of surface, chemical inertness, robustness, stability of response, low ohmic resistance, no need of internal solution and suitability for a variety of sensing and detection application [20–22]. Due to the above mentioned properties, carbon paste electrode seems to be especially promising.

On careful review of the literature, one report on determination of mercury(II) using a carbon paste electrode has been recently published [23] where the results are comparable to our findings with this electrode.

The present work describes construction, potentiometric characterization, and analytical application of a new modified carbon paste electrode selective for mercury ion based on salophen as ionophore Fig. 1. The results presented in this paper show that the sensor developed for Hg(II) ion using the above system has acceptable concentration range, low detection limit and gives reproducible results.

2. Experimental

2.1. Reagents

The ionophore (salophen), was prepared as reported [24] and was received as a gift from professor Salman M. Saadeh (chemistry department, the Islamic university, Gaza, Palestine). Freshly distilled water was used in preparing all solutions. Reagent grade pure graphite powder as well as the plasticizers, bis(2-ethylhexyl) adipate (DOA), dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (DOPh), dioctyl sebacate (DOS), tributyl phosphate (TPh) were purchased from Aldrich.

2.2. Electrode design and measurement of electrode potentials

The modified carbon paste electrode was made according to a general procedure as described elsewhere [23,25]. High purity graphite, ionophore and different types of plasticizers were intimately hand mixed in a Petri dish to obtain a very fine paste. A portion of the composite mixture was packed firmly into the end of a disposable polypropylene syringe (ca. 3 mm i.d. and 6 cm long) where electrical contact was established with a copper wire screw. To obtain stable electrochemical response, the outer layer of the carbon paste is renewed before each set of measurements by polishing the surface of the electrode. The sensor was used directly for

potentiometric measurements without pre-conditioning. Potential readings were recorded when stable values had been obtained after each addition and these values were plotted against the logarithm of mercury(II) activities.

The emf measurements were made relative to a saturated calomel electrode (SCE) with a digital millivoltmeter (SR-MUL-3800). pH measurements were made on a digital pH meter (HANNA pH 211) under stirring conditions at room temperature ($25.0 \pm 1.0\,^{\circ}$C) using the following galvanic cell: reference electrode|| sample solution| modified carbon paste electrode.

3. Results and discussion

Ionophores used in ISEs should have rapid exchange kinetics and adequate formation constants in the paste. In addition, they should have good solublility in the paste matrix and sufficient lipophilicity to prevent leaching from the paste into the sample solution [26].

The ionophore N,N'-bis(salicylaldehyde)-phenylenediamine (salophen) is nearly insoluble in water. It is a ligand with two nitrogens and two hydroxyl groups. The O and N atoms in ionophore play the role of an electron pair donor, and coordinate metals such as Hg(II) ions as electron acceptors, so it is possible to use it as an ion-selective ionophore [9].

3.1. Response of the electrode based salophen to Hg(II) ions

Potentiometric response of the salophen modified electrode was tested for different cations such as Na$^+$, K$^+$, NH$_4{}^+$, Ag$^+$, Li$^+$, Ca^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Ba^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Ce^{3+}, Al^{3+} and Cr^{3+} ions. As can be seen from Fig. 2, the slopes of the linear parts of the potential responses of the sensor for most of the tested cations are much lower than those expected by the Nernst equation. However, Hg^{2+} has the closest Nernstian response over a wide concentration range with low detection limit.
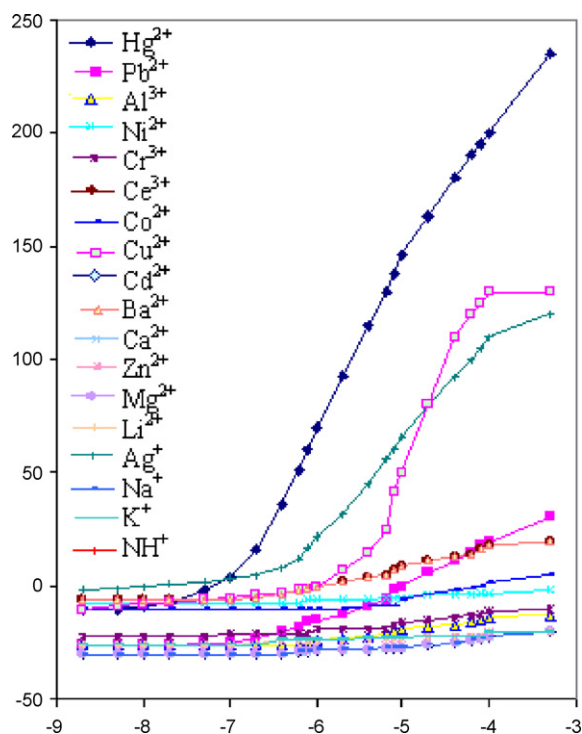

Fig. 2. Potential response of sensor for various metal ions.

Table 1
The paste compositions and the electrode characteristics of mercury(II) sensor.

No.	I	Composition (wt%)				Electrode characteristics			
		G	DOA	A	S (mV)	D.R. (M)	r^2	LOD (M)	R (s)
1	–	52.0	48.0	–	35.5 ± 0.2	3.5×10^{-5} to 3.0×10^{-4}	0.979	1.5×10^{-5}	≥ 40
2	0.1	54.8	45.1	–	41.9 ± 0.8	5.5×10^{-6} to 3.0×10^{-4}	0.985	3.1×10^{-6}	≥ 35
3	0.3	54.7	45.0	–	51.2 ± 0.1	9.5×10^{-7} to 3.5×10^{-4}	0.991	7.8×10^{-7}	≥ 25
4	0.7	54.5	44.8	–	56.5 ± 0.4	9.0×10^{-7} to 4.5×10^{-4}	0.990	7.5×10^{-7}	≥ 10
5	1.0	54.0	45.0	–	58.8 ± 0.3	3.2×10^{-7} to 3.2×10^{-4}	0.998	1.5×10^{-7}	≥ 10
6	3.0	53.0	44.0	–	53.5 ± 0.8	4.9×10^{-7} to 4.0×10^{-4}	0.991	2.2×10^{-7}	≥ 15
7	5.0	52.0	43.0	–	52.5 ± 0.5	5.6×10^{-7} to 3.8×10^{-4}	0.995	4.2×10^{-7}	≥ 25
8	1.0	57.0	42.0	–	56.6 ± 0.1	4.5×10^{-7} to 3.3×10^{-4}	0.990	3.1×10^{-7}	≥ 12
9	1.0	59.0	40.0	–	54.2 ± 0.7	4.5×10^{-7} to 3.3×10^{-4}	0.990	3.1×10^{-7}	≥ 12
10	1.0	47.0	52.0	–	48.6 ± 0.9	4.5×10^{-7} to 3.3×10^{-4}	0.990	3.1×10^{-7}	≥ 12
11	1.0	49.5	49.5	–	52.8 ± 1.2	5.8×10^{-7} to 4.0×10^{-4}	0.996	3.9×10^{-7}	≥ 15
12	1.0	54.0	45.0	0.3^a	20.2 ± 1.2	1.2×10^{-5} to 5.0×10^{-4}	0.965	8.1×10^{-6}	≥ 75
13	1.0	54.0	45.0	1.5^a	12.1 ± 0.6	5.0×10^{-5} to 3.0×10^{-4}	0.981	2.8×10^{-5}	≥ 65
14	1.0	54.0	45.0	0.3^b	13.0 ± 1.8	9.8×10^{-6} to 1.0×10^{-4}	0.986	6.5×10^{-6}	≥ 45
15	1.0	54.0	45.0	2.0^b	10.2 ± 1.4	1.8×10^{-5} to 4.0×10^{-4}	0.978	8.0×10^{-6}	≥ 55

G, Graphite; A, Additive; S, slope (mV/decade); D.R., Dynamic range (M); LOD, low of detection (M); R, response time (s) at high concentration of Hg(II).

^a Oleic acid.

a Oleic acid.
b Sodium tetraphenyl borate.

3.2. Optimization of the composition of the paste

It is well known that the sensitivity, linear dynamic range and selectivity obtained for a given electrode depend significantly on the composition of the paste [27,28]. Several compositions for the studied electrode were tested. They are presented in Table 1, along with their other characteristics.

3.2.1. Optimization of the amount of the modifier in the paste

For this purpose, electrodes with different percentages of the modifier were prepared namely 0.1%, 0.3%, 0.7%, 1.0%, 3.0%, and 5.0% (w/w). The slopes, concentration range, detection limit and response time of the above electrodes are given in Table 1. The electrode without the modifier (sensor No. 1) showed poor sensitivity to mercury cations, whereas, in the presence of the modifier, the electrode showed remarkable selectivity for Hg(II). The sensitivity of the electrode response increased with increasing modifier until the value of 1.0 wt% (electrode No. 5). However, further addition of the ionophore, (sensors No. 6 and 7), display somewhat smaller

slopes and sensitivity, most probably due to some inhomogeneities and possible saturation of the paste [29].

It is well known that the sensitivity and selectivity of the electrode depend on graphite/plasticizer ratio used [11]. The graphite/plasticizer ratios of 0.903–1.475 were examined. It is interesting to note that the ratio of ca. 1.20 showed the optimum physical properties and ensured high enough mobilities of their constituents [30]. Interestingly, oleic acid and sodium tetraphenyl borate disrupted the response of the electrode (sensors Nos. 12, 13, 14 and 15). It is argued that these commonly considered lipophilic additives adversely affect the mechanism of response of the salophen-based electrode.

3.3. Plasticizer selection

A plasticizer is an important constituent and influences the detection limit, selectivity and sensitivity of the electrode [31]. It should be noted that the partition coefficients of metals are strongly dependent on the solvation properties of the organic phase [32]
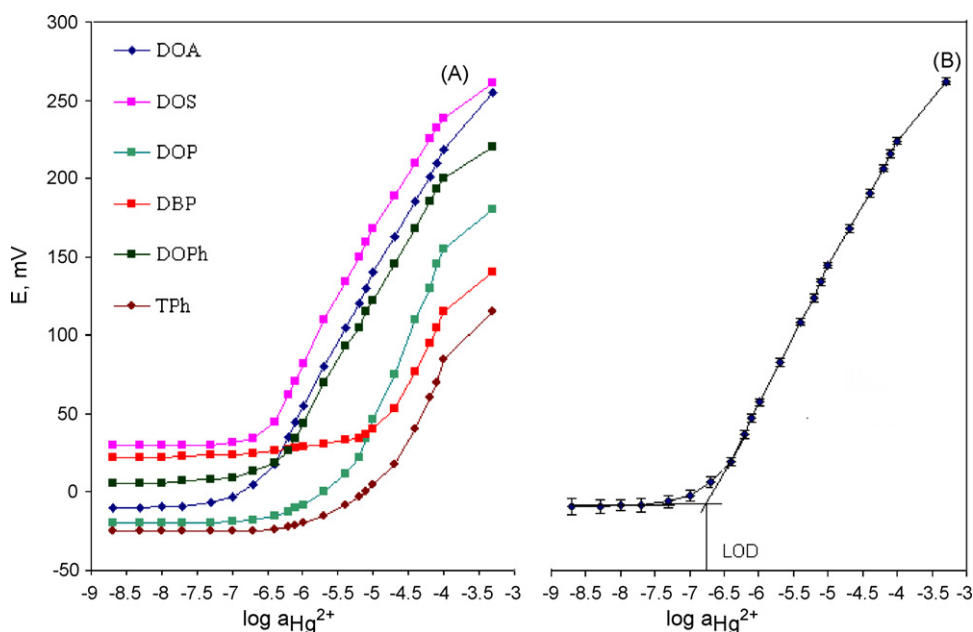

Fig. 3. (A) Variation of electrode potentials with different plasticizers. (B) Calibration curve for Hg(II) selective electrode based on plasticizer DOA.

Table 2
Effect of physical parameters of different plasticizers on characteristics of Hg(II) electrode.

	Physical parameters					Response characteristics			
	D.C.	$\log P_{TLC}$	$V(\eta)$	M.wt	S (mV)	D.R(M)	$R_{(s)}$	LOD (M)	RSD%
DOS	4.2	10.1	25.0	426	56.1 ± 0.7	5.1×10^{-7} to 3.8×10^{-4}	≥8	3.2×10^{-7}	0.66
DOA	3.9	6.1	13.0	371	58.8 ± 0.3	3.2×10^{-7} to 3.2×10^{-4}	≥10	1.5×10^{-7}	0.47
DOP	5.1	7.1	39.0	390	52.6 ± 0.5	3.6×10^{-6} to 3.2×10^{-4}	≥15	1.6×10^{-6}	1.08
DBP	6.4	4.5	15.7	278	43.8 ± 0.9	9.1×10^{-6} to 3.2×10^{-4}	≥25	7.9×10^{-6}	0.98
DOPh	4.8	10.2	11.0	435	55.6 ± 0.3	5.7×10^{-7} to 3.2×10^{-4}	≥10	4.1×10^{-7}	0.59
TPh	8.0	4.0	3.4	266	40.2 ± 0.8	1.7×10^{-5} to 3.2×10^{-4}	≥35	1.0×10^{-5}	1.32

D.C., Dielectric constant; $\log P_{TLC}$, lipophilicity; M.wt, molecular weight; S, slope; D.R. (M), dynamic range; R (s), response time; LOD (M), limit of detection; RSD, relative standard deviation.

which are mainly determined by the polarity of the plasticizer used in the electrode. In addition the nature of the plasticizer affects both the dielectric constant of the paste and the mobility of the ionophore and its complex [33]. Therefore, the influence of the polarity of the plasticizer on the cation selectivity of the paste was investigated. The plasticizers viz. DOA, DOS, DOP, DBP, DOPh and TPh were employed to study the effect on the electrochemical behavior of the electrodes (Fig. 3). Table 2 lists the values of the dielectric constant (ε), lipophilicity ($\log P_{TLC}$), viscosity (η) and molecular weight (M.wt) of the plasticizers used in the present work [34,35].

Generally, plasticizers improve certain characteristics of the electrodes, but in some cases, the response characteristics get affected adversely. In this study no relation between the physical parameters and the response characteristics was found. Nevertheless, better response characteristic values are obtained when these properties have intermediate values [36]. Comparatively, DOA with relatively moderate viscosity, lipophilicity, molecular weight and low dielectric constant, produced the best result and was used in further characterization as shown in Table 2.

3.4. Selectivity coefficients

The selectivity coefficients are the foremost important characteristics of the ISE, informing about the ability of the electrode in discriminating the primary ion against other ions of the same charge signs [37] and they are directly related to the thermodynamic equilibria in the membrane and at the membrane/surface interface [38]. The fixed interference method (FIM) and separate solution method (SSM) were recommended by IUPAC to determine the selectivity coefficient of the ISE [39]. Both of the methods, SSM and FIM, are based on Nickolsky-Eisenman equation. However, it has been shown that these methods suffer some limitations in

terms of the values for ions of unequal charges, a non-Nernstain behavior of interfering ions [40]. The recommendation report of IUPAC in 1995 on the determination of selectivity coefficient values emphasized the prerequisites of the SSM and MSM method and another method named the "matched potential method (MPM)" was recommended [41]. The MPM method is recommended when the primary ion and/or the interfering ion dissatisfies with the Nernst response or the involved ions are unequal in charge [42].

The effect of the interfering ions on the response behavior of the designed electrode was evaluated by the FIM, the separate solution method (SSM) and the matched potential method (MPM) methods. As can be seen from Table 3, most ions have negligible interference; the ions Ag(I) and Pb(II) show intermediate effect, which are common interfering ions on Hg(II) ion-selective electrodes as they have comparable size and characteristics to those of mercury ions[13]. Cu(II) has strong interference on the functioning of the electrode. Cu(II), being a strong Lewis acid will strongly coordinate the hard Lewis bases, nitrogen and oxygen donor atoms in salophen. On the other hand, the values of the selectivity coefficients of the univalent cations evaluated by the fixed interference method (FIM) and the separate solution method (SSM) seem to be somewhat large. It is noteworthy that such deceptively larger selectivity coefficient values arise from the term $a_B^{ZA/ZB}$ in Eq. as described elsewhere [41]. The smaller the charge of the interfering ion, n, the larger the selectivity coefficient, [43].

It is important to point out that the concentration level of the interfering ion that can be tolerated depends on the value of the selectivity coefficient. The smaller the selectivity coefficient the higher the concentration of the interfering ion can be tolerated [44]. Tolerance level for Cu (II)ion which has substantially higher selectivity coefficients was determined.

Therefore, to get an idea about the level of interference caused by Cu(II) ions at various concentrations, mixed run studies were performed. Fig. 4 shows that in the presence of 1.0×10^{-6}, 1.0×10^{-5} and 1.0×10^{-4} Cu(II) ion, the sensor can be used to determine Hg(II) in the reduced concentration ranges 3.5×10^{-7} to 3.2×10^{-4}, 8.5×10^{-7} to 3.2×10^{-4} and 3.5×10^{-6} to 3.2×10^{-4}, respectively.

3.5. Effect of acidity and calibration curve

The influence of the pH on the response of the carbon paste electrode was studied at 3.0×10^{-4} and 3.0×10^{-5} M mercury(II) ion for the pH range of 1.5–10.0. The pH was adjusted by 0.1 M solutions of hydrochloric acid or sodium hydroxide. It can be seen from Fig. 5 that the variation in potential is acceptable in the pH range 3.5–7.8. Under more acidic conditions, the ligand may be protonated thereby losing its capacity to complex with the metal ions. When the pH is nearly neutral, the fundamental cation is [Hg(OH)]$^+$, which reacts with the ligand. The drift in potential at pH 7.8 is attributed to formation of mercury(II) hydroxide [11]. Calibration curves were obtained for a selected electrode at different pH values. At pH 5.5–6.5, the ISEs showed a twice Nernstian response in the concentration range 3.9×10^{-7} to 3.2×10^{-4} with a slope

Table 3
Selectivity coefficient values for Hg(II) sensor.

Interfering ions	SSM	MPM	FIM
NH$^+$	1.9×10^{-2}	2.9×10^{-3}	5.8×10^{-2}
Na$^+$	3.2×10^{-2}	7.1×10^{-4}	4.3×10^{-2}
K$^+$	1.5×10^{-2}	4.3×10^{-3}	3.9×10^{-2}
Ag$^+$	1.1×10^{-1}	3.9×10^{-2}	9.7×10^{-2}
Cd^{2+}	3.2×10^{-3}	5.1×10^{-4}	2.5×10^{-3}
Mg^{2+}	8.1×10^{-4}	6.4×10^{-4}	1.9×10^{-3}
Ca^{2+}	6.3×10^{-4}	5.9×10^{-4}	6.1×10^{-4}
Ba^{2+}	4.5×10^{-4}	3.7×10^{-4}	3.9×10^{-4}
Zn^{2+}	7.3×10^{-4}	3.4×10^{-4}	2.2×10^{-3}
Ni^{2+}	4.7×10^{-4}	3.2×10^{-4}	5.3×10^{-4}
Li^{2+}	1.2×10^{-4}	1.5×10^{-4}	2.3×10^{-4}
Co^{2+}	6.2×10^{-3}	7.1×10^{-4}	4.1×10^{-3}
Cu^{2+}	2.5×10^{-1}	5.1×10^{-1}	1.4×10^{-1}
Pb^{2+}	2.2×10^{-2}	8.5×10^{-2}	1.1×10^{-2}
Ce^{3+}	9.1×10^{-5}	1.1×10^{-4}	2.7×10^{-4}
Al^{3+}	5.7×10^{-3}	2.9×10^{-2}	4.3×10^{-4}
Cr^{3+}	8.9×10^{-2}	6.4×10^{-2}	1.9×10^{-2}

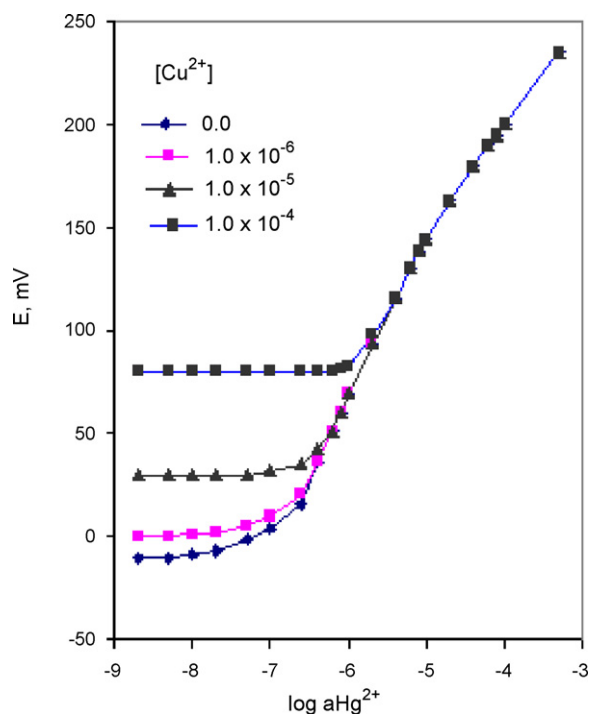**Fig. 4.** Variation of electrode potential as a function of Hg(II) ion in the presence of different concentrations of Cu(II) ions.

Fig. 6. Dependence of the response time on the change of concentration of mercury(II) (a) 0.00 to 3.0×10^{-7} M; (b) 3.0×10^{-7} to 3.0×10^{-6} M; (c) 3.0×10^{-6} to 3.0×10^{-5} M; (d) 3.0×10^{-5} to 3.0×10^{-4} M.

of 58.6 ± 0.8 mV/decade^{-1}. This is a typical value for monovalent cations. It is assumed that $[Hg(OH)]^+$ ion is present in this near neutral medium, because it is well known that, in pure water, Hg(II) can be found in two different forms, Hg^{2+} and $[Hg(OH)]^+$. At pH 3.8, the ISEs showed a Nernstian response in the concentration range 6.5×10^{-7} to 5.5×10^{-4} with a slope of 32.4 mV per decade. This is a typical slope value for a divalent cation and in this case the electrode can therefore be used for determination of Hg^{2+} species [12].

3.6. Dynamic response time, renewal surface and reproducibility of the electrode

For analytical applications, dynamic response time is a significant parameter for any sensor. The response time of the electrode is defined as the time between addition of the analyte to the sample solution and the time when a limiting potential has been reached [45].
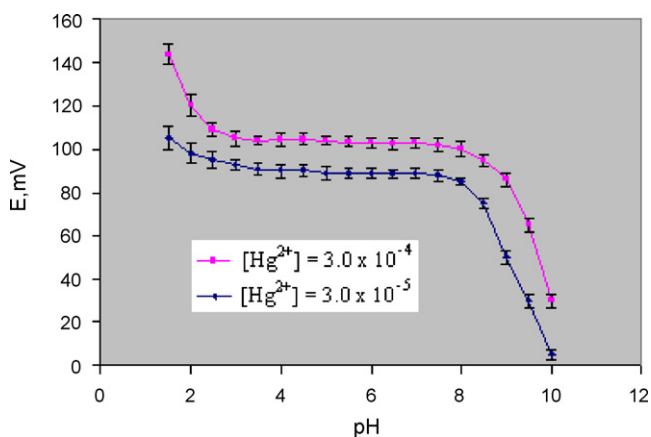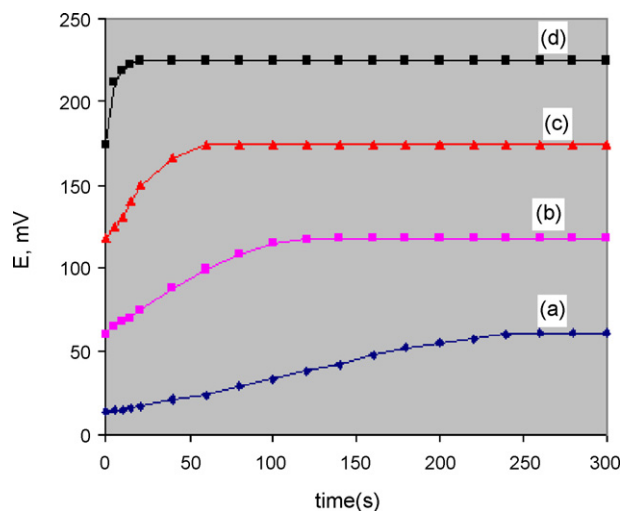
To measure the dynamic response time of the proposed sensor, the concentration of the test solution has been successively changed from 3.0×10^{-7} to 3.0×10^{-4} M. The resulting data depicted in Fig. 6 where the time depends strongly on the concentration change. At low concentration, 3.0×10^{-7} and 3.0×10^{-6}, the practical response time was longer (about 2.5–4.5 min) than that at higher ones, 3.0×10^{-5} and 3.0×10^{-4} (about 60–10 s). The short response time is most probably due to fast exchange kinetics of complexation–decomplexation of Hg(II) ion with the ionophore at the test solution-paste surface [46]. The potentials generated by this electrode remained stable for 15 min after which started deviation.

The slope of the calibration graph obtained by this electrode was found to decrease slightly after two times of use starting at 58.8 ± 0.3 mV and reaching 33.5 ± 0.7 mV at the last measurement. For the present electrode the decrease may be attributed to surface contamination and memory effect. Therefore, the electrode surface should be polished to expose a new fresh layer ready for use after each calibration. In this electrode, a new surface was obtained by squeezing out a small amount of the paste, scrapping off the excess against a printing paper and polishing the electrode on a smooth paper to obtain a shiny appearance again. Accordingly, a paste of optimum composition and suitable weight ($\sim$1.2 g) can be used for several months without any deterioration or change in the response of the electrode.

Fig. 5. Influence of pH on the response of the Hg^{2+} carbon paste electrode at 3.0×10^{-4} and 3.0×10^{-5} M.

Table 4
Recovery of mercury ions from different water samples.

Sample	M		$X \pm$ S.E.	RSD%
	Hg^{2+} added	Hg^{2+} found		
Mineral water				
	$(4.00) \times 10^{-5}$	$(4.02 \pm 0.01) \times 10^{-5}$	100.5 ± 0.012	0.52
	$(1.00) \times 10^{-4}$	$(9.91 \pm 0.01) \times 10^{-5}$	99.1 ± 0.036	0.88
Tap water				
	$(4.00) \times 10^{-5}$	$(9.82 \pm 0.01) \times 10^{-5}$	98.2 ± 0.072	0.45
	$(1.00) \times 10^{-4}$	$(9.68 \pm 0.01) \times 10^{-5}$	96.8 ± 0.046	0.89
Well water				
	$(4.00) \times 10^{-5}$	$(4.05 \pm 0.01) \times 10^{-5}$	101.2 ± 0.062	1.08
	$(1.00) \times 10^{-4}$	$(1.01 \pm 0.01) \times 10^{-5}$	101.0 ± 0.086	1.15

$X \pm$ S.E., recovery $\pm$ standard error; M, the molar concentration of Hg(II) samples; RSD, relative standard deviation.
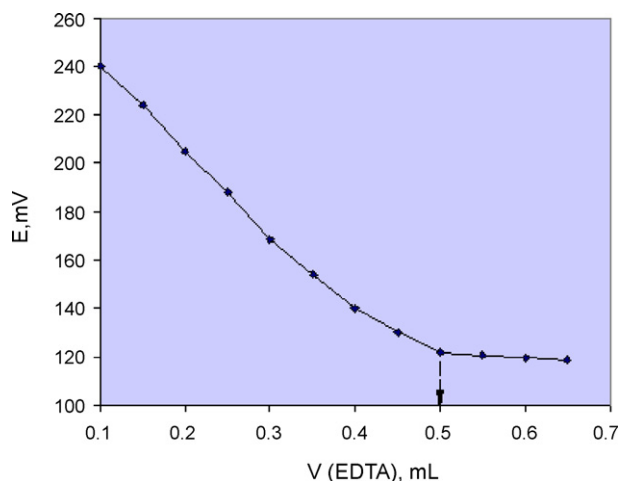
Fig. 7. Potentiometric titration curve of 5.0 ml of 1.0×10^{-3} M solution of Hg(II) with 1.0×10^{-2} M EDTA.

The reproducibility of the electrode was examined by determining a 1.0×10^{-6} and 1.0×10^{-5} M mercuric ion solution. The standard deviation in emf measurements for five replicate solutions was found to be 1.34 for 1.0×10^{-6} M solution and 0.36 for 1.0×10^{-4} M solution. Considering the low value of the standard deviation for these replicate measurements it is clear that the repeatability of the present electrode is satisfactory.

It is important to renew the electrode surface when the mercury solution is changed from a high concentration to a dilute solution because the residual mercury will still be adsorbed on the surface of the carbon paste electrode which will lead to poor reproducibility [47].

3.7. Analytical applications

The proposed sensor was found to work well under laboratory conditions. It is clear that the amount of Hg(II) ions can be accurately determined using the proposed sensor.

3.7.1. Determination of mercury in spiked treated, tap and well water

To assess the applicability of the proposed sensor to real samples, Hg(II) was measured in treated, tap, and well water. Each sample was analyzed in triplicate, using this sensor by the standard addition method. The results, in Table 4, show an average recovery of 98.5% with relative standard deviation (RSD) of 0.83% and indicates the utility of the proposed electrode.

3.7.2. Potentiometric titration

The sensor was successfully applied as an indicator electrode in potentiometric titration of 5.0 ml of 1.0×10^{-3} M HgCl$_2$ against 1.0×10^{-2} M EDTA. Typical results of titration of Hg(II) is shown in Fig. 7. The added titrant caused a decrease in the potential as a result of a decrease in free Hg(II) ion due to formation of a complex with EDTA. The amount of Hg(II) ions in solutions can be accurately determined from the resulting titration curves.

4. Conclusion

In this study, a new chemically modified carbon paste electrode based on N,N′-bis(salicylaldehyde)-phenylenediamine (salophen) as ionophore was used for Hg(II) determination. The electrode shows high sensitivity (1.5×10^{-7}), reasonable selectivity, fast static response, long term stability and applicability over a wide concentration range (3.2×10^{-7} to 3.2×10^{-4}). The modified electrode

was applied as indicator electrode in potentiometric titration and successfully used to determine mercury(II) in water samples with satisfactory results.

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