Int. J. Electrochem. Sci., 11 **(2016)** 10732 – 10747, doi: 10.20964/2016.12.30

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Manufacture of Lead-Specific Screen-Printed Sensor Based on Lead Schiff Base Complex as Carrier and Multi-Walled Carbon Nanotubes for Detection of Pb(II) in Contaminated Water Tests

Tamer Awad Ali[1,*], *Abeer M.E. Hassan*[2], *Gehad G. Mohamed*[3]

[1] Egyptian Petroleum Research Institute (EPRI), 11727, Cairo, Egypt.
[2] Analytical Chemistry Department, Faculty of Pharmacy, October 6 University, Giza, Egypt.
[3] Chemistry Department, Faculty of Science, Cairo University, Giza,12613, Egypt.
[*]E-mail: dr_tamerawad@yahoo.com

Received: 7 June 2016 / *Accepted:* 11 September 2016 / *Published:* 10 November 2016

A novel screen-printed electrode (SPE) based on [Pb(L)] complex (H_2L = 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylidene amino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol) was prepared for selective determination of Pb(II)ion. The ligand and its Pb(II) complex were prepared and characterized using elemental analysis, spectroscopic (IR and ^{1}H NMR) and molar conductance. Different individual variables were optimized using IUPAC recommendation such as graphite powder, plasticizer, amounts of [Pb(L)] complex ionophore and multi-walled carbon nanotubes (MWCNT). Their possible interactions were investigated. In this potentiometric method, fabrication of screen-printed (SPE; electrode V) and multi-walled carbon nanotubes-screen-printed (MWCNT-SPE; electrode IX) sensors was described. [Pb(L)] complex alone or with MWCNT was used as modifier in case of electrodes V and IX, respectively. Optimum composition resulted in enhancement in the sensitivity and selectivity of the SPE toward Pb(II)ions significantly over the concentration range of 1.0×10^{-7} -1.0×10^{-1} and 4.6×10^{-8} -1.0×10^{-1} mol $L^{-1}$of Pb(II)with detection limit of 1.0×10^{-7} and 4.6×10^{-8} mol L^{-1} and a Nernstian slope of 28.98±0.92 and 30.28±0.70 mV decade^{-1} for electrodes V and IX, respectively. No significant change in response was observed over the pH range of 3.0-8.0 and 2.5-8.5 with response time lower than 9 and 7s for electrodes V and IX, respectively. The potentiometric selectivity coefficients were calculated and the results obtained showed the good selectivity of the modified SPE electrodes (V and IX) for Pb(II) ion over other metal ions. Finally, these electrodes were precisely applied for the determination of Pb(II) ions in real spiked water samples. The results obtained using both the proposed potentiometric method and atomic absorption spectrometer (AAS) showed satisfactory agreement.

Keywords: Screen-printed electrodes; Schiff base; Pb(II)-Schiff base complex; Real water samples.

1. INTRODUCTION

Pipes, ammunition, solder, paint and petrol were the various products containing Lead. The use of lead as a petrol additive was considered as the major source of lead in the environment [1]where many countries have phased-out the use of lead in petrol due to atmospheric pollution by lead has caused considerable concern in the past [2]. However, it already was cycled through the biogeochemical cycle, and originally its release into the atmosphere has ended up in ground waters and surface and [3, 4]. Many serious illnesses such as anaemia, kidney diseases, nervous disorders and sickness, or even mortality among adults were resulted mainly due to its accumulation in bones, brains, kidneys and muscles [5]. Physical and mental development in children can be delayed due totheirexposure to lead in drinking water above the standard level [6]. Maximium limit of 15 ppb lead was allowed in drinking water according to the United States Environmental Protection Agency (US-EPA) and World Health Organization (WHO) [7, 8]. There is a great tendency to develop selective and sensitive detection methods for controlling toxic heavy metal ions as the results of their significant hazard effect[9]. Therefore, many techniques including atomic absorption/emission spectrometry [10], inductively coupled plasma mass spectrometry [11], colorimetric spectrometry [12], fluorescence spectrometry [13] and electrochemical method [14, 15] were developed. The electrochemical method was widely used due to they had many advantages' including high sensitivity, inherent simplicity, ease of miniaturization for in-situ measurement, low power consumption and capability of short analytical time[16]. Lead (II)–ion-selective electrodes (ISEs) were previously reported such that most of them based on polymeric membrane containing highly sensing ionophores [17-19] that had strong affinity for a particular metal ion with low or even no response to others. In this regard, Pb(II) ion selective electrodes were constructed using crown ethers [20-22], calixarenes [18, 23], and Schiff base [24, 25] as ionophores. Of their advantages [26-30] are simplicity, low cost, accuracy and reasonable selectivity and repeatability that candidate them for more extensive application in analytical chemistry [31], even for more complicated matrices such as soil and industrial wastewater [32]. In the development of potentiometric sensors, the specific metal–ligand interaction is the most important recognition mechanism that can be utilized [33-35]. Therefore, this work reports the first time of preparation, potentiometric characterization, and analytical application of a novel Pb(II)-screen-printed electrodes based on the use of [Pb(L)] complex (H_2L = 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylidene amino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol) as ionophore and plasticizer for the determination of Pb(II). The fabricated SPE was applied for the potentiometric calibration methods of Pb(II) in its analytical grad solution and different water samples.

2. EXPERIMENTAL

2.1. Reagents

Every one of the reagents was of the explanatory review and deionized water was utilized all through the trials. Lead nitrate was supplied from Sigma-Aldrich. While 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylidene amino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol)Schiff base

(SB) was set up as per the beforehand distributed strategy [36]. Sodium tetraphenylborate was purchased from Fluka. Polyvinyl chloride (PVC, relative high molecular weight) and graphite powder (synthetic 1–2 µm) (Aldrich) were of high purity and used for the fabrication of different electrodes. Multi-walled carbon nano tube (MWCNT) with the highest purity (diameter within 10–20 nm) was purchased from Merck and tricresylphosphate (TCP; Alfa-Aesar) were utilized. Different sorts of plasticizers, to be specific dioctylphthalate (DOP), dibutylphthalate (DBP) and o-nitrophenyloctylether (o-NPOE) were bought from Sigma, Merck and Fluka, individually.

Chloride salts of zinc, potassium, manganese, cobalt, magnesium, cadmium, chromium, nickel, calcium, sodium, ferrous, ferric and aluminum were utilized as meddling particles.

2.1.1. Samples

Water samples included wastewater (Sample 1 was supplied from Egyptian Petroleum Research Institute, Nasr City, Cairo), cooling tower waters (Egyptian Petrochemical Company (sample 2) and Sidpec Petrochemical Company (sample 3), Amryia, Alexandria, Egypt) and formation water (Faras (22) (sample 4) and Raml (2) (sample 5), Western Desert, Agiba Petroleum Company.

2.2. Apparatus

All potentiometric measurements were performed utilizing Jenway 3505 pH-meter. Ag/AgCl double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrode was used. A companied glass pH electrode (Thermo- Orion, model Orion 3 stars, USA) was used for all pH measurements. All glasswares used were washed deliberately with distilled water and dried in the stove before use.

2.3. Synthesis of diamine [36]

2.5 g of sodium hydroxide was dissolved in a minimum amount of distilled water. 7.75 g of 2-aminophenol was added in ice bath. At that point 10 mL of H_2O_2 (30%, w/w) was added to the solution with continuous stirring for 2 h. A yellow precipitate was obtained, washed by distilled water, filtered off and crystallized from ethanol.

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2.4. Preparation and characterization of Schiff base ligand (H_2L) [36]

An appropriate amount of diamine was added to stirred solution of 5-methoxysalicylaldehyde in methanol over a period of 2h at room temperature to obtain light orange (H_2L) precipitate. The product was filtered off and washed with methanol then crystallized from dichloromethane/methanol mixture. The analysis of the yield was as follows: % Found (calculated) for $C_{28}H_{22}N_2O_4S_2$, C = 65.12 (65.37), H = 4.02 (4.28), N = 5.22 (5.45) and S = 12.63 (12.45). ^{1}H NMR, δ (ppm) = 3.73 (s, 6H, O−CH_3), 6.90–7.91 (m, 14H, Ar-H), 8.95 (s, 2H, HC=N), 12.07 (s, 2H, OH). FT-IR (KBr cm^{-1}) 1615 (C=N), 1274 (C−O).

2.5. Synthesis of [Pb(L)] complex

The Pb(II) complex was prepared by dissolving the appropriate amount of Schiff base ligand (H_2L, 3.2 g, 6.23 mmol) in ethanol and Pb(II) nitrate (2.062 g, 6.23 mmol) in water in 1:1 ratio. The solution was refluxed for 2 h to give a light yellow precipitate. The precipitate was filtered and washed with ethanol and water. Analytical characteristics for [Pb(L)]: %Found (calculated) for $C_{28}H_{20}N_2O_4S_2Pb$, C = 46.42 (46.60), H = 3.03 (2.77), N = 4.22 (3.88) and S = 8.56 (8.88). ^1H NMR, δ (ppm) = 3.70 (s, 6H, O−CH_3), 6.85–7.94 (m, 14H, Ar-H), 8.93 (s, 2H, HC=N). FT-IR (KBr cm^{-1}) 1610 (C=N), 1270 (C−O).

2.6. Fabrication of (SPEs)

Altered SPEs were printed in arrays of six couples consisting of the working electrodes following the procedures previously described [37-42]. A polyvinyl chloride flexible sheet (0.2 mm) was used as a substrate which was not affected by the curing temperature or the ink solvent and easily cutted by scissors. The working electrodes were printed using homemade carbon ink (prepared by mixing 2.5-18.0 mg ionohopre, 450 mg TCP, 6.0 mg MWCNT, 1.25 g of polyvinyl chloride (8%) and 0.75 g carbon powder) and cured at 50 ^oC for 30 min. A defined rectangular shaped (5 × 5 mm) working area and a similar area (for the electrical contact) on the other side were left after putting a layer of an insulator onto the printed electrodes. Fabricated electrodes were stored at 4 ^oC and used directly in the potentiometric measurements.

2.7. Performance characteristics of the potentiometric response

Sensor alignment comprised on the recording of potential after accumulated microadditions of concentrated primary ion solution over a fixed initial volume. The lower detection limit (LD) was taken as the intersection of the two asymptotic behaviors of the calibration curve, as prescribed by IUPAC [43-45]. Reproducibility was inspected by repeated monitoring of the slope and the LD of calibration curve.

The activity coefficients of ions in solution were calculated according to the Debye–Hückel formalism [46]. Selectivity attributes were resolved by IUPAC recommended matched potential method (MPM) [47, 48] and separate solutions method (SSM)[49].

pH impudence, determined as the Reilley diagram [50-52] was recorded in a NaOH solution at two concentration of $Pb(NO_3)_2$ solution (of 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1}) varying the pH from 1.0 to 9.0 with HNO_3 or NaOH.

The response time ($t_{90\%}$) of tested sensors was determined as the time required to achieve 90% of steady potential [34, 53]. It corresponds to five additions of primary ion, when the concentrations were rapidly increased.

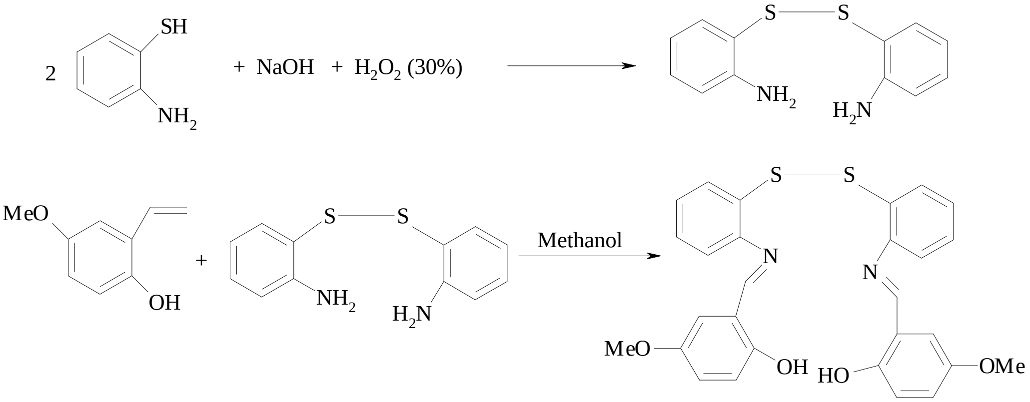
2.8. Determination of Pb(II) in spiked genuine water tests

Around 5 ml water tests were spiked with a definite Pb(II) ion concentration and then transferred to a 25 ml measuring flask and adjusted to pH 4 then content was assessed through potentiometric calibration utilizing SPEs as sensing electrodes. The technique was rehashed a few times to check the accuracy and reproducibility of the proposed method [54, 55].

3. RESULTS AND DISCUSSION

3.1. Investigation of complexion amongst ionophore and analyte

It is realized that the Schiff base ligands frame extremely fixed complex with transition metal ions. The exceptional way of N- giver Schiff bases is upgraded by the presence of a generally spread π-conjugation framework [36]. Moreover, the compound formed between Pb(II) ion and H_2L ligand in ethanol-water dissolvable was investigated and they were described by elemental analysis, IR, ^1H NMR and molar conductance procedures. The structure of the Schiff base ligand is given in Scheme (1) [36].



Scheme 1. Structure of Schiff base ligand (H_2L).

3.2. Effect of ionophore structure

The structure of a paste assumes an imperative part in deciding the sensitivity and selectivity of an ionophore [56-60]. The impact of various different parts like TCP plasticizer, ionophore and MWCNT additive were investigated where ten SPE-paste with different structure were readied and the potential responses of the electrodes towards comparing Pb(II) cations were acquired (Table 1). ISEs utilizing SPEs based on (Pb(II)-SB) complex as an ionophore were observed to be profoundly receptive to Pb(II) ion regarding a few different cations. In this way, the execution of the electrodes for

Pb(II) ions was initially examined in detail. By including a little measure of added substance, MWCNT, the potentiometric response amended. It is significant to specify that the nearness of lipophilic added substance increases the selectivity of the paste by lessening the anionic impedance impacts, enhances the potential reactions of SPEs by diminishing the reaction time, and also diminishes the paste ohmic resistance by expanding the cation extraction productivity [53, 61]. Clearly, the nonattendance of lipophilic added substance brings about the abatement of transducer upper recognition limit because of anionic obstructions. In any case, the slope of potential response was enhanced from sub-Nernstian estimation of 28.98 mV decade^{-1} to a Nernstian estimation of 30.28 mV decade^{-1} was obtained by addition of MWCNT to (Pb(II)-SB) complex as an appropriate amount to the paste. Moreover, the additional measure of lipophilic added substance may likely execute as a particle exchanger and brought about super Nernstian response, which diminished the selectivity and affectability of the SPE towards comparing Pb(II) metal particles.

Table 1. Enhancement of the screen-printed fixings

Structure % (W/W)					Performance and characteristics		
No.	GP[a]	TCP	((Pb(II)-SB) complex	MWCNTs[b]	Slope (mV decade^{-1})	LR (mol L^{-1})	R
I	50	50	-	-	14.34±1.83	1.0 × 10^{-5} – 1.0 × 10^{-1}	0.878
II	53	47	-	-	15.61±1.92	6.1 × 10^{-6} – 1.0 × 10^{-1}	0.903
III	50	47.5	2.5	-	25.98±1.60	8.2 × 10^{-7} – 1.0 × 10^{-1}	0.945
IV	49	46	5	-	27.01±1.01	2.0 × 10^{-7} – 1.0 × 10^{-1}	0.974
V	**48**	**44.5**	**7.5**	**-**	**28.98±0.92**	**1.0 × 10^{-7} – 1.0 × 10^{-1}**	**0.999**
VI	47	43	10	-	27.33±1.55	1.0 × 10^{-7} – 1.0 × 10^{-1}	0.980
VII	47	42.5	7.5	3	29.10±0.44	7.0 × 10^{-8}– 1.0 × 10^{-1}	0.984
VIII	46	41.5	7.5	5	29.39±0.77	5.0 × 10^{-8}– 1.0 × 10^{-1}	0.989
IX	**46**	**40**	**7**	**7**	**30.28±0.70**	**4.6 × 10^{-8} -1.0 × 10^{-1}**	**0.999**
X	45	39	7	9	29.62±0.81	4.6 × 10^{-8} – 1.0 × 10^{-1}	0.991

[a] Graphite powder.

[b] Multi-walled carbon nanotubes (MWCNTs).

3.3. Calibration graphs, construction and reaction qualities of the SPE

To get greater specificity and enhance SPE figures of authenticity need strong connection amongst transporter and Pb(II) ions. To evaluate the particular connection of the suggested SPE with Pb(II) ions, an electrode with the composition 7.5 mg of carrier ((Pb(II)-SB) complex), 450 mg plasticizer, 1.25 g of PVC and 735 mg of graphite powder (electrode V) was readied and it's reaction towards different metal particles in the focus range from 1.0× 10^{-7} to 1.0 ×10^{-1} mol L^{-1} was researched. The outcomes are appeared in Fig. 1. The exhibited outcomes affirm the Nernstian conduct and the most touchy reaction for Pb(II) ions over a wide focus range, while poor affectability and lower straight range for different particles were acquired.

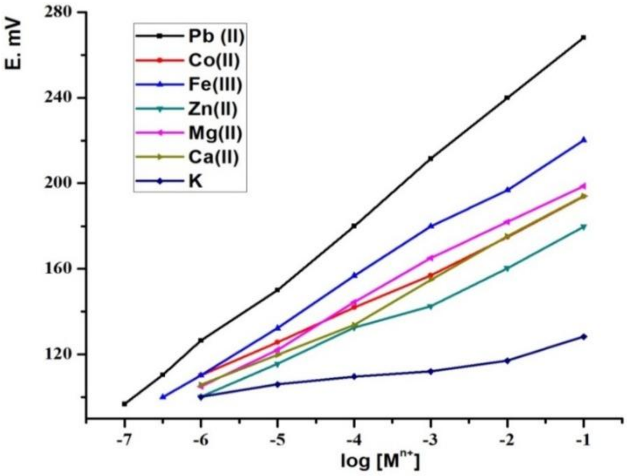


Figure 1. Potential response of Pb(II)-SPE of different metal ions (electrode V).

3.4. Effect of plasticizer

Pb(II)-screen-printed electrode (electrode IX) incorporating (Pb(II)-SB) complex ionophore, MWCNT and distinctive plasticizers having different dielectric constants (e.g. TCP, DBP, DOP and o-NPOE) were arranged and tried. Screen-printed electrode based on (Pb(II)-SB) complex ionophore, MWCNT plasticized with TCP ($\varepsilon = 17$), DBP ($\varepsilon = 4$), DOP ($\varepsilon = 7$) and o-NPOE ($\varepsilon = 24$) demonstrates calibration slopes of 30.28, 25.94, 27.58 and 30.80 mV decade^{-1} with lower identification points of confinement of 4.6×10^{-8} (Fig. 2).

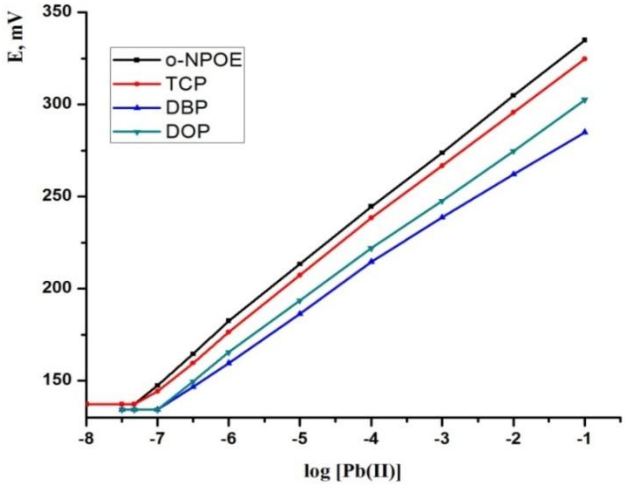


Figure 2. Profile of plasticizer sort on adjustment of altered SPEs (electrode IX).

3.5. Impact of pH

The impact of pH on the potentiometric response of the manufactured transducers over the scope of 1.0 - 10.0 at 1.0×10^{-3} and 1.0×10^{-5}mol L^{-1} of Pb(II) particle arrangement was explored (Fig. 3). The operational extent was examined by adjusting the pH of the test solution with either HNO_3 and/or sodium hydroxide solutions. As is clear, the potentials stay steady in the pH scope of 3.0-8.0 and 2.5-8.5 for transducers IV and IX, individually.

Furthermore it was observed that the drift at higher pH value due to the hydroxyl-complex of Pb(II) ion is formed. While the protonation of proposed carriers is responsible for the decline saw in potential at low pH values. Since the pH of Pb(II) particle solution over the direct range is in this reach, it was chosen as a working extent without including any buffer.

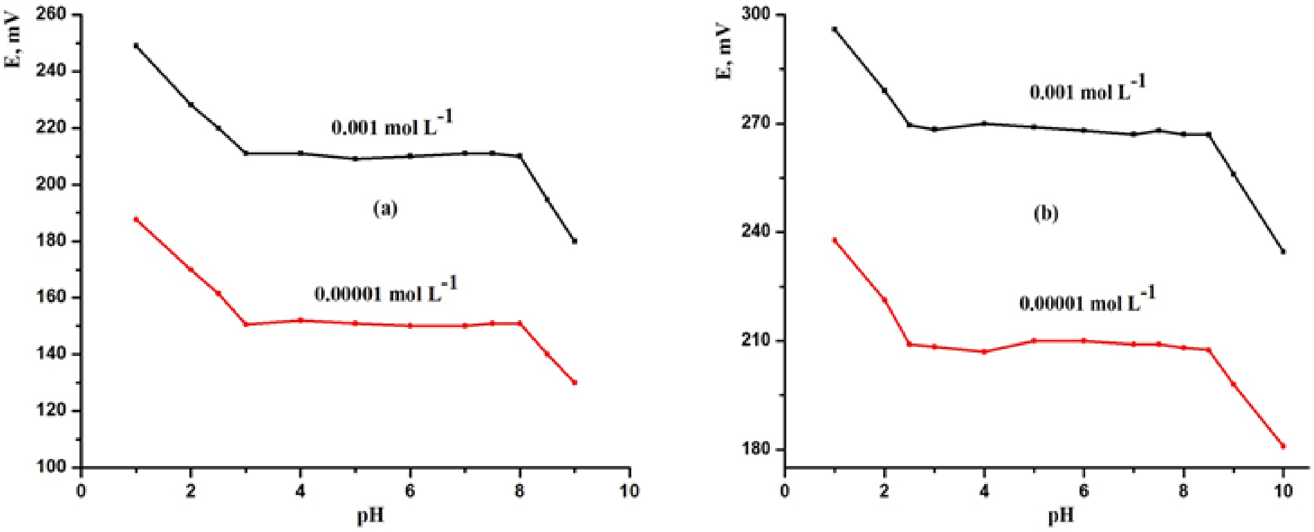


Figure 3. The performance of pH of test solutions on the response of (a) electrode (V) and (b) electrode (IX).

3.6. Influence of temperature of the test solution

In order to determine the isothermal coefficient (dE^0/dt) of the electrodes, alignment graphs (electrode potential (E_{elec}) versus p[Pb(II)]) were developed at different test solution temperatures (10-55 °C) in order to determine the isothermal coefficient (dE^0/dt) of the electrode. The standard electrode potentials (E^0) at various temperatures were acquired from calibration graphs as the intercepts at p[Pb(II)] = 0 were plotted versus (t−25), where t was the temperature of the test solution in °C (Fig. 4). A straight-line plot is obtained according to Antropov’s equation [37-39]:

$$E^0 = E^0_{(25)} + (dE^0/dt)(t-25)$$

Where $E^0_{(25)}$ is the standard electrode potential at 25 °C. The isothermal coefficient of the electrode was determined from the slope of the straight-line which is found to be 0.00173 and 0.00094 V/°C for electrodes IV and IX, separately. It is demonstrated from the values of the obtained isothermal coefficient of the electrodes that the electrodes have genuinely high thermal stability within the investigated temperature range. The investigated electrodes were observed to be usable up to 55 °C without noticeable deviation from the Nernstian behavior (Fig. 4).

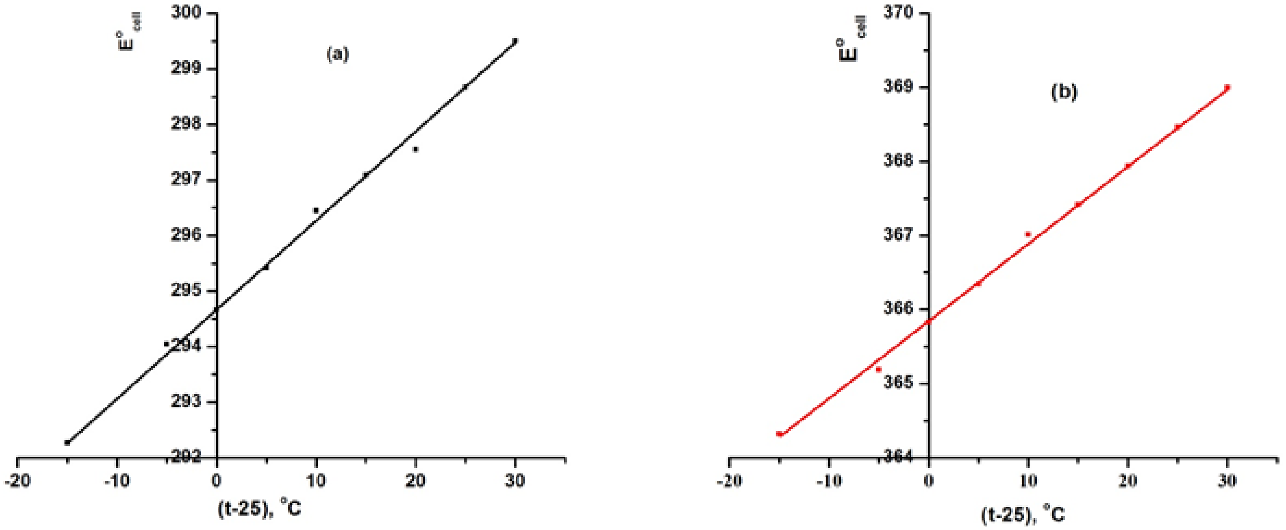


Figure 4. Impact of temperature on the response of (a) electrode (V) and (b) electrode (IX).

3.7. The reaction time of the transducers

The dynamic reaction time is a vital parameter for analytical applications of any sensor [42, 47]. In this study, practical reaction time was recounted by enhancing the Pb(II) ions concentration in solution from 1.0 $\times 10^{-7}$ to 1.0 $\times 10^{-2}$ mol L^{-1}. The outcomes portrayed in Fig. 5, unmistakably shows that the deliberate reaction time is 9 and 7s for electrodes IV and IX, individually.

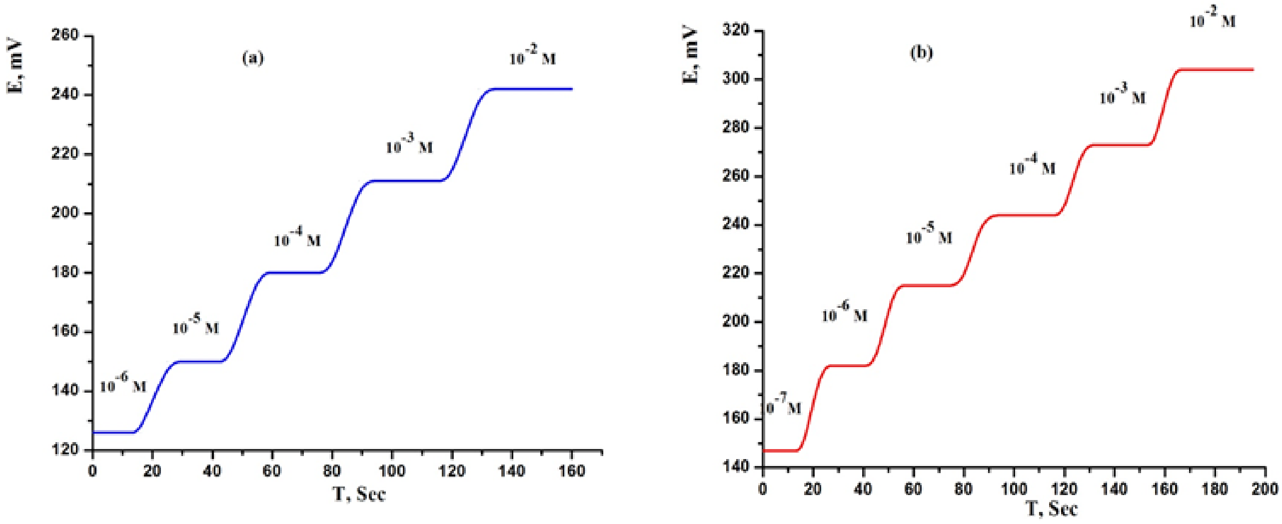


Figure 5. Reaction time of (a) sensor (V) and (b) sensor (IX) acquired by progressive increment of Pb(II) ion concentration.

Table 2. Potentiometric selectivity coefficients of various ions utilizing electrode (V) and electrode (IX).

Interfering ions	$-\log K^{SSM}_{A,B}$ (a) electrode (V)	$-\log K^{SSM}_{A,B}$ (a) electrode (X)	$-\log K^{MPM}_{A,B}$ (b) electrode (V)	$-\log K^{MPM}_{A,B}$ (b) electrode (X)
Co^{2+}	3.34	3.52	3.72	3.81
Zn^{2+}	5.01	5.09	5.15	5.22
Mg^{2+}	2.67	2.43	2.74	2.80
Ni^{2+}	5.21	5.26	5.29	5.30
Cd^{2+}	5.03	5.05	5.10	5.14
Cu^{2+}	1.99	1.94	2.01	2.03
Hg^{2+}	2.03	2.04	2.08	2.05
Ca^{2+}	3.84	3.86	3.88	4.00
Mn^{2+}	5.11	5.15	5.17	5.19
Fe^{3+}	1.01	1.05	1.03	1.07
Cr^{3+}	4.24	4.43	4.26	4.47
Ce^{3+}	4.52	4.59	4.57	4.61
Al^{3+}	3.31	3.35	3.42	3.44
Na^{+}	6.02	6.04	6.09	6.10
K^{+}	6.20	6.21	6.27	6.30
I^{-}	5.60	5.63	5.66	5.68
Br^{-}	5.72	5.71	5.73	5.75
Maltose	-	-	6.12	6.18
Glycine	-	-	5.78	5.82
Starch	-	-	5.84	5.91
Urea	-	-	6.01	6.05

[a] Selectivity coefficients found by separate solutions method

[b] Selectivity coefficients found by matched potential method.

3.8. Selectivity characteristics

The potentiometric selectivity coefficients ($K_{A,B}^{pot}$) of Pb(II) sensors were assessed at various concentrations of both lead(II) and the interferents according to IUPAC proposals. The "separate solutions method (SSM)" was utilized in event of different cations (Al^{3+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, Cu^{2+},Ni^{2+}, Ce^{3+}, Zn^{2+}) [36], and the "matched potential method (MPM)" [37] in the event of nonpartisan species (maltose, glycine, starch, and urea).In "(SSM)", the "Nicolsky-Eisenman" condition [49] was utilized:

$$\log K^{pot}_{A,B} = \text{"}((E_B-E_A)/S) + (1-(Z_A/Z_B))\text{"} \operatorname{Log} a_A \qquad (1)$$

Where E_A and E_B mean the potentiometric response of a_A and a_B, individually. a_A and a_B are the primary ion activity and the activity of an meddling ion, respectively. The 'Debye-Hückel' condition was used to compute the single ion activity [61]. In this work, a_A (1.0×10^{-3} mol·L^{-1} Pb(II) ion) and a_B (1.0×10^{-3} mol·L^{-1} meddling particle) were utilized to quantify the selectivity coefficients. S is the Nernstian slope, Z_A and Z_B are the charges of the primary and meddling ions, individually.

By applying the matched potential method, the selectivity coefficient was determined by measuring the adjustment in potential after expanding the primary ion activity from an initial value of a_A to $a_{A'}$ and a_B represents the activity of interfering ion added to the reference solution of primary ion of activity a_A which likewise brings the same potential change. It is given by expression:

$$K_{A,B}^{MPM} = \frac{a'_A - a_A}{a_B}$$

Hence a_A and $a_{A'}$ were fixed at 1.0×10^{-4} and 1.5×10^{-5} mol L^{-1}Pb(II) and a_B was experimentally determined. The outcomes got summarized in Table 2 demonstrate that the sensors show great selectivity coefficient values for lead(II) ion over the majority of the tried basic species.

3.9. Shelf life

The average shelf life of the developed transducers was studied. The suggested transducers tenderly washed with refined water, dried and put away at room temperature when not being used. The potential estimations were recorded each day over a timeframe to decide the shelf life of the transducers. As it can be seen from Fig. 6, preceding 28 or 31 weeks, no significant change in the execution of the transducers was watched. There was a slight slow decline in the slants from 28.98 to 28.10 and 30.28 to 29.04 mV decade^{-1} for transducers IV and IX, separately. This demonstrated the shelf life of the proposed Pb(II) transducers was around 7 to 8 months for cathodes V and IX.

3.10. Reproducibility and accuracy of the electrode

To assess the repeatability of this transducer, a arrangement of films (five) with comparative structure (IV and IX) prepared and the reaction of these sensors to Pb(II) particales concentration were tried. The outcomes demonstrated that the average of inclines, detection limits and straight dynamic reaches were (28.53±1.0 and 30.05±0.48) mV decade^{-1}, ($1.0 (\pm0.33) \times 10^{-7}$ and $4.6 (\pm0.33) \times 10^{-8}$) mol L^{-1} and ($1.0 (\pm0.46) \times 10^{-1}$ to $1.0 (\pm0.33) \times 10^{-7}$ and $1.0 (\pm0.16) \times 10^{-1}$ to $1.0 (\pm0.10) \times 10^{-8}$ mol L^{-1}) for transducers IV and IX, individually. The standard deviation of estimations of 1.0×10^{-4}mol L^{-1} of Pb(II) solution with these five transducers was ± 1.0 mV.

It can be described as the technique is fit for creating comes about with high precision. Additionally, the accuracy was notified in terms of percentage of outright blunders acquired in the estimation of known concentrations. They got outcomes are inside the worthy scope of < 1%.

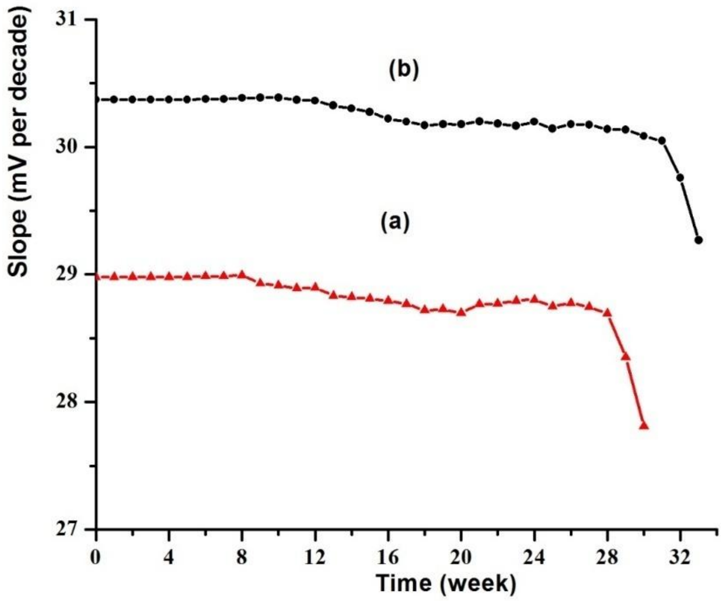


Figure 6. The lifetime of (a) electrode V and (b) electrode IX.

Table 3. Evaluation of Pb(II) ions in spiked water samples using sensor (V) and sensor (IX).

Samples	[Pb(II)] (µg L^{-1})									
	(Electrode IV)				(Electrode IX)			AAS		
	Added	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)
1	3.0	2.95	0.968	98.33	2.98	0.146	99.33	2.96	1.005	98.67
	3.5	3.47	0.231	99.14	3.49	0.096	99.71	3.47	0.093	99.14
2	5.0	4.93	0.728	98.60	4.97	0.106	99.40	4.95	0.107	99.00
	5.5	5.44	0.532	98.91	5.46	0.162	99.27	5.45	1.006	99.09
3	4.5	4.46	0.097	99.11	4.49	0.084	99.78	4.44	1.153	98.67
	5.5	5.43	0.421	98.73	5.47	0.103	99.45	5.42	1.235	98.55
4	3.0	2.96	0.394	98.67	2.97	0.153	99.00	2.95	1.231	98.33
	3.5	3.47	0.096	99.14	3.48	0.163	99.43	4.46	1.352	98.86
5	3.0	2.94	1.008	98.00	2.98	0.184	99.33	2.96	1.084	98.67
	3.5	3.42	1.106	97.71	3.44	0.252	98.29	3.43	1.351	98.00

3.11. Examination of the genuine specimens

The technique become effective to the assess of trace amounts of Pb(II) in a wide variety of real samples. The specimens were also scrutinized after spiking with various concentrations of the analyte. The explanatory results are displayed in Table 3. In perspective of the high selectivity gave by atomic absorption spectrometer (AAS), the recuperation of spiked specimens is acceptable, which demonstrated the capability of the framework in the estimation of analyte in genuine water specimens with various matrices.

3.12. Correlation of Previous Works with the Current Study

The Features of the created particular sensors based on (Pb(II)-SB) complex alone or with MWCNTs ionophores were compared with the reported Pb(II) specific sensors taking into account different macrocyclic compounds and methods. As it can be seen in this study (Table 4), the created sensors showed a fast response time and excellent dynamic working range with low detection limit compared to previously reported electrodes [54, 56, 58, 59]. Also, the potential reactions of the created sensors are pH independent over an attractively wide range. It can be presumed that the created sensors can be applied effectively for exact and precise estimation of lead(II) concentration in genuine specimens.

Table 4. Comparing of the proposed Pb(II)- sensors (Sensors V and IX) Features with some of the already reported Pb(II)-ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
Proposed electrode (V)	28.98	9	3.0 – 8.0	<6	1.0×10^{-7} - 1.0×10^{-1}	1.0×10^{-7}
Proposed electrode (IX)	30.28	7	2.5 - 8.5	<7	4.6×10^{-8} - 1.0×10^{-1}	4.6×10^{-8}
54	30.37	15	4.0 - 8.0	<2	6.31×10^{-8} –3.98×10^{-2}	2.51×10^{-8}
56	29.5	10	2.8 - 7.0	4	5.0×10^{-7} –1.0×10^{-1}	2.5×10^{-7}
58	29.84	<5	4.0–7.5	<4	2.5×10^{-9} – 1.0×10^{-1}	2.5×10^{-9}
59	30.7	14	4.0-6.0	-	8.5×10^{-7} – 1.0×10^{-2}	1.5×10^{-7}

4. CONCLUSIONS

New screen-printed specific sensors to Pb(II) particles were made utilize 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylideneamino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol)-Pb(II) Schiff base complex and multi-walled carbon nanotubes (MWCNTs) as a novel charged carrier without use of anionic additives. The developed electrodes enable the determination of Pb(II) ions in the concentration range from 1.0×10^{-7} to 1.0×10^{-1} and 4.6×10^{-8} to 1×10^{-1} mol L^{-1} and can be used in complex matrixes in different water specimens. The preparation of the electrodes is simple, not costly and the lifetime is about 7 to 8 months. The very quick response may empower its utilization in routine examination. Most of them were less specific and had long reaction time; their steadiness was likewise not effective.

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