

New Ion Selective Sensitive Electrode of Pd (II) as Multisensor Based on IRA-410 via Low Cost Oxidation Reduction Process

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Abstract

A novel ion selective IRA-410 membrane disc sensor for Pd (II) ions has been prepared and studied. This electrode has a wide linear dynamic range from 10^{-1} to 2.5×10^{-6} mol $^{-1}$ with a Nernstian slope of 16.5 ± 0.2 mV decade $^{-1}$ and low detection limit of 1.6×10^{-6} mol l $^{-1}$. It has a fast response time (<1 s) and good selectivity with respect to different metal ions. IRA-410 based electrode was suitable for aqueous solutions of pH range from (1.0- 9.0). It can be used for about 10 months with complex with Pd (II) was calculated by using segmented sandwich membrane method. The formation constant of ionophore of IRA-410 and its Pd (II)-Complex is examined using Fourier-transform infrared analysis and elemental analysis techniques. The proposed electrode has been used successfully as an indicator electrode in potentiometric determination in aqueous nitrate and /or chloride media.

Keywords: Membrane sensor; Nernstian slope; IRA-410 based electrode; Ionophore complex; Aqueous and nitrate media.

Introduction

Separation of palladium by strongly basic anion exchangers IRA-410 and IRA-900 from intermediate radioactive liquid waste in chloroacetic acid/nitrate medium containing thirteen elements have been achieved. Different conditions have been studied, the effect of NaNO₃ as salt content, chloroacetic acid and hydrogen ion concentration have been investigated. Selective recovery of palladium from the [ILLW] solution was achieved using the column technique. The selectivity increased by using chloroacetic acid/nitrate than in nitrate medium. The elution of palladium was carried out via reduction with formic acid [1-3] where the rate of the reduction process was increased by decreasing

the formic acid concentration till 50% followed by dissolving the separated palladium by nitric acid. Selective efficient method is used for separation of palladium [4-12] by strongly basic anion exchangers IRA-410 and IRA-900 from intermediate radioactive nitrate medium different conditions for exchange behaviour of palladium from (ILLYO solutions containing number of elements were investigated by batch technique. Selective recovery of palladium from (ILLW) solution was achieved using column technique the elution [13] of palladium was carried out via reduction with formic acid. Ion-selective electrode based potentiometry has become a well-established electro-analytical technique. In this technique the most exciting and fastest growing area of research is the use of ion sensitive membrane electrodes for analysis of wastewater containing heavy metals. Using this approach the applicability of the potentiometric method has been greatly extended [14-17] enabling the simple and accurate determinations of many heavy metal ions and has led to a search for suitable materials that can be used for preparation of sensitive and selective ion-sensors, chemical sensors or more commonly ion-selective electrodes ((ISEs) [18,19]. Ion selective electrode based on palladium (II) dichloride acetylthiophene fenchone azine (I) has been developed.

Experiment

Reagents and chemicals

The strongly basic anion exchanger was used as previously described [4]. The plasticizers were obtained from Aldrich (Milwaukee, WI). While poly vinyl chloride powder (PVC) were obtained from Fluka (Buchs, Switzerland). The chloride salts of all cations studied (Figure 1).

XRD and SEM characterization of Amberlite-410

As it is shown in Figures 2, 3a and 3b, Pd (II) was chosen as the

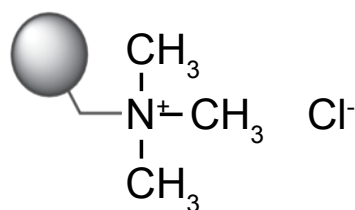


Figure 1: Structure: Amberlite IRA- 410 in chloride medium.

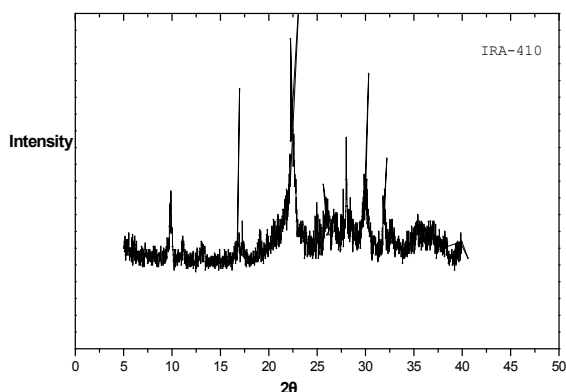


Figure 2: XRD Pattern for PVC on pd after.

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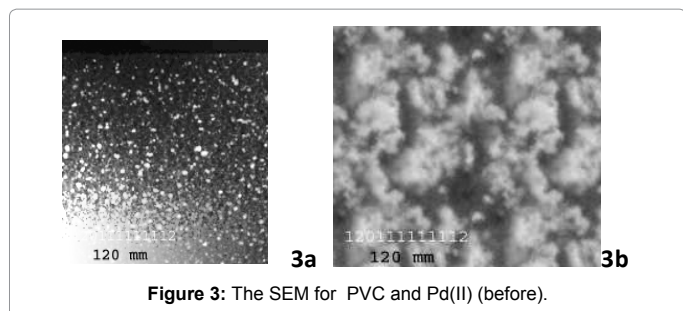


Figure 3: The SEM for PVC and Pd(II) (before).

Resin	C%	N%	O%	Cl%
IRA-410	85	12	2.33	0.67

Table 1: Elemental analysis results after addition the IRA-410.

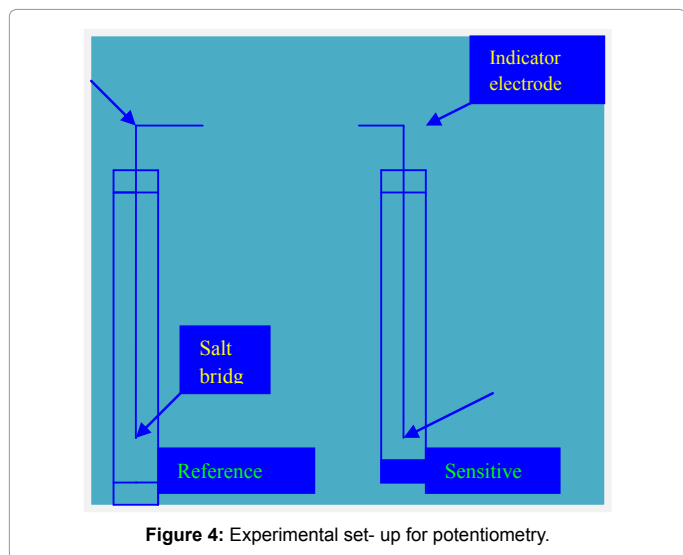


Figure 4: Experimental set-up for potentiometry.

Membrane	PVC	Composition % Plasticizer	NBPP	Additive	Slope/mV decade ⁻¹
1	60	2,NaTFPB	-----	2,KTCIPB	12.5 ± 0.2 mV
2	60	2,NaTFPB	-----	2,KTCIPB	28.4 ± 0.2 mV
3	60	2,NaTFPB	0.8	4,KTCIPB	14.6 ± 0.2 mV
4	60	4,NaTFPB	1.2	4,KTCIPB	9.8 ± 0.2 mV
5	60	2,NaTFPB	1.6	3,KTCIPB	12.4 ± 0.2 mV

Table 2: Optimization of membrane ingredients.

appropriate sorbent for the sorption of Amberlite-410 among all the sorbents tested in this work. X-ray powder diffraction (XRD) characterization showed that the natural samples of Amberlite-410, Figure 2: XRD pattern of acid-treated. Amberlite-410 with 2MHCl almost pure. Elemental content of the mineral was revealed using energy dispersive X-ray spectroscopy (EAR). The percentages of the elements are given in Table 1. The values given correspond to an average of Data points selected randomly on the surface of Amberlite-410. A scanning electron microscope (SEM) micro image is provided in Figures 2, 3a and 3b. This Figures show typical Amberlite-410 crystals with sizes varying up to several μm .

Powder XRD pattern of Pd nanoparticles is shown in Figure 2. The d-spacing corresponding to XRD lines is 2.236, \AA . These d-spacing values correspond to (111), (planes with lattice constant, $a = 3.871 \text{\AA}$). This observation confirms the presence of metallic Pd with fcc structure. XRD line corresponding to {111} plane is found to be

unusually intense. SEM images of black particles are shown in Figure 3a and 3b. Aggregates of irregular-shaped particles are observed and the size of Pd particles varies from 8 to 25 nm. Of particles are formed due to the self-assembling nature of palladium tetra chloroacmplox on IRA-410. This self-assembly of the particles also confirms the capping ability of Pd on IRA-410.

Apparatus: Potentiometric measurements were performed at $25 \pm 1^\circ\text{C}$ using a Fisher scientific-computer aided pH/ millivoltmeter (Model 450) with a palladium PVC matrix membrane electrodes in conjunction with a double junction $\text{Hg}|\text{HgCl}_2|\text{KCl}(\text{sat.})$ reference electrode (Cole-Parmer Co., Chicago, Illinois 60648). A Fisher Accumet Model 825 MP pH-meter (accuracy ± 0.00 1 pH) with a glass pH electrode (Fisher electrode no. 13-639-90) was used for all pH measurements). Figure 4: using the KBr technique was used for infrared measurements. (Figure 3a,b) (Figure 4) (Table 2).

Calibration Curve: Figure 5: These sensors exhibit the maximum working concentration range of 1.0×10^{-7} to $1.0 \times 10^{-3} \text{M}$ with a slope of $>16 \text{ mVdecade}^{-1}$ of activity (Sensor of Pd (II) ion selective electrode). The PVC-membranes were prepared and aggregation into sensor electrodes using established procedures [20-24]. The prepared membranes contained 1.2 mg ionophore (IRA-410), 0.60 mg lipophilic salt, 60 mg PVC and 10 mg membrane solvent were mixed with 0.5 ml (THF) I mixed together very well and making compact disk with diameter 0.5 cm and thickness 0.2 cm and drying. In the glass dish with an diameter of 30 mm resting on a smooth mould. THF tetrahydrofuran was allowed to evaporate for 48 h standing at room temperature. Transparent PVC membranes were obtained with a thickness of 0.2 mm. A 11 mm diameter piece was cut out from the PVC membrane and attached to a PVC tube by means of PVC-THF solution Figure 6: wavelength(nm)

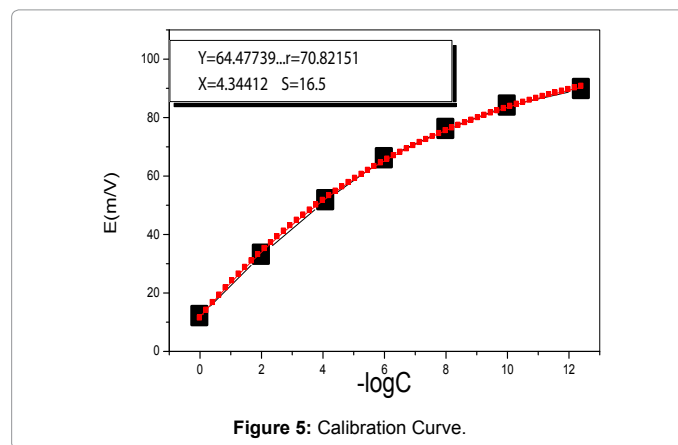


Figure 5: Calibration Curve.

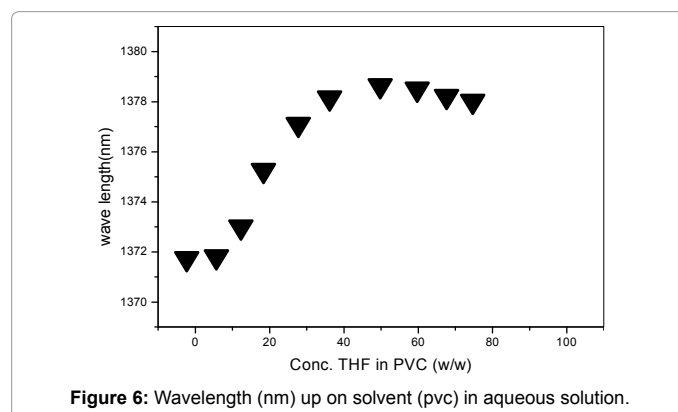


Figure 6: Wavelength (nm) up on solvent (pvc) in aqueous solution.

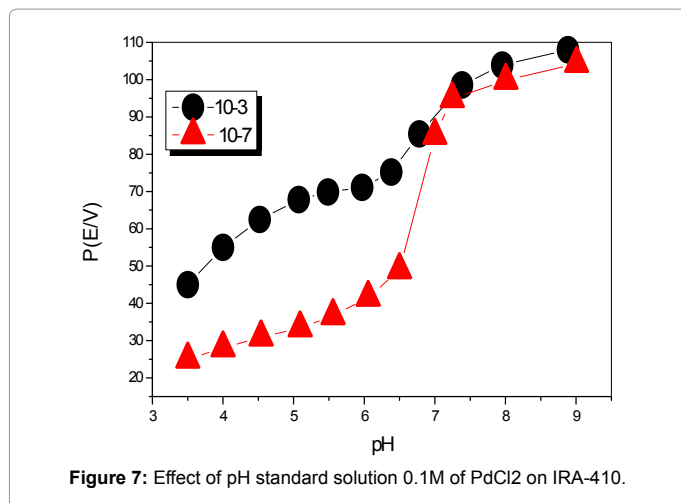


Figure 7: Effect of pH standard solution 0.1M of PdCl₂ on IRA-410.

upon solvent(PVC)in aqueous solution as previously described [25]. The PVC tube with the membrane was then incorporated into an Hg|HgCl₂ |KCl inner electrode (1.0 mm diameter). The dried tube was filled with internal solution contained 10⁻³ mol l⁻¹ pdCl₂ and 10⁻³ mol l⁻¹ KCl. Then, the electrode was conditioned for 1 h in 10⁻³ mol l⁻¹ pdCl₂ solution [26].

Preparation of PVC-membrane: The PVC-membranes were prepared and aggregation into sensor electrodes using established procedures (20-24). The prepared membranes contained 1.2 mg ionophore (IRA-410), 0.60 mg lipophilic salt, 60 mg PVC and 10 mg membrane solvent were mixed with 0.5 ml (THF) I mixed together very well and making compact disk with diameter 0.5 cm and thickness 0.2 cm and drying. In the glass dish with a diameter of 30mm resting on a smooth mould. THF tetrahydrofuran was allowed to evaporate for 48 h standing at room temperature. Transparent PVC membranes were obtained with a thickness of 0.2 mm. A 11 mm diameter piece was cut out from the PVC membrane and attached to a PVC tube by means of PVC-THF solution as previously described (25). The PVC tube with the membrane was then incorporated into an Hg|HgCl₂ |KCl inner electrode (1.0 mm diameter). The dried tube was filled with internal solution contained 10⁻³ mol l⁻¹ pdCl₂ and 10⁻³ mol l⁻¹ KCl. Then, the electrode was conditioned for 1 h in 10⁻³ mol l⁻¹ pdCl₂ solution [26].

Potential measurement: All potential measurements were performed at 25 ± 1°C using a Fisher scientific-computer aided pH/milivoltmeter (Model 450). The electrochemical system for this electrode can. The performance of the electrode was investigated by measuring its potential in palladium chloride solutions prepared in the concentration range (10⁻¹ to 10⁻⁷) mol l⁻¹ by gradual dilution of stock standard solution 0.1 mol l⁻¹ of pdCl₂, with triply distilled water. The potentiometric selectivity coefficients (log K Pot Pd, B) were measured using the separation solution method (SSM) and the mixed solution method (MSM) [27,28]. Dependence of pH on electrode response was examined (Figure 7): Adjusting the pH of the measured standard solution with 1x10⁻³ mol l⁻¹ hydrochloric acid or sodium hydroxide solutions (Figures 6 and 7).

Underwent response Sensors palladium according the equation Nernstian with selectivity similar and the knowledge that the sensors palladium prepare traditional because we prepare palladium disc, and put the bottom of reference electrode .The electrode signal feels palladium in another solutions whether the sample solution sea water or others and, of course, used plastic films made of PVC, which showed

long-term response to sensitivity this led to the use of sensors for a long period of more than 6 months and under the continued use of this investigation.

Results and discussion

Dynamic response time

Dynamic response time of the Pd (II) sensor: The determination of palladium (II) by potentiometric titration based on the formation of a water-insoluble ion pairs of PdX₄²⁻ and PdX³⁻ complexes (X = Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻) [29] with a cationic titrant such as alkyl ammonium [30-32], alkylphosphonium [33-35] and crystal violet [36] were published. An important requirement for preparation of an ion selective sensor is that membrane electroactive material should have high lipophilicity and strong affinity for a target metal ion and poor affinity to the others.

It is well known that coordination abilities of ligands containing sulfur atom, are very selective to the transition metal ions. However, most of these show some limitations in their working activity range, selectivity, response time, pH range and lifetime. Thus, the development of reliable sensing ion selective sensors for palladium ion is considerable importance for environment and human health. To improve the analytical selectivity, it is essential to search novel carrier compounds that would interact with palladium ion with high selectivity. Because of the ligand that contain sulphur highly selective for Pd (II), classified as a “soft” Lewis acid. The use of IRA-410 as an ionophore is reported in the construction of a Palladium (II)-PVC membrane electrode and their characteristic and properties of selective electrode were studied. The novelty comes from that it can be used in aqueous and solid phases. The washing was used by elution of palladium absorbed palladium via reduction of palladium by formic acid. It is used for reducing of palladium producing palladium metal and sensing it in metallic palladium. The reduced palladium can be used as sensor hydrogen.

Time response, when total solution effect of the time according the equation (1)

$$y(t) = \{Kt + K(t_0 - T) e^{-t/\tau}\} \quad (1)$$

Where Kt represent yp (t)..... K(t₀-T) e^{-t/τ} yH(t)

The first term from equation describe the particular solution the end term is homogeneous solution. The dynamic response time of the Pd (II) (ISE)s selective electrode , of the most important factors .study

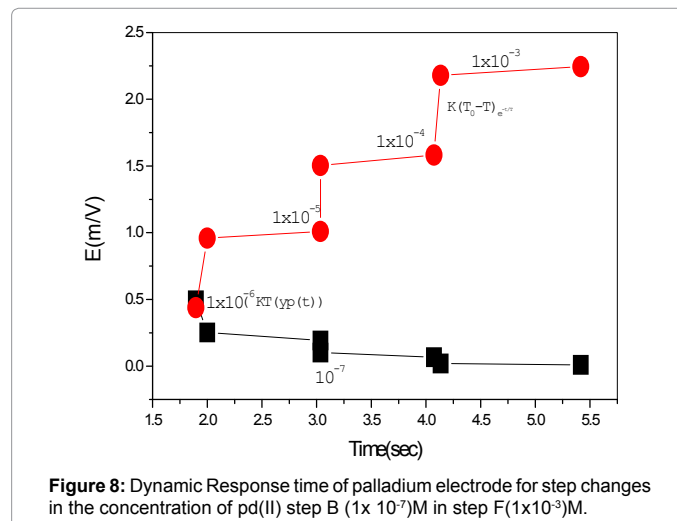


Figure 8: Dynamic Response time of palladium electrode for step changes in the concentration of pd(II) step B (1x 10⁻⁷)M in step F(1x10⁻³)M.

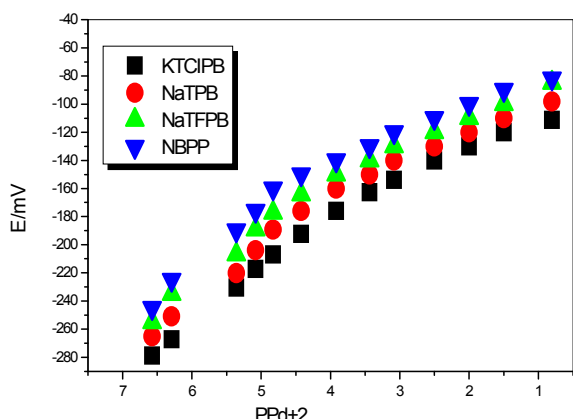


Figure 9: The Potential responses of pd(II) membrane ISEs prepared with different types of potential.

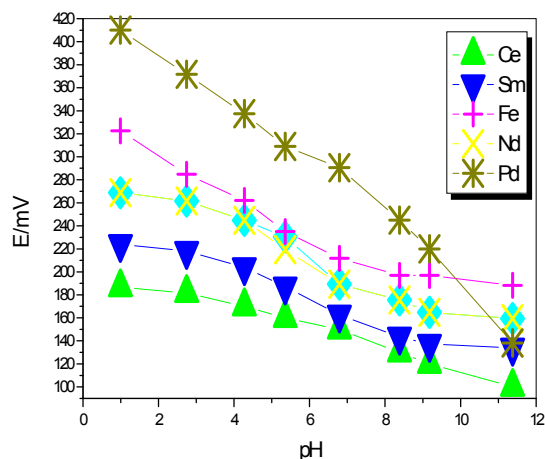


Figure 10: Effect of pH on the potential responses of Pd(II) ion-selective electrode.

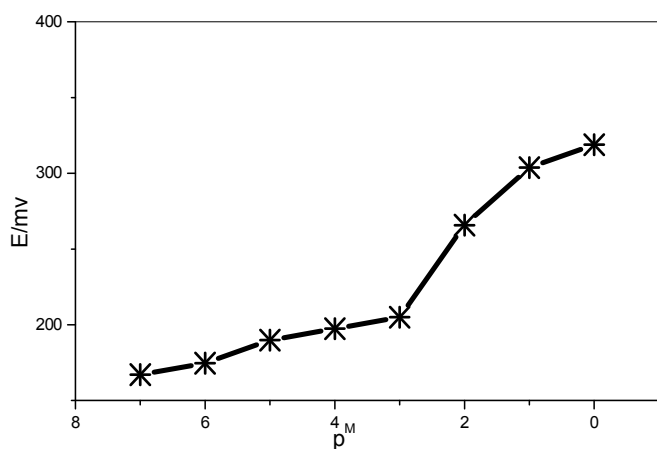


Figure 11: Potential response of various ion-selective membrane based on IRA-410.

the practical for response time of the ion selective electrode recorded by changing of the Pd(II) concentration in solution from (1.0×10^{-7}) to

1.0×10^{-3})M. The potentials versus time traces are shown in Figure 8. As can be seen, the whole concentration range of plasticized membrane electrode reaches its equilibrium responses in a very short time ($<1s$)

Membrane composition

Due to some similarities between the functional groups of IRA-410 with those of the previously reported ligating molecules for lanthanide ions, and especially for palladium ion [2–6] as well as its negligible water solubility, we decided to examine the suitability of IRA-410 as potential ionophore in constructing some lanthanide ion-selective electrodes. Our preliminary solution studies revealed that, NBPP forms a quite stable complex with Pd (II) ion, which readily precipitates out from dioxan solution. While the extent of complexation of transition metal ions as well as other lanthanide such as Fe (III), Nd (III) and Sm (III) with IRA-410 was found to be much lower, as was examined by segmented sandwich membrane method [37]. Subsequently, the ligand IRA-410 was tested as an ionophore for the preparation of a variety of ions, mono, di, and trivalent metal ion-selective electrodes. The potential response of various ion-selective electrodes based on the proposed ionophore is shown in Figure 10. As expected, among different cations tested, Pd (II) with the most sensitive response seems to be suitably determined with the PVC membrane based on ligand NBPP. While the response slope of the other ion-selective electrodes are much lower the values expected from Nernstian equation, although in a limited concentration range. The response of membrane electrode depends on some parameters such as plasticizer-PVC ratio, amount of ionophore and additive used since; the nature of plasticizer influences the dielectric constant of the membrane phase both the mobility of ionophore molecules and the state of ligands [38-41]. It was expected to play a key role in the determining the ion-selective electrode characteristics. Polar plasticizers lead to the lowering of the membrane resistance as compared with polar plasticizers, which contain other functional groups with potential coordination sites which might [42] compete with carrier Thus, several solvents such as THBE, EHBS, DOP, o-NDPE, o-NPPE, and were tested (Figures 9-11). In fact, the Pd (II) ion-selective electrode based on IRA-410 better than the other examined mediators. It has a good Nernstian slope of 19.5 ± 0.2 mV decade⁻¹ over a wide of concentration range from 10^{-1} to 2.5×10^{-6} mol l⁻¹, with detection limit of 1.6×10^{-6} mol l⁻¹. On the other hand, THBE, EHBS, DOP, o-NDPE and o-NPPE solvents give non-Nernstian slopes of 12.5, 28, 14.6, 9.8, and 12.4, respectively.

Response of different anions: In preliminary experiments, various PVC-membrane ion-selective electrodes with the synthesized ion pair were prepared and tested for different anions. The potential response of the electrode for different anions is shown in Figure 9: The results exhibited significantly high selectivity to palladium ion over other anions. Hence, ion pair was selected as a carrier for preparation of palladium selective electrode.

Preparation of sandwich membrane

A potentiometric method to determine ionophore complex formation constants in solvent polymeric membrane phases, it requires membrane potential measurements on two-layer sandwich membranes, where only one side contains the ionophore. If both membrane segments have the same ionic strength, it is convenient to assume that the activity coefficients for the complexed and uncomplexed ions are approximately equal. In that case, they can be omitted and the complex constant is related to the potential. This relationship allows for the convenient determination of formation constants of ionophore complexes within the membrane phase on the basis of transient membrane potential

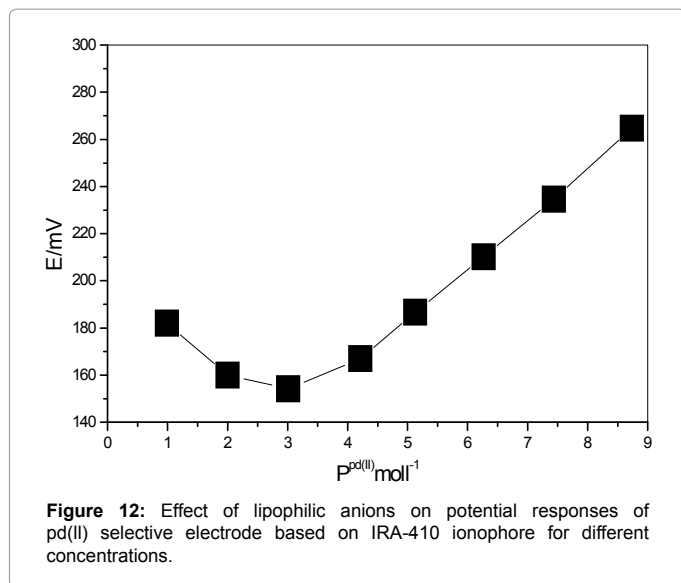


Figure 12: Effect of lipophilic anions on potential responses of pd(II) selective electrode based on IRA-410 ionophore for different concentrations.

Interfering ions	$\log K_{p(II)}^{MPM}$
Ce ³⁺	-3.00
Sm ³⁺	-2.89
Fe ³⁺	-3.02
Nd ³⁺	-3.10

Table 3: Comparison of the selectivity coefficients of different pd(II) electrodes.

measurements on two-layer sandwich membranes can be if ion pairing neglected. Ion-selective electrode membranes were cast by mixing the recorded membrane components to give a total cocktail mass of 181.8 mg in 2 ml of THF. The solvent THF allowed evaporating overnight. A series of disks were cut with a cork borer from the parent membrane. These disks were conditioned overnight in each of metal chloride 0.01 M salt solutions shown in Figure 10 of Ce (III), Sm (III), Fe (III) and Nd (III). All membrane electrode potential measurements were performed at laboratory ambient temperature in unstirred salt solution (identical to the conditioning and inner filling solution) versus Ag/AgCl reference electrode. Sandwich membrane was made by pressing two individual membranes (ordinary one without ionophore and one with the same components and additional ionophore) together immediately after blotting them individually, dry with tissue paper. The combined segmented membrane was then rapidly mounted into the electrode body and immediately measured. The time required from making the membrane sandwich contact until final membrane potential measurement was less than 1 min.

Sample preparation

Determination of palladium sample by Potentiometric titrations: THF (15.0 mL) was placed in the titration vessel and the required volume of the investigated acid and two drops of the indicator solution were added. The indicator electrode, either H₂/Pd or glass electrode and a SCE as the reference one were immersed in the investigated solution and connected to a pH-meter. The solution was then titrated with standard solution of (potassium hydroxide or sodium methylate) and the potential was read after each addition of titrant. The test solution was stirred magnetically under a continuous stream of dry nitrogen (Figures 9-11).

The optimization of permselectivity of membrane sensors

The optimization of permselectivity of membrane sensors is known to be highly dependent on the incorporation of addition a membrane components. In fact it has been demonstrated that, the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain cation-selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity [43,44]. Some of the lipophilic ions such as, potassium tetrakis (4-chlorophenyl) borate (KTCIPB), sodium tetra phenyl borate (NaTPB), sodium tetrakis (1-imidazolyl borate) (NaIB) and sodium tetrakis (4-fluorophenyl) borate dehydrate (NaTFPB), were tested (Figure 12). It has been found that, the suitable lipophilic additive which improves the sensitivity of Pd (II) electrode was KTCIPB with a good Nernstian slope of 19.5 ± 0.2 mVdecade⁻¹. While the other lipophilic ions have slopes of 21, 13.6 and 9, respectively (Figure 11). Shown that the potential response of various ion-selective membranes based on IRA-410. The amount of ionophore has effect on the electrode sensitivity. So that, amounts of NBPP carrier (0.8, 1.2 and 1.6 mg) were examined. The results indicate that, the membrane containing 1.20 mg NBPP ionophore exhibits a good Nernstian slope of 19.5 ± 0.2 mV decade⁻¹ and high selectivity of Pd (II) ion.

Effect of internal solution, response time and pH

The working of membrane electrode in relation to variation of reference solutions was investigated. It was found that, the variation of the concentration of the internal solution (10^{-1} to 10^{-4} mol⁻¹ of KCl solution) causes significant effect on corresponding potential response. However a solution of 10^{-3} mol⁻¹ KCl mixed with 10^{-3} mol l⁻¹ [pdCl₄]⁻⁴ would be used as a suitable internal solution, it had a good slope 19.5 ± 0.2 mV decade⁻¹. The detection limit, taken at the point of intersection of the extrapolated linear segment of the calibration curve, was 1.6×10^{-6} mol l⁻¹. The static response time of the membrane electrode thus obtained was <10 s. The sensing behavior of the electrode remained unchanged when the potential recorded from low to high concentrations or vice versa. The life time of the present electrode was at least 3 months. During this time, the detection limit of the electrode remained almost constant and the slope of the response decrease from 16.5 ± 0.2 to 16.1 ± 0.15 mV decade⁻¹. After this time the electrochemical behavior of the electrode gradually deteriorates. The effect of pH on the response of the electrode was studied over the pH range from 1 to 11 at different concentrations (10^{-2} to 10^{-5} mol⁻¹) of Pd (II) solution. The pH of solutions was adjusted with either HCl or NaOH solutions. Potential remains constant at pH range from 4 to 8 (Figure 12). The increase of potential below pH~ 4 may be ascribed to interference by H⁺ ion and the decrease of potential above pH= 8 may be due to formation of some hydroxyl complex of the pd(II) ions in solution from hydrolysis of palladium chloride. The performance of the electrode was assessed in partially non-aqueous media using ethanol-water mixture; it is observed that the electrode functions well in presence of up to 10% (v/v) non-aqueous (alcoholic) content. Higher alcoholic content disturbs the functioning of system (Figure 12).

Electrode selectivity

The influence of interfering ions on the response behavior of ion-selective membrane electrode is usually described in terms of selectivity coefficient $\log K_{Potpalladium B}$. The potentiometric selectivity coefficients $\log K_{Potpalladium B}$ of palladium electrode were evaluated by (SSM) and (MSM)(27,30,31). The resulting values of the selectivity coefficients are summarized in Table 3. It is evident from the selectivity coefficients data, that the sensor exhibits a high performance for Pd

(II) ion compared with alkali, alkaline-earth, transition and heavy metal ions. Comparison of the main analytical features of some of the previously described pd(II) ion-selective [18-22] electrodes) with the proposed Pd (II) electrode revealed that, the present electrode exhibited a better selectivity, especially in the presence of Hg (II) and Fe (III). This participation of these functional groups in the binding with pd(II) ions. Elemental analysis of NBPP and its Pd (II) complex was examined and showed that, the formation of NBBP-pd(II) complex for a membrane segment may form with the complex stoichiometry $n = 1$. Membrane potential values emf for the examined metal salt solutions of Ce (III), Sm (III), Fe (III) and Nd (III) were determined by subtracting the cell potential for a membrane without ionophore from that of the sandwich membrane. The determined formation constants ($\log \beta_{ILn}$) for the examined different complexes were recorded in Table 3. A careful analysis of the data in, reveals that pd(II) has significant cation-binding characteristics. A comparison between the potentiometric behaviors of the proposed electrode with the previously reported ISEs for Pd (II).

Determination of cations in some pharmaceutical samples.

Samples containing 50 ml of distilled water and stirred for 3 h in thermostat adjusted to $25 \pm 1^\circ\text{C}$ and allowed to stand to 2 that the same temperature before potential measurement. The palladium selective electrode and reference electrode were immersed in the precipitate solution. The concentration of soluble pd(II) ions was measured and Solubility product was calculated for cerium oxalate was 2.2×10^{-26} while reference was 3.2×10^{-26} and for cerium phosphate was 2.3×10^{-23} while reference was 1×10^{-23} with small deviation of reference (Table 3).

Determination of palladium in some water and radioactive waste samples

As discussed before palladium cation can be determined in water and radioactive waste samples

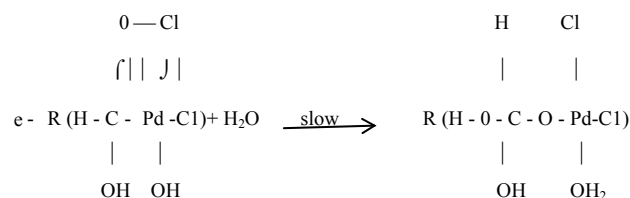
Reaction mechanism

The formation of $[\text{PdCl}_4]^{2-}$ species are suggested to be bounded to the resin. This concept is supported by the considerable stability of the formed palladium tetrachloro complex ($\text{PdClO}_4=15$). The complex formation of palladium tetrachloro complexes explains the fast loading of palladium on the resin phase as a brown zone which may be formed as a tetrachloro complex. It, also, explains the difficulty of elution which is attributed to the stability of $[\text{PdCl}_4]_2$ complex. Therefore, the separation of the complexed palladium from the solid phase can be carried out via reduction using the weak complexing agent; formic acid [1]. To explain the reduction steps of palladium chloride by formic acid, the reduction using ethylene was consulted [2] in comparison to the following reduction reaction case. In this respect the following steps are suggested [1]. Sepaon Mechanism: The formation of a complex for a metal ion M^+ with the following steps is also suggested;

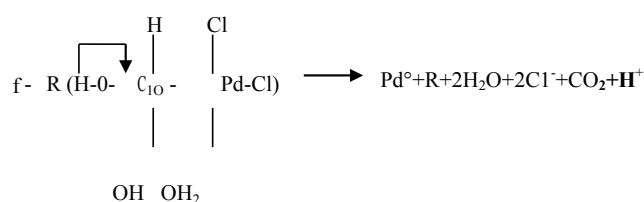
The following steps are also suggested

- $\text{HCOOH} + \text{R}[\text{PdCl}_4]^{2-} \xrightarrow{K_1} \text{R}[\text{PdCl}_3(\text{HOOH})] + \text{Cl}^-$
- $\text{R}[\text{PdCl}_3(\text{HOOH})] + \text{H}_2\text{O} \xrightarrow{K_2} \text{R}[\text{Pd}(\text{HCOOH})(\text{OH})_2\text{Cl}_2] + \text{Cl}^-$
- $\text{R}[\text{Pd}(\text{HCOOH})(\text{OH})_2\text{Cl}_2] \xrightarrow{\sim K_3} \text{R}[\text{Pd}(\text{HCOOH})(\text{OH})\text{Cl}_2] + \text{H}^+$
- Step (c) indicates that the rate of the reduction process is reversibly proportional to the H^+ concentration which explains its increase by decreasing the formic acid concentration.

The complexed species formed in step (c) are suggested to go via possible rearrangements through an addition of an OH group [14]; as in (d):



Step (d) is suggested to be the rate determining step where the addition of the hydroxide ion to the coordinated formic acid occurs. This step is followed by a proposed fast reaction as in (e):



Conclusion

New ion selective sensitive electrode of Pd (II) as multisensor based on IRA-410 via low Cost oxidation reduction process as membrane disc sensor from. It can be used as sensor in HCl solution as $(\text{PdCl}_4)^{2-}$ in, Pdo sorbed on solid phase IRA-410 and eluted as $\text{Pd}(\text{NO}_3)_2$ in nitrate medium. This electrode has a wide linear dynamic range d low detection limit of $1.6 \times 10^{-6} \text{ mol l}^{-1}$. It has a fast response time ($< 1 \text{ s}$) and good selectivity with respect to different metal ions in pH range from (1.0-9.0). It can be used for about 10 months with complex with Pd (II) was calculated by using segmented sandwich membrane method. The proposed electrode has been used successfully as an indicator electrode in potentiometric determination in aqueous nitrate and /or chloride media.

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