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## Development of Electrochemical Sensor for Determination of Lead (II) Ion

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### Abstract

A PVC membrane based on 1, 5-diphenylthiocarbazon (dithizone) as an ionophore. The lead (II) coated graphite electrode exhibits a near Nernstian response of  $29.11 \pm 1$  mV/decade over a relatively wide concentration range ( $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mole  $\text{dm}^{-3}$ ) with a detection limit of  $6.7 \times 10^{-7}$  mole  $\text{dm}^{-3}$ . The response time of the electrode is 9 sec. The proposed membrane electrode revealed very good selectivity in the pH range of 2 to 8.2 and can be used for at least 3 months without any measurable deviation in response properties. The proposed electrode was used for the determination of lead ion in groundwater, wastewater manufactory with very good performance against atomic absorption spectroscopy method and also as an indicator electrode for potentiometric titration of lead ions with NaCl solution.

**Keywords:** Coated graphite electrode, Dithizone, Lead, Stability constant, Potentiometry

### 1. Introduction

Lead is a universal and versatile metal, which has been used by mankind for many years. It is the most serious environmental pollutant among the toxic heavy metals all over the world [1-2]. The common sources of its exposure are use of certain products such as paints, cosmetics, environmental emission containing lead, lead acid batteries, lead glasses, optical sensors [3-4]. Lead has no biological benefit to human and wildlife. When lead starts accumulating gradually in human blood, they induce abdominal cramps, reproductive toxicity, learning disability, attention deflect disorder and brain damage [5-7]. Due to environmental and biological toxicity of lead, the detection of lead at low level especially in drinking water has forced particular attention of analytical chemists. Presently, the most common analytical methods used for the determination of lead in different samples are atomic absorption spectroscopy (AAS) [8] and inductively coupled plasma atomic emission spectroscopy (ICPAES) [9]. Although both these techniques show good selectivity and low detection limit to lead ions, both of these methods are expensive and complicated to perform online and inline determination of lead in drinking water. Conversely, electrochemical techniques are cheap, portable, robust, and easy to handle [10-14].

In the recent years many research worker has use ionophore ligand as sensing materials for selective electrodes due to their unique properties. One of the most important characteristics of ISEs is the selectivity towards a specific analyte, which is generally limited by the interaction of ionophore within the membrane with other ions in solution. The use of complexing agents offers the possibility of designing ligands with a wide range of functional groups and, consequently, different abilities to form complexes. Several neutral compounds with oxygen, nitrogen and sulphur donor atoms have been examined as ionophores for lead selective electrodes. Dynamic response of ion-selective electrode (ISE) is generated by the selective complexation of the target ion by the ion carrier that is dispersed in a poly (vinyl chloride) (PVC) matrix. The Lead ion ISEs that are based on polymeric membranes incorporated with dithizone ionophores are well known and very useful tools for clinical, chemical and environmental analysis [26-30].

Dithizone or 1, 5-diphenylthiocarbazon (H2DZ) is an organic chelating reagent was discovered by Helmut Fischer that was initially used for calorimetric determination of trace metal ions [31]. From number of years applications of dithizone become widely used and continue to be expended in many analytical researches. Dithizone shows good capability ions interesting redox chemistry, the electrochemical behavior of dithizone has been studied by Jeanne, E. P. and *et al* [32]. It has the presence of azo and sulfhydryl groups, the oxidation and reduction of dithizone can be characterized.

### Cespondence

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Previous studies shown that dithizone has been exploited in chemically modified electrode as a modifier for determination of metal ions [33-34]. The aim of the present paper is to develop lead ion selective electrode which has greater mechanical stability, good dynamic response time, high selectivity, wider concentration range, good durability and its applicability for the determination of lead ion in groundwater samples. The coated graphite lead ion selective electrode based on 1, 5-diphenylthiocarbazone (dithizone) have been developed to achieve all the above characteristics.

## 2 Experimental

### 2.1 Materials and Methods

All the chemicals used are of analytical grade and used without any further purification. Double distilled water was used for preparing all aqueous solutions. High molecular weight polyvinyl chloride (PVC), dioctyl phthalate (DOP), dibutyl phthalate (DBP), Tetrahydrofuran (THF), dithizone and sodium tetraphenyl borate (NaTPB), and salts of nitrates or chlorides were obtained from Merck.

### 2.2 Electrode preparation

The coated graphite electrodes were prepared according to previously reported method [15-21]. Graphite rods (3 mm diameter and 10 cm long) were prepared from spectroscopic grade graphite. The electrode was rinsed with distilled water and allowed to dry. A mixture of PVC, plasticizer, NaTPB and ionophore: 30 : 61 : 3 : 6 respectively was added to about (total mass 100 mg) 3 ml of THF.

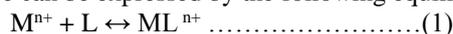
The polished graphite electrode was then coated by repeated dipping (several times, a few minutes between dipping) into the membrane solution and solvent was allowed to evaporate at room temperature. A membrane was formed on the graphite surface, electrode allowed to stabilize overnight. The coated graphite electrode was finally conditioned by soaking in  $1 \times 10^{-2}$  M lead nitrate solution for 24 hrs until it produced stable and reproducible potential. The potentiometric measurements were carried out using following electrochemical cell assembly:

CGE | Test Solution || Hg – Hg<sub>2</sub>Cl<sub>2</sub> | KCl (sat.)

## 3 Results and Discussion

### 3.1 Determination of Stability Constants

The formation constant of the ion-ionophore complex within the membrane phase is an important parameter that indicates the selectivity of the sensor. The Complexation behavior of L (ionophore) with different cations was measured conductometrically, at room temperature in order to establish the stability and sensitivity of the resulting complexes. The 1:1 binding of the cations with the ionophore can be expressed by the following equilibrium



The complex formation,  $K_f$  were evaluated by the molar conductance mole ratio data obtained by using the equations given below:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f(M^{n+})}{f(M^{n+})fL} \dots \dots \dots (2)$$

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{\Lambda_M - \Lambda_{obs.}}{(\Lambda_{obs.} - \Lambda_M)L} \dots \dots \dots (3)$$

$$K_f = CL - \frac{CM(\Lambda_M - \Lambda_{obs.})}{\Lambda_{obs.} - \Lambda_M} \dots \dots \dots (4)$$

Where  $[C_M]$ ,  $[M^{n+}]$  and  $[L]$  represents equilibrium molar concentration of complexes, free cation and free ligand respectively.  $\Lambda_M$  is the molar conductance of the cation before addition of the ligand,  $\Lambda_M$  is the molar conductance of the complex,  $\Lambda_{obs}$  molar conductance of the solution

during titration and  $C_L$  is the analytical concentration of the ionophore. The complex formation constant  $K_f$  and the molar conductance of the complexes. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values ( $\log K_f = 6.86 \pm 0.05$ ) of the resulting 1:1 complexes in Table 1 show the high selectivity of the proposed ionophore to Pb<sup>2+</sup> ions. The results showed that the ionophore dithizone had a good discriminating ability towards Pb<sup>2+</sup> ions over a wide variety of alkali, alkaline earth, transition, and heavy metal ions. Therefore, the Dithizone ionophore can be used as potential ionophore for preparing coated graphite Pb (II) ion selective electrode.

### 3.2 Effect of Membrane Composition

Several membranes of different compositions were prepared. The ratios of PVC, ionophore, NaTPB and plasticizers were varied [22]. Some of the results of this study are summarized in Table 2. It is clear from these results that the composition of the membrane highly affects the response and performance of the electrode. The ratios of all constituents should be optimized for best performance of the sensor.

The membrane composition which is suitable with regard to Nernstian slope was found to contain 30 mg PVC, 6 mg dithizone as an ionophore, 61 mg DBP as plasticizer and 3 mg NaTPB as an ionic additive.

### 3.3 Effect of pH

The effect of pH on the potentiometric response of the coated graphite electrode was tested for solutions of  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M Pb<sup>2+</sup> ions. To achieve the required pH of the test solution, HNO<sub>3</sub> and NaOH were used. As shown in Figure 1, the potential records were constant at pH ranged from 2 to 8.2.

The decrease in the observed potential at pH values higher than 8.2 may be due to the formation of lead hydroxide in solution. On the other hand, its decrease at pH values lower than 2 may be due to the liberation of protons from dithizone in the basic medium which helps on the reaction between lead ions and dithizone [23]. Accordingly, it was decided to perform all measurements at pH of 8.2.

**3.4 Calibration curve and Statistical Data:** The developed coated graphite electrode provides a linear response to the concentrations of lead ion in the range of  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mole dm<sup>-3</sup> with a cationic slope of  $29.11 \pm 1$  mV/decade, which is very close to the Nernstian slope value as shown in Figure 2. The limit of detection was  $6.7 \times 10^{-7}$  M. The prepared electrode could be used for at least 3 months without any measurable divergence and when not in use was stored in  $1.0 \times 10^{-2}$  M lead ion solution.

### 3.5 Response Time

The response time of the electrode was evaluated by potential reading for the electrode dipped into two solutions of lead ions  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-3}$  M, respectively [24]. The actual potential versus time is shown in Figure 3. As can be seen, the electrode reaches its equilibrium response in about 9 sec.

### 3.6 Selectivity

The selectivity coefficient (K) is very important source of information concerning interference on the electrode response. In the present work, fixed primary ion method

(FPM) based on semi-empirical Nikolsky-Eisenman equation was employed to determine logarithmic selectivity coefficient ( $\log K_{A,B}^{Pot}$ ) of proposed Pb (II) coated Graphite Electrode [25].

The emf of a cell comprising an ion selective electrode and a reference electrode is measured for solutions of constant activity of the primary ion,  $a_A$  and varying activity of the interfering ion,  $a_B$ . The emf values obtained are plotted vs. the logarithm of the activity of the interfering ion. The intersection of the extrapolated linear portions of this plot indicates the value of  $a_B$  that is to be used to calculate  $K_{A,B}^{Pot}$  from the following equations:  $K_{A,B}^{Pot} = a_A/a_B^{z_A/z_B}$ . The obtained data as shown in Table 3 indicate that the developed electrode exhibits a good selectivity for  $Pb^{2+}$  among most of the tested metal ions.

### 3.7 Analytical Application

**Potentiometric titration:** The coated graphite lead ion selective electrode was used for monitoring direct titration of 20 ml of  $5.0 \times 10^{-3}$  M  $Pb^{2+}$  with  $1.0 \times 10^{-2}$  M of NaCl. The obtained results are presented in Figure 4. As can be seen, the electrode works well under laboratory conditions.

### 3.8 Determination of $Pb^{2+}$ ion concentration in ground water samples

In order to test the analytical applicability of the proposed sensor system, it has been applied for the determination of lead in ground water samples collected from 10 different sampling stations in and around logistic park of Bhiwandi area of Thane District. No further treatment for the sample was given except filtration of sample by Whatmann filter

paper no.42. The  $Pb^{2+}$  concentration in the ground water samples was determined directly by using the calibration method. The  $Pb^{2+}$  concentration in the ground water samples was also determined by atomic absorption spectroscopy (AAS). The data obtained by using present ion selective electrode are in good agreement with the AAS and it is given in Table 4.

### 3.9 Comparison of the proposed $Pb^{2+}$ sensor with some of the best previously reports

The Nernstian slope, detection limit, concentration range and response time of proposed Pb (II) ion electrode with some of the best previously reports are compared in Table 5.

### 4. Conclusion

According to the obtained results in the present work, the proposed electrode is easy to be prepared and used. Developed electrode exhibited excellent selectivity, sensitivity, high pH range, fast response time and large concentration range with no interference observed from diverse ions. It is successfully applied as an indicator electrode in potentiometric titration of Pb (II) ion solution with NaCl. Its high selectivity permits the direct measurement of Pb (II) ions in different ground water samples. The reliability of proposed electrode has been checked statistically by using AAS.

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**Table 1:** Stability formation constants of different metal ions with Dithizone

Metal ions	Formation Constant (log K <sub>f</sub> )	Metal ions	Formation Constant (log K <sub>f</sub> )
<b>Pb<sup>2+</sup></b>	<b>6.86 ± 0.05</b>	Na <sup>+</sup>	2.55 ± 0.05
Ni <sup>2+</sup>	3.58 ± 0.02	Cr <sup>3+</sup>	3.45 ± 0.03
Fe <sup>3+</sup>	2.69 ± 0.01	K <sup>+</sup>	3.24 ± 0.03
Zn <sup>2+</sup>	3.12 ± 0.02	Ca <sup>2+</sup>	3.33 ± 0.04
Cd <sup>2+</sup>	3.36 ± 0.03	Cu <sup>2+</sup>	4.11 ± 0.08

**Table 2:** Optimization of membrane composition.

No	Composition (w/w, %)				Slope (mV/ decade)
	Ionophore	PVC	Plasticizer	NaTPB	
1	0	30	66 (DOP)	4	N.R
2	2	32	63 (DOP)	3	17.4
3	3	31	64 (DBP)	2	21.8
4	5	30	62 (DBP)	3	26.57
<b>5</b>	<b>6</b>	<b>30</b>	<b>61 (DBP)</b>	<b>3</b>	<b>29.11</b>
6	7	30	60 (DBP)	3	23.64
7	9	29	60 (DBP)	2	14.2
8	6	30	61 (DOP)	3	25.9
9	5	30	61 (DOP)	4	19.27
10	6	31	60 (DOP)	3	24.71

**Table 3:** Selectivity coefficients of various ions

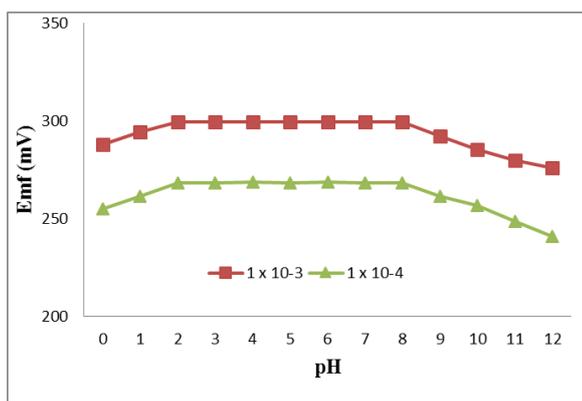
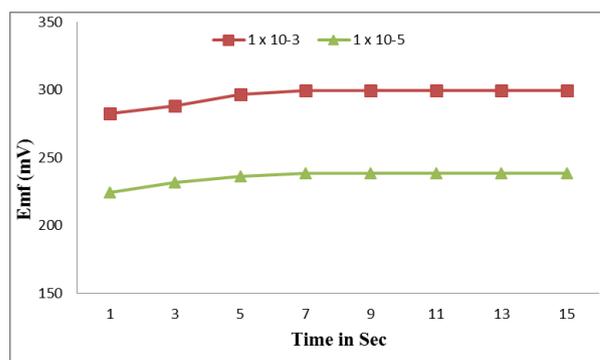
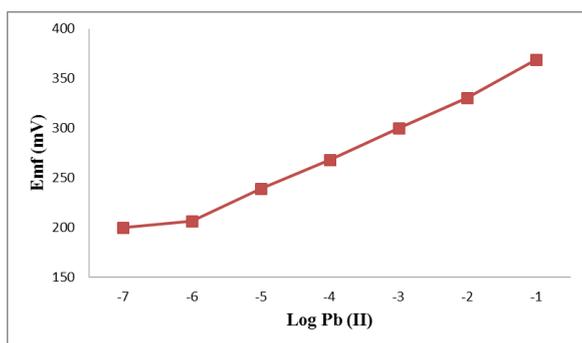
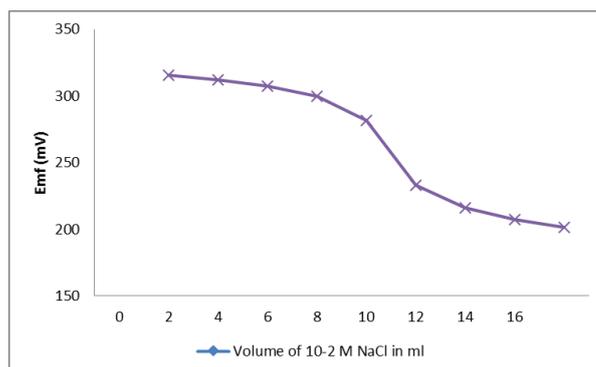
Interfering Ions (10 <sup>-3</sup> )	Selectivity coefficients (K <sub>Pb<sup>2+</sup>, B</sub> )	Interfering Ions (10 <sup>-3</sup> )	Selectivity coefficients (K <sub>Pb<sup>2+</sup>, B</sub> )
Ni <sup>2+</sup>	3.49 x 10 <sup>-3</sup>	Na <sup>+</sup>	4.26 x 10 <sup>-4</sup>
Fe <sup>2+</sup>	Precipitate	K <sup>+</sup>	4.10 x 10 <sup>-4</sup>
Zn <sup>2+</sup>	4.14 x 10 <sup>-4</sup>	Ca <sup>2+</sup>	4.12 x 10 <sup>-3</sup>
Cd <sup>2+</sup>	3.77 x 10 <sup>-4</sup>	Cu <sup>2+</sup>	precipitate

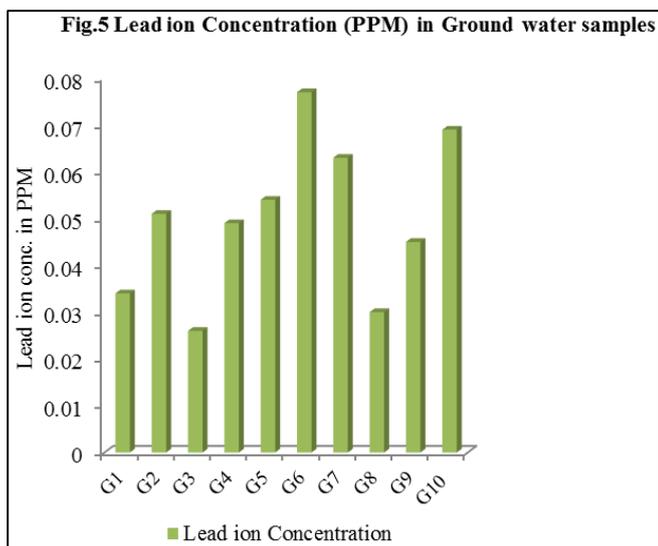
**Table 4:** Determination of  $Pb^{2+}$  in different ground water samples

Sample No.	Sample No.	Sampling Stations	AAS (ppm)	Proposed Sensor (Coated Graphite ion selective Electrode (ppm)
G1	1	Kalher ( borewell)	< 0.1	0.034
G2	2	Kalher pipeline (tubewell)	< 0.1	0.051
G3	3	Purna (borewell)	< 0.1	0.026
G4	4	Khandagale estate (tubewell)	< 0.1	0.049
G5	5	Batco godown (borewell)	< 0.1	0.054
G6	6	Jaipur golden godown (well)	< 0.1	0.077
G7	7	Super logistic godown (well)	< 0.1	0.063
G8	8	Anjurphata (borewell)	< 0.1	0.030
G9	9	Kopar (tubewell)	< 0.1	0.045
G10	10	Manibhadra complex (borewell)	< 0.1	0.069

**Table 5:** Comparison of the proposed  $Pb^{2+}$  ion electrode and the some previously reports.

Ionophore	Slope	Concentration range (M)	Detection limit (M)	Response time (s)	Ref.
Crown Ether Nitrobenzo18-Crown-6	30.5	$1 \times 10^{-2}$ - $1 \times 10^{-5}$	$8.9 \times 10^{-6}$	6	26
1-((3-((2-Hydroxynaphthalen-1-yl) Methyleneamino)-2,2-Dimethylpropyl imino) Methyl) Naphthalen-2-ol	25.79	$0.1$ - $1.0 \times 10^{-6}$	$4.0 \times 10^{-7}$	10	27
1,10-dibenzyl-1,10-diaza-18-crowne-6	29.1, 28.9	$1.0 \times 10^{-1}$ - $5 \times 10^{-6}$	$3 \times 10^{-6}$ , $5 \times 10^{-6}$	10<	28
N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane(I)	30	$1.0 \times 10^{-1}$ - $8.2 \times 10^{-6}$	$8.2 \times 10^{-6}$	10<	29
1,2- bis(salicylidin aminooxy)ethane	26.49	$1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$	$7.6 \times 10^{-7}$	10<	30
This work	29.11	$1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$	$6.7 \times 10^{-7}$	9	---

**Figure 1:** Effect of pH of the test solution ( $1 \times 10^{-3}$  and  $1 \times 10^{-4}$ ) on the response potential of the electrode**Figure 3:** Static response time of the proposed electrode by changing the  $Pb(II)$  concentration from  $1 \times 10^{-5}$  to  $1 \times 10^{-3} M$ **Figure 2:** Calibration curve for  $Pb(II)$  Ion Selective Electrode**Figure 4:** Titration of  $20 \text{ ml } 5 \times 10^{-3} M Pb^{2+}$  ion with  $10^{-2} M NaCl$  by using the proposed lead ion selective electrode as an indicator electrode



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