International Journal of Advanced Educational Research
ISSN: 2455-6157
Impact Factor: RJIF 5.12
www.educationjournal.org
Volume 3; Issue 2; March 2018; Page No. 107-113

Acrylonitrile copolymer based membrane sensor for selective detection of Pb^{2+} ions in aqueous medium

[1] Shyam Lal, [2*] Sunita Hooda, [3] Amit Kumar, [4] Subodh Kumar, [5] Aarushi Singh, [6] Snigdha Singh, [7*] Ramesh Chandra, [8] Vikrant Kumar, [9] Vandana Uberoi, [10] Geetu Gambhir, [11] Drashya
[1- 4, 8- 11] Department of Chemistry, Acharya Narendra Dev College, University of Delhi, Delhi, India
[5-7] Department of Chemistry, University of Delhi, Delhi, India
[*]Corresponding author

Abstract

A lead (II) ion selective sensor has been facilely fabricated from Styrene - Acrylonitrile (SA) copolymer as a neutral carrier, sodium tetra phenyl borate (NaTPB) as an anionic excluder and tri butyl phosphate (TBP) as a plasticizing solvent mediator. Fabricated sensor, over a concentration range of $1x10^{-5}$-$1x10^{-1}$ mol L^{-1} revealed a best Nernstian response for Pb (II) ions with a slope of 39.60 mV/decade. Potentiometric selectivity coefficient values as determined by Fix Interference Method (FIM) and Match Potential Method (MPM) indicated that the electrode has good selectivity of Pb^{2+} ion over other heavy metal ions. The performance of proposed sensor in non aqueous mixtures up to 20 % (v/v) ethanol was satisfactory. The effect of surfactant and detergent on the working of Pb^{2+} ion selective electrode was also studied. The electrode can be used for the determination of lead ion pollution in waste water sample.

Keywords: styrene, acrylonitrile, copolymer, ion selective electrode, potentiometric sensor

Introduction

A large number of heavy metals and their compounds are found in the industrial waste and responsible for the environmental pollution. The major sources of lead wastes are lead battery effluent, paint and leather industry. World Health Organization (WHO) [1] has recognized an action level of 10 ppb (µg/L) for lead in drinking water. Therefore, reliable and convenient determination of lead (II) ion is significantly important and emergent in monitoring human health effects and the environment. Lead is a strong poison and tends to accumulate in the bone structure when ingested in the level exceeding the natural elimination rate of about 300g Pb/day[2]. Prolonged lead exposure disturbs the biosynthesis of hemoglobin and its accumulation in the body and It may results as the severe and permanent brain damage, [3] metabolic disturbance, convulsion and death[4]. As per Indian standard institution (ISI) specifications, the tolerance limit for the discharge of lead in drinking water is 0.05 mg/L and in land surface is 0.1 mg/L [5]. These effects comply with the requirement for efficient monitoring of toxic metal by rapid and simple analytical methods.

One main reason for the interest in conducting polymers (CPs) is that small perturbations at their surface or in their bulk can generate strong changes in their electro activity, which can be probed by potentiometric, additionally CPs are biocompatible, and therefore are convenient for binding biomolecules [6]. Conventional methods for precise determination of heavy metal ions are atomic absorption spectrometer [7], inductively coupled Plasma - Mass Spectroscopy (ICP-MS) [8], ICP-AES [9] and Mass Spectroscopy [10] etc. These are elaborate, time consuming methods and involve sophisticated equipment that might not be available in most analytical laboratories [11]. To monitor lead metal, membrane sensors are well-known analytical tools used for the selective and direct measurement of a wide variety of different ions in complex biological and environmental samples. Potentiometric sensors is a direct method that does not require a pretreatment of samples and has noticeable advantages including simple instrumentation, fast response, wide dynamic range, high analyte selectivity, minimal use of toxic solvents, superior detection limit, inexpensive and convenient method for the analysis of heavy metal ions in solutions over most of the other methods. Huang *et al* [12] designed and synthesized a new Pb(II) ionophore on the polymer chains by a direct chemical oxidative polymerization of m-phenylene diamine and 2-hydroxy-5-sulfonic aniline for fabricating robust long-lived Pb(II)-sensor, signifying the potential suitability of such novel materials for inexpensive sensitive detection of Pb(II) ions. Chang *et al* [13] synthesized cysteine-functionalized graphene oxide (SGO) which can be used to effectively adsorb and remove Pb^{2+} ions in water samples. Other groups like Swager *et al.* [14] have studied that conducting organic polymers show great promise as sensory materials for detection of various analytes. Likewise, Ginnetto *et al.* [15] have studied the new ion selective electrode of Acrylonitrile - Butadiene polymeric membrane with tetra phenyl borate as an ion exchange functionalized with allylic moieties[16]. Various coworkers have synthesized polymeric based sensors for the detection of heavy metal ions [17] [18]. Overviews on electrochemical sensors have also been reported by various coworkers [19] [20]. The evaluation of heavy metal ions in ground water as well as in various other samples have already been reported [21] [22] [23] [24]. Lead (II) ion selective potentiometric sensors based on nanoparticle have also been studied recently [25]. Among various modification approaches, conducting polymers (CPs) have received huge interest due to their superior electrical conductivities, good adhesion properties and easy preparation. In addition, CPs also demonstrated anti-fouling capability, which is an important practical advantage over conventional electrode materials. However, a large number of ion selective electrodes (ISE) were developed using new polymer membranes, although the development of a good sensor for lead ion has long been a subject of concern to analytical chemists and lot of efforts has been made in this direction in the last decades.

In this work, a new lead (II) ion selective membrane sensor based on Styrene - Acrylonitrile (SA) copolymer has been synthesized. The proposed membrane sensor shows promising selectivity towards Pb^{2+} ion over wide range of heavy metal ions. The membrane sensor exhibits a super Nernstian response over a wide concentration range of $1x10^{-5}$-$1x10^{-1}$ mol L^{-1} of Pb^{2+} ion. It is expected that these selective membrane sensor will succeed in on-site Pb^{2+} ion measurements with excellent performance, reliable and convenient measurement, low cost and environmental effectiveness.

Experimental

Reagent and apparatus

All the chemicals and reagents used were of analytical grade and used without further purification. Styrene, Acrylonitrile, Dioctyl phthalate (DOP), Dibutyl phthalate (DBP), Dibutyl butyl phthalate (DBBP), Tributyl phosphate (TBP), Sodium tetra phenyl borate (NaTPB), Chloro Naphthalene (CN), and Lead nitrate were received from Merck. Standard solutions of metal salts were prepared in double distilled water. Working solutions of different concentrations were prepared by stock solution. pH of the solutions was adjusted with 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} NaOH solution.

Synthesis of Styrene-Acrylonitrile Copolymer (SA)

Styrene and Acrylonitrile monomers were purified by vacuum distillation under nitrogen atmosphere at 60°C. Benzoyl peroxide was purified by dissolving in chloroform and re-precipitating in methanol. Styrene-acrylonitrile (SA) copolymers were synthesized by free radical bulk polymerization using benzoyl peroxide as an initiator at 60°C. The copolymers were precipitated by addition of methanol in reaction mixture. Styrene-acrylonitrile copolymers were purified by successive re-dissolution and re-precipitation in tetrahydrofuran and methanol respectively (Scheme I).

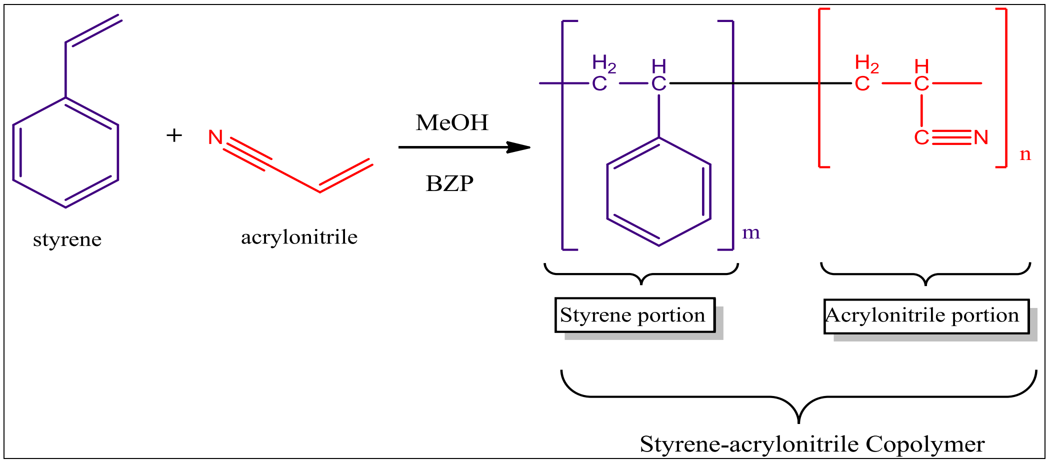

Fig 1: Schematic representation for synthesis of Styrene-Acrylonitrile copolymer.

Preparation of SA Copolymer Membrane

A saturated solution of styrene - acrylonitrile copolymer with and without additive was prepared in tetrahydrofuran (THF) as a solvent. When the solution got viscous it was poured in a cyclic ring resting on a smooth glass plate. The solution was allowed to evaporate for overnight at room temperature. A stable, uniform, transparent, flexible, and homogeneous membrane of about 1 mm thickness was obtained. Membranes of different composition were prepared and investigated. A number of membranes containing varying amount of neutral carrier, anion excluder and plasticizer were prepared.

Equilibration of Membrane

The ion selectivity is determined by the ion exchange equilibrium at the interface between membrane and the aqueous sample. For equilibration, remove the membrane and glued it to one end of a hollow tube and dip in 0.1 mol L^{-1} lead nitrate solution for 48-72 hours. The interaction between SA copolymeric membrane and Pb^{2+} ion is shown in scheme II. The potentials obtained after this equilibrium period were quite stable and reproducible.

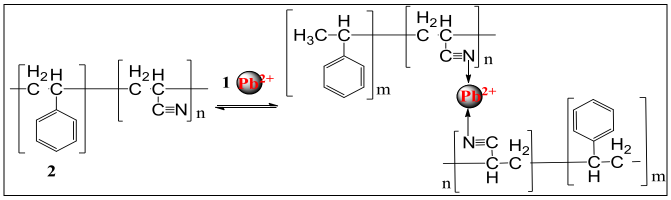

Fig 2: Proposed complexation of Styrene-Acrylonitrile copolymer with Pb^{2+}ion.

Potential Measurement

The potential of co-polymeric membrane was measured by electrochemical cell. All the membrane electrode potential measurements were performed at constant temperature (25 ± 0.5^{0}C) using the following cell assembly set up:

Internal reference electrode (SCE)/ 0.1 mol L^{-1} $Pb(NO_3)_2$ internal solution / membrane// Test solution / External reference electrode (SCE).

Saturated calomel electrode (SCE) was used as a reference electrode and the cell potentials were measured by varying the concentration of test solutions in the range $1x10^{-7}$-$1x10^{-1}$ mol L^{-1} by gradual dilution. The response time of membrane sensor was recorded by measuring the potentials at different time period. All the measurements were reported after 5 minutes.

Results and discussion

Styrene - acrylonitrile (SA) copolymers of different composition were prepared by free radical bulk polymerization. Following studies were carried out on SA copolymer membrane sensors.

Effect of internal solution

The internal solution may be affecting the sensor response when the membrane internal diffusion potential is appreciable. Thus, the effect of the internal solution on the functioning of the membrane sensor was studied by measuring the potential at varying activity of internal solution, viz. 1.0 x 10^{-1}, 5.0 x 10^{-2} and 1.0 x 10^{-2} mol L^{-1} Pb^{2+} ion. It was found that, the best result in terms of slope and working concentration range were obtained with internal solution of activity 1.0 x 10^{-1} mol L^{-1}. Thus, the activity of the internal solution was kept 1.0 x 10^{-1} mol L^{-1} in all studies.

Working concentration range and slope

The potential of the membrane SA1, SA 2 and SA 3 were investigated as a function of Pb^{2+}ion activity in the range of 1.0 x 10^{-7}-1.0 x 10^{-1} mol L^{-1} and the result obtained are shown in Fig. 1. In order to achieve permselectivity, it is essential that no significance of counter ion should enter the membrane phase. Sodium tetra phenyl borate (NaTPB) was added to all the prepared membrane to reduce the interference from anions, optimize sensing selectivity and to reduce bulk membrane impedance[26] . It can be seen from Fig. 1, that SA 2 sensor having the membrane without plasticizer shows linear response over a working concentration of 1.0 x 10^{-5}-1.0 x 10^{-1} mol L^{-1} with a slope of 32.80 mV/decade of activity (Table 1). The slope of the membrane is near Nernstian and the working concentration range is narrow. The improvement in the performance was attempted by the addition of appropriate amount of plasticizer to the membranes. It is well documented that the addition of the plasticizer not only improve the workability of the membrane but also contribute significant towards the improvement of detection limit, stability and shelf life of the sensor [27]. It is achieved that the zero-current ion fluxes from the membrane ingredients in to the solution through judiciously optimize membrane ingredients and inner electrolyte composition. Thus, five plasticizers namely DOP, DBP, TBP, CN and DBBS were added in order to improve the performance of the sensors. The results obtained are shown in Fig. 2 and all performance characteristics of the sensors are compiled in Table 2. The addition of five different plasticizers in SA-2 membranes (sensor no. 1-8), improve the working concentration range, response time and the slope (Fig. 2 and Table 2). However, the best performance membrane ratio (NaTPB:SA2:TBP::1:100:06) i.e. sensor 7, showed a working concentration range of $1x10^{-5}$-$1x10^{-1}$ mol L^{-1} with a super Nernstian slope of 39.60 mV/ decade of lead ion concentration and a response time of about 05s. Repeated monitoring of potentials on the same portion of the sample gave a standard deviation of ± 0.4 mV. The standard deviation of the slope was 0.5-1.20 mV, which shows good reproducibility. The membrane electrode can thus be used to estimate lead ion in above mentioned range of concentrations.

Response time

The response time of a sensor is evaluated by measuring the average time required to achieve a stable potential with in ± 0.1mV of the final steady state potential for $1x10^{-4}$ mol L^{-1} solution, when lead ion concentration increased tenfold from $1x10^{-5}$ to $1x10^{-4}$ mol L^{-1}. The membrane without any plasticizer exhibited the response time of 60s. The addition of plasticizer improved the response time of membrane. In this work, response time of about 5 seconds was obtained for the proposed sensor when contacting various lead ion solutions from $1x10^{-4}$-$1x10^{-1}$ mol L^{-1} and nearly 15s at lower concentration.

Life time

The average life time for most of the reported sensor is in the range of 6-12 weeks. After this period, the slope and potential of the sensor will decreased. In the present studies, the sensor was used extensively for 4 hours per day. The proposed sensor can be used for 10 weeks. During this period, membrane did not show any significant change in working concentration range and the slope. After this period a drift in potential and slope was observed.

Detection limit

The detection limit of sensor is evaluated by extrapolating the linear portion of the calibration curve. In this work, the detection limit of the proposed sensor was 6.1 $x10^{-5}$ mol L^{-1} which was calculated by extrapolating the two segments of calibrating curve (Fig. 3).

Effect of pH

In order to determine the useful pH range over which the electrode can be used without any pH interference, the potential of the electrode was determined over a pH range of 1.0-13.0. In the present studies, effect of pH variations over the membrane sensor was tested at fixed concentrations ($1x10^{-4}$ mol L^{-1}) and ($1x10^{-5}$ mol L^{-1}). The potential determined at different pH values are shown in Fig. 4. It has been seen from the figure that potential is constant in pH range of 2.0-7.0, as in this pH range the potential does not change with pH. Therefore membrane sensor works well in acidic medium.

Effect of Solvent

The performance of membrane sensor was further tested in partially non-aqueous media using ethanol-water, acetone-water and acetonitrile-water mixtures. The membrane sensor exhibits the same response in partially non-aqueous mixtures having up to 20 % (v/v) non-aqueous content. Thus, the sensor can be used in partially non-aqueous media containing up to 20% ethanol, acetonitrile and acetone. The slope and working concentration range reduce when the non-aqueous media exceeds this concentration limit.

Potentiometric Selectivity

The most important characteristic of any ion sensitive sensor is its response for the primary ion over others ions present in solution. This is measured in the term of potentiometric selectivity coefficient ($K^{pot}Pb^{2+}$) which was evaluated using both Match Potential method (MPM) and Fixed Interference Method (FIM) [28] [29]. In MPM, selectivity coefficient ($K^{pot}Pb^{2+}$) was determined by the following expression: $K^{pot}Pb^{2+} = a' - a / {}^{a}B$

In this experiment, values of a' and a, were taken as $1x10^{-4}$ and $5x10^{-5}$ mol L^{-1} respectively. The value of ${}^{a}B$ was determined by addition of interfering ion to maintain the same potential. FIM is the most widely used method as per IUPAC recommendation for the determination of selectivity coefficients for various cations and anions. In FIM, selectivity coefficient was determined from potential measurement on solution containing a fixed amount of foreign ion ${}^{a}B$ ($1x10^{-4}$ mol L^{-1}) and varying concentration of lead ion, ${}^{a}A$. The potential values obtained are plotted versus concentration of the primary ion. The intersection of the extrapolation of linear portions of this curve will indicate the value of ${}^{a}A$, which is to be used to calculate selectivity coefficient ($K^{pot}Pb^{2+}$) from the equation:

$$K^{pot}Pb^{2+} = \frac{{}^{a}A}{{}^{a}B^{Z}B \,/\, {}^{Z}A}$$

Where both ${}^{Z}A$ and ${}^{Z}B$ have the same signs, positive or negative. A smaller value of selectivity coefficient shows the better response of primary ion over the foreign ion. If the value of selectivity coefficient is 1.0, it indicates the same response to both primary and foreign ion. If the value of selectivity co-efficient is greater than 1, it shows insufficient response of primary ion over the interfering ion. The selectivity co-efficient values in Table 3 indicate that the electrode is more selective to lead ion over other ions. However, Na^{+}, Cd^{2+} and Cu^{2+} cations exhibit slightly higher interference at higher concentration, but at low concentrations these cations do not cause any interference. The values of selectivity coefficients have been calculated for monovalent, bivalent and trivalent ions. The values of selectivity coefficients were found to be more for monovalent ions than bivalent and trivalent ions.

Effect of Surfactant and Detergent

The effect of surfactant and detergent on the measurements of lead ion concentration has also been investigated. It was noticed that potential remains unchanged in the presence of appreciable amount of surfactant (sodium lauryl sulphate) but there occurs appreciable change in potential in the presence of small amount of detergent which shows the effect of detergent and surfactant on the working of Pb^{2+} ion selective electrode.

Analytical Applications

The analytical use of this sensor was investigated using it as an indicator electrode in the potentiometric titrations for the determination of lead ion in various water samples. The potentiometric titration was performed for the titration of 10^{-3} mol L^{-1} lead nitrate solution with 10^{-3} mol L^{-1} EDTA solution using proposed Pb^{2+} ion selective electrode. The inflexion point in titration curve in Fig. 5 corresponds to the stoichiometric ratio of EDTA required to remove lead ions. Table 4 shows the results obtained by direct potentiometry of synthetic samples containing various ions. It was found that results obtained from proposed lead sensor are in good agreement with composition of synthetic samples as depicted in Table 5 which shows the comparison of sensors parameters of proposed Pb^{2+} ion selective sensor with other existing electrodes reported by other researchers [30] [31] [32] [33]. The proposed sensor exhibits better performance for the determination of lead ions as compare to other already existing electrode. SA 2 copolymer based membrane sensor has been successfully used for the detection of Pb^{2+} ion concentration in ground, rain and running water collected from different part of India as shown in Table 6. The present data shows that the amount of lead ion determined in water by proposed sensor is in close agreement with that determined by atomic absorption spectroscopy [34] (AAS).

Conclusions

The proposed ion selective electrode based on SA 2 copolymer has appreciable selectivity for Pb^{2+} ion in the presence of various other metals ions. As development of easy and rapid renewable sensors for the detection of different species is one of the most important tools of analytical chemistry, a simple SA 2 co-polymeric membrane sensor for the determination of Pb^{2+} ion in various water samples has been recommended here. The sensitivity, working concentration range, selectivity, response time, potential stability and life time depend on the amount and nature of the membrane's components. It can be seen from our investigation that response time of membrane were improved by addition of plasticizers. The calibration of resulting Pb^{2+} ion sensor has confirmed the good response in the concentration range of $1x10^{-5}$-$1x10^{-1}$ mol L^{-1}. It is noticed that potential remains unchanged in the presence of appreciable amount of surfactant but it changes significantly in the presence of small amount of detergent. It was used as an indicator electrode in the potentiometric titration of Pb^{2+} ion with EDTA. On exploration we have proposed Pb^{2+} ion sensor as simple, rapid and low cost detection of heavy metal ion in environmental, biological and real samples.

Acknowledgment

Authors are thankful to UGC (University Grant Commission), New Delhi, India, for providing financial assistance to carry out this work. We are thankful to Dr. Savithri Singh, Principal, Acharya Narendra Dev College for providing research facility in college.

Table 1: Variation of Characteristics of Membrane Sensor with Composition of Styrene-Acrylonitrile Copolymers

S. No.	Sensors	Acrylonitrile In Feed (%) in Copolymer	Working concentration range (M)	Slope (mV/decade)	Response time (s)	Life time (days)
1	E (SA1)	30	$5x10^{-5}$ - $1x10^{-1}$	29.8	45	60
2	E(SA2)	50	$1x10^{-5}$ - $1x10^{-1}$	32.8	30	70
3	E (SA 3)	70	$5x10^{-5}$ - $1x10^{-1}$	27.4	50	50

Table 2: Composition and Response Characteristics of Lead (II) Selective Sensor

S. No.	Percentage(w/w) of component in membrane							Working Conc. Range (M)	Slope(mV/decade)	Response time(s)
	NaTPB	DOP	TBP	DBP	CN	DBBP	SA 2			
1	1	40	-	-	-	-	100	$1x10^{-5}$ - $1x10^{-1}$	13.7	25
2	1	-	40	-	-	-	100	$5x10^{-6}$ - $1x10^{-1}$	15.2	10
3	1	-	-	40	-	-	100	$1x10^{-5}$ - $1x10^{-1}$	6.5	15
4	1	-	-	-	40	-	100	$5x10^{-5}$ - $1x10^{-1}$	18.3	30
5	1	-	-	-	-	40	100	$1x10^{-5}$ - $1x10^{-1}$	8.2	20
6	1	6	-	-	-	-	100	$1x10^{-6}$ - $1x10^{-2}$	36.8	15
7	1	-	6	-	-	-	100	$1x10^{-5}$ - $1x10^{-1}$	39.6	05
8	1	-	-	6	-	-	100	$1x10^{-5}$ - $1x10^{-1}$	29.0	05

Table 3: Selectivity Coefficient Values for Pb (II) Selective Electrode as Calculated by Fixed Interference Method and Match Potential Method

S. No.	Interfering Ion	Selectivity co-efficient Values (KPb, M^{2+}) (MPM)	Selectivity co-efficient Values (KPb, M^{2+}) (FIM)
1	K^+	0. 200	0. 250
2	Na^+	0.300	0.320
3	Sr^{2+}	0.022	0.020
4	Ni^{2+}	0.025	0.026
5	Cu^{2+}	0.026	0.028
6	Mn^{2+}	0.044	0.049
7	Ba^{2+}	0.045	0.042
8	Al^{3+}	0.003	0.005
9	Fe^{3+}	0.0035	0.0032
10	Co^{3+}	0.005	0.006
11	Hg^{2+}	0.0003	0.0004

Table 4: Potentiometric Results Obtained From Synthetic Samples

S. No.	Composition of Synthetic Samples	Pb^{2+} ion observed by proposed sensor (μg/ml)	% Recovery
1	0.001 M $Pb(NO_3)_2$ + 0.01 M $Cu(NO_3)_2$ + 0.001 M $Co(NO_3)_2$	304	92.0
2	0.001 M $PbCl_2$ + 0.01 M $Cu(NO_3)_2$ + 0.001 M $Co(NO_3)_2$	306	92.4
3	0.01 M $Pb(NO_3)_2$ + 0.01 M $HgCl_2$ + 0.1 M $LaCl_3$	312	94.2

Table 5: Comparison of Proposed Sensor with Existing Sensors

Sensor no.	Electro active phase	Slope	Working concentration range (mol L-1)	References
1	*N,N'*- bis(salicylidene)-2,6-Pyridine diamine	29.4	$1x10^{-6}$ - $1x10^{-1}$	25
2	Bis(acetyl acetone)-*p*-phenylene diamine-lead(II) $[Pb(NO_3)_2]H_2O$ complex ionophore	30.0 ± 0.2	$1x10^{-5}$ - $1x10^{-1}$	26
3	*N,N'*-bis(5-methyl salicylidene)-*p*-diphenyl enemethane Diamine	29.4	$5x10^{-6}$ - $1x10^{-1}$	27
4	*N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diaza cyclo octadecane (I)	30.0± 0.1	$8.2x10^{-6}$ - $1x10^{-1}$	28
5	4'-vinylbenzo-15-crown-5	59	$1x10^{-6}$ -$1x10^{-3}$	29
6	N,N'-dimethyl cyano diaza- 18-crown-6	29	$1x10^{-7}$ - $1x10^{-2}$	30
7	dibenzodiaza-15-crown-4	29	$5x10^{-6}$ - $1x10^{-2}$	31
8	p-(4-n-butyl phenyl azo) calix[4]arene	29.0± 0.1	$9.2x10^{-6}$ - $1x10^{-1}$	32
9	Styrene-Acrylonitrile copolymer(Proposed sensor)	39.60 ± 0.1	$1x10^{-5}$ - $1x10^{-1}$	This work

Table 6: Quantification of Pb^{2+} ion in Real Water Samples by AAS and Proposed Sensor

S. No.	Water sample	Observed by AAS sensor (mg/L)	Observed by Proposed Sensors (mg/L)
1	Water sample-I (Ganga canal, Khatoli)	0.017 ± 0.03	0.018± 0.02
2	Water sample-II (Rain water Okhla Industrial Area)	0.055 ± 0.03	0.057± 0.01
3	Water sample-III (Hindan River, Noida)	0.063 ± 0.02	0.061± 0.01

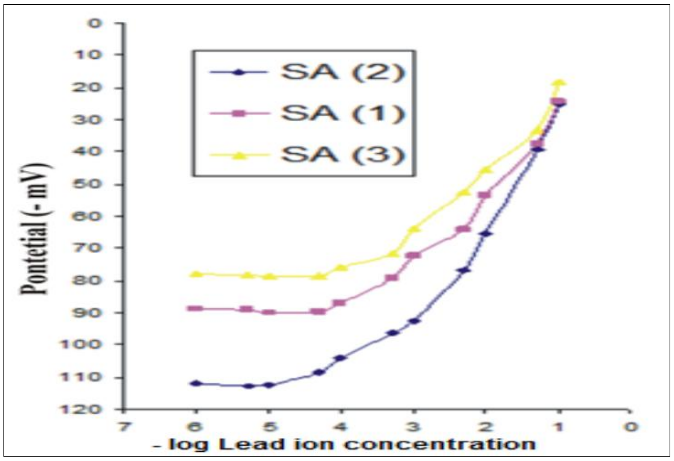

Fig 1: Variation of Potential of Different Copolymer Membranes Over Wide Range of Concentration.

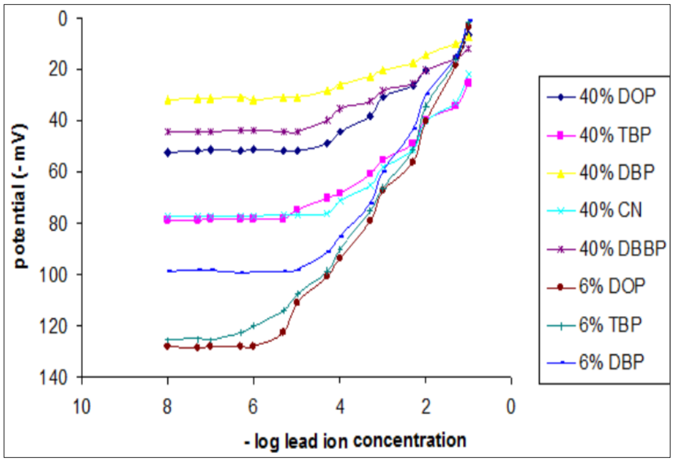

Fig 2: The Effect of Plasticizers on the Working of Proposed Electrode.

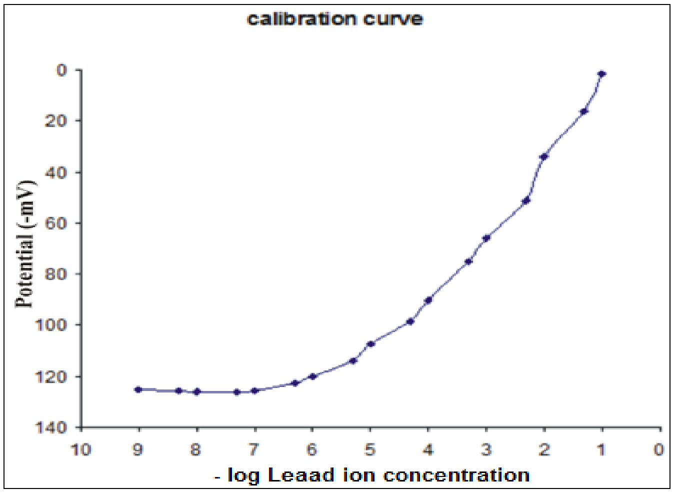

Fig 3: Calibration curve indicating the variation of potential with -log Lead ion concentration.

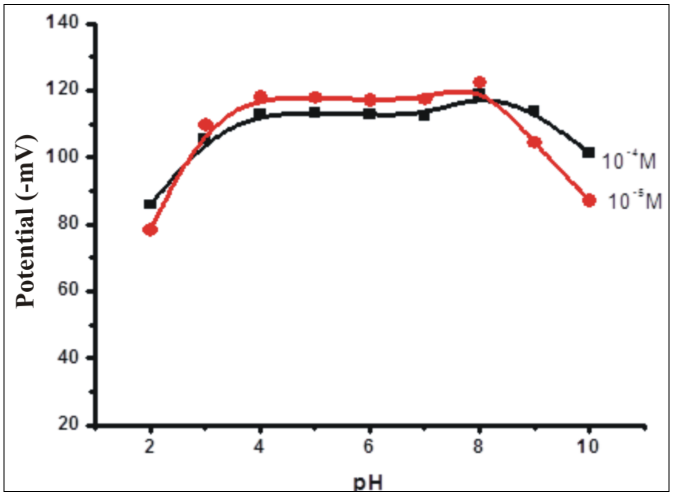

Fig 4: Variation of Potential with pH of Solution.

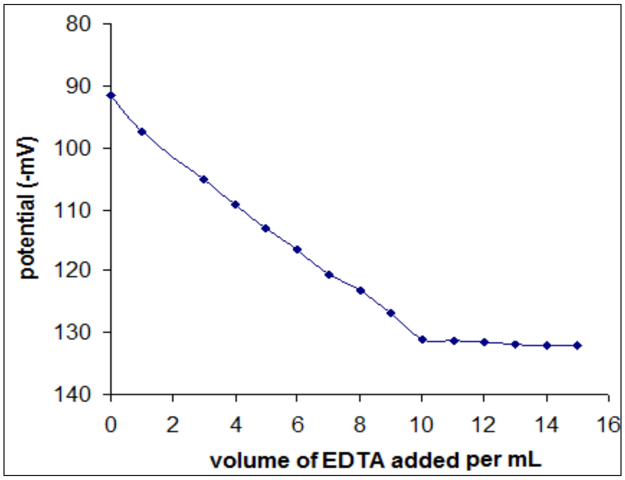

Fig 5: Potentiometric Titration of Lead Nitrate Solution with EDTA Solution Using Proposed Pb (II) Ion Selective Electrode.

References

1. Pittet D, Allegranzi B, Boyce J, Experts WHO. The World Health Organization guidelines on hand hygiene in health care and their consensus recommendations, Infection Control & Hospital Epidemiology. 2009; (30):611-622.
2. Kausar A. Pb (II) Selective Sensor of Poly (vinyl chloride-vinyl acetate)/Polyaniline/Carbon Black, International Journal of Instrumentation Science, 2017; (6):8-11.
3. Gupta V, Jain A, Kumar P. PVC-based membranes of N, N′-dibenzyl-1, 4, 10, 13-tetraoxa-7, 16-diazacyclooctadecane as Pb (II)-selective sensor, Sensors and Actuators B: Chemical. 2006; (120):259-265.
4. Bhat VS, Ijeri VS, Srivastava AK, Coated wire lead (II) selective potentiometric sensor based on 4-tert-butylcalix [6] arene, Sensors and Actuators B: Chemical. 2004; (99):98-105.
5. Adam V, Zehnalek J, Petrlova J, Potesil D, Sures B, Trnkova L, *et al*., Phytochelatin modified electrode surface as a sensitive heavy-metal ion biosensor, Sensors. 2005; (5):70-84.
6. Li Z, Chen J, Liu M, Yang Y, Supramolecular solvent-based microextraction of copper and lead in water samples prior to reacting with synthesized Schiff base by

flame atomic absorption spectrometry determination, Analytical Methods. 2014; (6):2294-2298.

7. Su S, Chen B, He M, Hu B, Graphene oxide–silica composite coating hollow fiber solid phase microextraction online coupled with inductively coupled plasma mass spectrometry for the determination of trace heavy metals in environmental water samples, Talanta. 2014; (123):1-9.
8. Beltrán B, Avivar J, Mola M, Ferrer L, Cerdà V, Leal L O. Automated method for simultaneous lead and strontium isotopic analysis applied to rainwater samples and airborne particulate filters (PM10), Environmental science & technology. 2013; (47):9850-9857.
9. Dal Borgo S, Jovanovski V, Hocevar SB, Antimony film electrode for stripping voltammetric measurement of Hg (II) in the presence of Cu (II), Electrochimica Acta. 2013; (88):713-717.
10. Dong X, Chen J, Ma Y, Wang J, Chan-Park M B, Liu X, *et al*. Superhydrophobic and superoleophilic hybrid foam of graphene and carbon nanotube for selective removal of oils or organic solvents from the surface of water, Chemical communications. 2012; (48):10660-10662.
11. Seenivasan R, Chang WJ, Gunasekaran S, Highly sensitive detection and removal of lead ions in water using cysteine-functionalized graphene oxide/polypyrrole nanocomposite film electrode, ACS applied materials & interfaces. 2015; (7):15935-15943.
12. Sugiyasu K, Swager TM, Conducting-polymer-based chemical sensors: transduction mechanisms, Bulletin of the Chemical Society of Japan. 2007; (80):2074-2083.
13. Giannetto M, Bello A, Gennari M, Marchiò L, Mori G, New membrane electrodes based on a functionalized tetraphenylborate covalently bound to the polymeric backbone, Sensors and Actuators B: Chemical. 2008; (133):235-240.
14. Zhu M, Jiang Z, Jing W. Fabrication of polypyrrole–glucose oxidase biosensor based on multilayered interdigitated ultramicroelectrode array with containing trenches, Sensors and Actuators B: Chemical. 2005; (110):382-389.
15. Jin P, Yamaguchi A, Oi F A, Matsuo S, Tan J, Misawa H. Glucose sensing based on interdigitated array microelectrode, Analytical sciences. 2001; (17):841-846.
16. Gupta VK, Goyal RN, Sharma RA, Novel PVC membrane based alizarin sensor and its application; determination of vanadium, zirconium and molybdenum, Int J Electrochem Sci. 2009; (4):56-172.
17. Sak-Bosnar M, Grabaric Z, Grabaric BS, Surfactant sensors in biotechnology Part 1-electrochemical sensors, Food Technology and Biotechnology. (2004; (42):197-206.
18. Stetter JR, Penrose WR, Yao S, Sensors, chemical sensors, electrochemical sensors, and ECS, Journal of The Electrochemical Society. 2003; (150):11-16.
19. Herdan J, Feeney R, Kounaves SP, Flannery AF, Storment CW, Kovacs GT, *et al*. Field evaluation of an electrochemical probe for in situ screening of heavy metals in groundwater, Environmental science & technology. 1998; (32):131-136.
20. Nolan MA, Kounaves SP. Failure analysis of microfabricated iridium ultramicroelectrodes in chloride media, Sensors and Actuators B: Chemical. 1998; (50):117-124.
21. Mittal SK, Sharma HK, Kumar AS, Samarium (III) selective membrane sensor based on tin (IV) boratophosphate, Sensors. 2004; (4):125-135.
22. Gupta K, D'Arc MJ, Cadmium Ion-Selective Electrode Based on Cyanocopolymer, Electroanalysis. 2000; (2):1408-1413.
23. Liu Y-Q, Zhang M, Yin B-C, Ye B-C, Attomolar ultrasensitive microRNA detection by DNA-scaffolded silver-nanocluster probe based on isothermal amplification, Analytical chemistry. 2012; (84):5165-5169.
24. Shamsipur M, Shirmardi Dezaki A, Akhond M, Sharghi H, Khalife R, Synthesis, characterisation and application of two new lariat crown ethers in construction of PVC membrane, coated wire and coated graphite electrodes: application to flow injection potentiometry, International Journal of Environmental and Analytical Chemistry. 2011; (91):33-48.
25. Rounaghi G, Kakhki RMZ, Sadeghian H. A new cerium (III) ion selective electrode based on 2, 9-dihydroxy-1, 10-diphenoxy-4, 7-dithia decane, a novel synthetic ligand, Electrochimica Acta. 201; (56):9756-9761.
26. Vlascici D, Fagadar-Cosma E, Popa I, Chiriac V, Gil-Agusti M, A novel sensor for monitoring of iron (III) ions based on porphyrins, Sensors. 2012; (12):8193-8203.
27. Birinci A, Eren H, Coldur F, Coskun E, Andac M. Rapid determination of trace level copper in tea infusion samples by solid contact ion selective electrode, journal of food and drug analysis. 2016; (24):485-492.
28. Kumar P, Mittal SKNN. N′′′-tris (2-pyridyloxymethyl) ethane as ionophore in potentiometric sensor for Pb (II) ions, Journal of Chemical Sciences. 2014; (126):33-40.
29. Q Memon S, Memon N, Mallah A, Soomro RY, Khuhawar M, Schiff Bases as Chelating Reagents for Metal Ions Analysis, Current Analytical Chemistry. 2014(10):393-417.
30. Mani GK, Rayappan JBB. Novel and facile synthesis of randomly interconnected ZnO nanoplatelets using spray pyrolysis and their room temperature sensing characteristics, Sensors and Actuators B: Chemical. 2014; (98):125-133.
31. Gupta VK, Singh AK, Kumawat LK, Thiazole Schiff base turn-on fluorescent chemosensor for Al3+ ion, Sensors and Actuators B: Chemical. 2014; (19):98-108.
32. Zheng J, You SL. Construction of Axial Chirality by Rhodium-Catalyzed Asymmetric Dehydrogenative Heck Coupling of Biaryl Compounds with Alkenes, Angewandte Chemie. 2014; (126):13460-13463.
33. Kong D, Yan F, Han Z, Xu J, Guo X, Chen L, Cobalt (ii) ions detection using carbon dots as an sensitive and selective fluorescent probe, RSC Advances. 2016; (6):67481-67487.
34. Yu JS, Liu YL, Tang J, Wang X, Zhou J. Highly Efficient On Water Catalyst-Free Nucleophilic Addition Reactions Using Difluoroenoxysilanes: Dramatic Fluorine Effects, Angewandte Chemie International Edition. 2014; (53):9512-9516.