Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1138327

57 (2016) 23893–23902
October

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of graphene Th(IV) phosphate composite cation exchanger: analytical application as lead ion-selective membrane electrode

Tauseef Ahmad Rangreez, Inamuddin*

Faculty of Engineering and Technology, Department of Applied Chemistry, Aligarh Muslim University, Aligarh 202002, India, Tel. +91 571 2700920, ext. 3008, Tel. +91 9557414508; email: inamuddin@rediffmail.com *(Inamuddin)*

Received 19 February 2015; Accepted 28 December 2015

ABSTRACT

A Pb^{2+} ion-selective membrane electrode (ISME) based on graphene Th(IV) phosphate composite cation-exchange material was fabricated using solution casting method. The effect of membrane composition on the proton conductivity was investigated using varying amounts of electroactive material. The membrane with 250 mg of electroactive material and 10 μL of plasticizer exhibited highest proton conductivity. The optimized membrane composition was used for the fabrication of ISME which exhibited a typical Nernstian response towards Pb^{2+} ions in the concentration range 1.0×10^{-1} to 1.0×10^{-7} M with a sub-Nernstian slope of 27.65 mV per decade change in Pb^{2+} ion concentration. The response time of this electrode for Pb^{2+} ions was found to be 10 s and the electrode can be used for 120 d without any considerable divergence in response potential and can be used in the pH range from 3.0 to 7.0. It was found selective for Pb^{2+} ions in the presence of various monovalent and multivalent interfering ions. It was also employed as an indicator electrode in the potentiometric titration of Pb^{2+} ions using ethylenediamine tetraacetic acid, disodium salt as titrant.

Keywords: Composite cation exchanger; Potentiometric determination of Pb^{2+} ions; Graphene Th(IV) phosphate; Membrane electrode; Selectivity

---

1. Introduction

Lead ion has attracted a lot of attention due to its adverse and wide spread effects on the environment. It poses a serious threat to the plant, animal and human health due to its non-biodegradable and toxic nature [1–8]. Owing to its persistent and harmful effects, lead has been placed on the priority list of environmental pollutants by various environmental protection agencies [9–12]. An advisory panel (2012) to the Centre for Disease Control recommended the lowering of the current blood lead level of concern in children (10 μg/dL); as the harmful effects may occur even at lower levels [13]. According to the National Institute for Occupational Safety recommendations, workers must not be exposed to lead levels greater than 100 μg/m^3 for up to 10 h. The Indian Standard drinking water specification (Second Revision), recommends the tolerance limit of lead in drinking water as 0.01 mg/L [14]. It is widely dispersed throughout the environment due to both natural and anthropogenic activities. It is used in storage batteries, paints, solders, water pipes and gasoline [15–17]. Lead exposure is related to several health problems in humans. It

---

*Corresponding author.

severely affects brain, kidneys, reproductive and central nervous system [18–20]. As a result, it has become more important to monitor and determine the quantities of lead in environment by developing methods that are not only sensitive but also selective in nature. Several analytical techniques have been used for the determination of lead. These methods include atomic absorption spectroscopy [21,22], electro thermal atomic absorption spectroscopy, atomic emission spectroscopy and inductively coupled plasma [23,24]. However, all these methods are very costly, time-consuming and require sophisticated equipment and well-skilled manpower [25,26]. Owing to these shortcomings, there has been a continuous need for development of other methods for easy and on spot determination of heavy metals. The electrochemical methods have been used to overcome these limitations. The ion-selective membrane electrodes (ISME) have several attractive features as simple operation, high sensitivity and selectivity, low cost, portability and fast response for determination of heavy metal ions [27–33].

The ion-selective electrodes consisting mainly of a perm-selective ion-conducting material are primarily membrane-based devices/sensors. The membrane responds more selectively to a particular species; present on one side of this membrane while the other side has the same ion at varying concentrations, giving rise to the membrane potential. The potential of membrane is obtained from the electromotive force value of the complete electrochemical cell, consisting of ion-selective electrode and the external reference electrode [34]. Membranes with higher selectivity bind the analyte ion, leaving interfering ions behind. Thus, different materials are used to impart ion-recognition properties to the membrane electrodes and hence higher selectivity.

Composite materials are the latest development for making electrochemical sensors for determination of heavy metals [35,36]. In this study, a Pb^{2+} ion-selective membrane electrode (ISME) graphene Th(IV) phosphate composite cation exchanger is prepared and successfully used for the potentiometric determination of Pb^{2+} ions.

2. Experimental

2.1. Reagents and instruments

The reagents used in the synthesis were thorium nitrate ($Th(NO_3)_4 \cdot 5H_2O$) (99%), Orthophosphoric acid (H_3PO_4) (85%), Nitric acid (HNO_3) (71%) and N-Cetyl-N,N,N-trimethyl ammonium bromide (CTAB) (98%). These reagents were purchased from Central Drug House, India. Graphene was procured from Sigma Aldrich Pvt. Ltd, USA. All reagents and chemicals were of analytical reagent grade. The instruments used during the study were a hot air oven (Biogen, India), magnetic stirrer (LMMS-300, LABMAN, India), potentiostat/galvanostat (302N Autolab, Switzerland) and a digital pH/mV meter (ELICO LI 120, India).

2.2. Preparation of the reagent solutions

A solution of thorium nitrate (0.1 M) was prepared in nitric acid (1 M) while orthophosphoric acid (2 M) was prepared in demineralized water (DMW). A dispersion of graphene was prepared in CTAB (1 mmol). A solution of $Pb(NO_3)_2$ (0.1 M) was prepared by dissolving $Pb(NO_3)_2$ in 100 ml of DMW, while other standard $Pb(NO_3)_2$ solutions (1.0×10^{-1} to 1.0×10^{-10} M) were prepared by stock dilution method.

2.3. Synthesis of composite cation exchanger

Inorganic precipitates of thorium phosphate were obtained by adding various volumes of thorium nitrate (0.1 M) slowly at a flow rate of 0.5 mL to a solution of orthrophosphoric acid (2 M) with continuous stirring using a magnetic stirrer at a temperature of 90 ± 5˚C for 5 h. Further, a dispersion of graphene in CTAB (1 mmol) was added to the above slurry and stirred for 3 h (Table 1). The resultant blue coloured gel was kept overnight at room temperature (25 ± 3˚C) for digestion. The supernatant liquid was decanted and the gel was filtered off and then repeatedly washed with DMW to remove excess of acid. The

Table 1
Conditions of preparation and the ion-exchange capacity of graphene Th(IV) phosphate composite cation-exchange material

	Mixing volume ratios (V/V)				
Sample	0.1 M $Th(NO_3)_4 \cdot 5H_2O$ in 1 M HNO_3	2 M H_3PO_4	Graphene dispersion in 1 mmol CTAB (mg)	Appearance of beads after drying (color)	Na^+ IEC (meq dry g^{-1})
S-1	1	1	50	Light blue	1.48
S-2	1	1.5	100	Light blue	1.56
S-3	1	2	150	Light blue	1.56
S-4	1	2.5	200	Light blue	1.56

product was dried in an oven maintained at 40 ± 1°C. The dried product was ground into small granules and converted to H^+ form by treating with HNO_3 (1 M) for 24 h with occasional removal of supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW, dried at 50 ± 1°C and stored in a desiccator.

The ion-exchange capacity (IEC) of the graphene Th(IV) phosphate composite cation exchanger was determined by standard column process as described elsewhere [37]. Conditions of preparation and the IEC of the composite cation exchanger are given in Table 1.

2.4. Characterization of the cation-exchange composite material

2.4.1. Fourier transform infrared study

The Fourier transform infrared (FTIR) spectra of the inorganic Th(IV) phosphate and composite graphene Th(IV) phosphate in the range 4,000–500 cm^{-1} were recorded using FTIR spectrometer (Spectrum-Two, Perkin-Elmer, USA).

2.4.2. X-ray diffraction study

The X-ray diffraction (XRD) pattern of the graphene Th(IV) phosphate (S2) composite cation exchanger was recorded by an X-ray diffractometer (mniflex-II, Rigaku, Japan) with Cu Kα radiations.

2.4.3. Thermal studies

Simultaneous TGA and DTA studies of the composite cation exchange material (S2) were carried out using thermogravimetric analyser (Pyris 1-HT, Perkin Elmer, USA) at a heating rate of 10°C min^{-1} from 0 to 600°C in N_2 atmosphere.

2.5. Distribution studies

The selectivity of the material was determined by the distribution behaviour of the metal. The distribution coefficient (K_d-values) for various metal ions on graphene Th(IV) phosphate were determined by batch method in various solvent systems as discussed elsewhere [38].

2.6. Preparation of membrane and determination of proton conductivity

The electroactive material i.e. graphene Th(IV) phosphate composite cation exchanger was ground to fine powder and mixed thoroughly with PVC dissolved in 10 mL of tetrahydrofuran (THF) and finally mixed with 10 μL of dioctylphthalate used as a plasticizer [39]. The mixing ratio of the ion exchanger was varied with a fixed content of PVC to obtain a composition for best performance of the electrode. The solutions were carefully poured into a glass-casting ring (diameter 10 mm). These rings were left for slow evaporation of THF to obtain thin films. In this way, four sheets of master membranes with varying thickness were obtained.

Proton conductivities of membranes were determined by an impedance analyzer (FRA32M.X), connected with Autolab 302N modular potentiostat/galvanostat. The membranes were immersed in demineralized water for 1 h before performing the experiment and proton conductivity (σ) was calculated using the following equation:

$$\sigma = \frac{L}{R \times A} \tag{1}$$

where σ is proton conductivity (S cm^{-1}), L is the membrane thickness (cm), A is cross-sectional area of composite membrane (cm^2) and R is the resistance (ohm).

2.7. Fabrication of ion-selective electrode

The membrane sheet (M-2) of 0.30 mm thickness was cut in the shape of a disc and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. The glass tube was filled with $Pb(NO_3)_2$ (0.1 M) solution. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE)	Internal electrolyte Pb^{2+} (0.1M)		Membrane		Sample solution	External reference electrode (SCE)

2.8. Electromotive force measurement

The response potentials of the ISME were measured by varying the concentration of $Pb(NO_3)_2$ in a range between 1.0×10^{-10} and 1.0×10^{-1} M. The membrane electrode was conditioned by soaking in a $Pb(NO_3)_2$ (0.1 M) solution for 5–7 d and for 1 h at least before use. After performing the experiment, membrane electrode was removed from the test solution and kept in a $Pb(NO_3)_2$ solution (0.1 M) to maintain the activity.

Potential measurements of the membrane electrode were plotted against the logarithmic function of selected concentrations of the respective ions. The characteristics of the electrode were studied by evaluating the following parameters: lower detection limit, slope response curve, response time, working pH range, and the effect of interference of various metal ions.

The response time was measured by recording the electromotive force (e.m.f.) of the electrode as a function of time when it was immersed in the solution to be studied. The electrode was first dipped in 1.0×10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH 4.0) of 1.0×10^{-2} M ion concentrations of the same ion (10-fold higher concentration). The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution and afterwards recorded at the intervals of 5 s. The time during which the potential attains a constant value represents the response time of the electrode. The lifetime of the membrane electrode was determined by periodically recalibrating the potentiometric response to Pb^{2+} ions in standard $Pb(NO_3)_2$ solutions.

The influence of pH of the test solution on the potential response of ISME was tested at 1×10^{-2} M concentration of lead over the pH range 1–9. The standard solutions of 1.0×10^{-2} M concentration of lead over the pH range 1–9 were prepared using standard pH solutions. The value of the electrode potential at each pH was recorded and plotted against pH.

The cationic interference on the selectivity of ISME was determined by the mixed solution method [40]. A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1.0×10^{-3} M) and varying concentrations (1.0×10^{-1} to 1.0×10^{-10} M) of the primary ion. The potential measurements were made using the membrane electrode assembly and plotted against the logarithmic of the concentration of ions under study**.**

3. Results and discussion

In this study, graphene Th(IV) phosphate composite cation exchanger was prepared by sol–gel precipitation method. The material (S2) possessed the ion-exchange capacity of 1.56 meq dry g^{-1} determined through the standard column process (Table 1). The FTIR spectra of the inorganic phosphate and composite cation exchanger are shown in Fig. 1. The FTIR spectrum of the composite (S2) exhibits a broad band in the region −3,400 cm^{-1} (O–H stretching) [41], a band around −2,900 cm^{-1} (C–H stretching) [42], a band at −1,620 cm^{-1} (C=C) [43], a sharp peak around −1,050 cm^{-1} (P=O stretching) and the presence of two bands at −630 and −500 cm^{-1} may be attributed to the presence of metal oxygen bond [44,45]. The XRD pattern of this material (S2) shows the absence of sharp peaks indicating the amorphous nature of the composite cation exchanger (Fig. 2). TGA curve (Fig. 3) shows distinct water loss. The TGA curve shows −12% initial weight loss around 150˚C which may be due to removal of external water molecules [46]. Around 300˚C, there is again about 8% loss of mass which may be due to condensation of phosphate to pyrophosphate group, and after that the sample shows almost negligible weight loss indicating the good stability in this region. These structural changes are also confirmed by the prominent DTA peak with a maxima of 150˚C and a very small peak at 250˚C. No additional peaks are observed beyond this temperature indicating absence of any phase change in the sample material in the range studied. Table 2 shows the distribution studies of this composite cation exchanger.

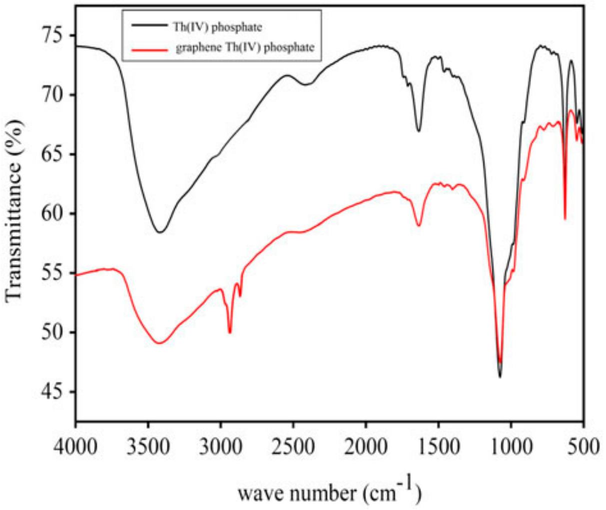

Fig. 1. FTIR spectra of as prepared Th(IV) phosphate and graphene Th(IV) phosphate.

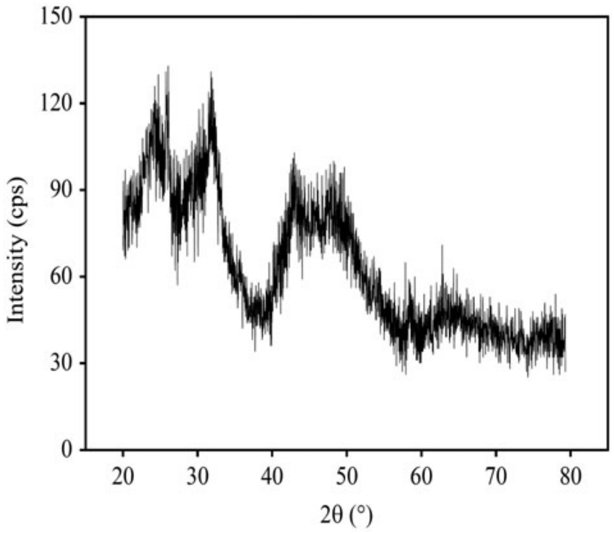

Fig. 2. Powder XRD pattern of graphene Th(IV) phosphate composite cation exchanger.

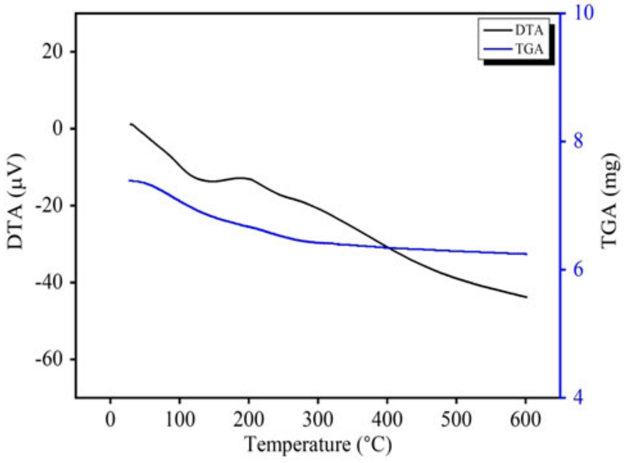

Fig. 3. Simultaneous TGA-DTA curves of graphene Th(IV) phosphate composite cation exchanger.

These studies revealed that this composite cation exchanger is highly selective for lead ions. Thus, the membrane of this cation exchanger can be selectively utilized for the fabrication of ion-selective membrane electrode. The ISME was characterized to optimize the selectivity and working concentration range. The ISME was fabricated by preparing various membranes by solution casting method. The proton conductivity of the membranes was determined by impedance analysis [47–49]. The proton conductivity was found to be 1.42×10^{-4} S cm^{-1} at room temperature for membrane M-2 (Table 3). On the basis of highest proton conductivity, membrane M-2 was selected for further studies. It is well known that the extent of proton conductivity is responsible for the selective exchange of counter ions with the other metal ions and the exchange takes place stiochiometrically.

The linear part of the calibration curve is considered as the measuring range of an ion-selective electrode for the determination of a particular ion. The measurements of an ion using an ion-selective electrode can be performed in this range only. The membrane electrode prepared by using the membrane having highest proton conductivity M-2, exhibited a sub-Nernstian response to the concentration of Pb^{2+} ions in the concentration range of 1.0×10^{-1} to 1.0×10^{-7} M with a slope of 27.65 ($R^2 = 0.99$) mV/decade change in concentration of Pb^{2+} ions as shown in Fig. 4. Thus, the linear part of the calibration curve of membrane electrode was considered the working concentration range for Pb^{2+} ions. The limit of detection for an ion-selective electrode can be determined by extrapolating the linear part of the ion-selective electrode calibration curve. The limit of detection for this electrode calculated by extrapolating the two segments of the calibration curve was found to be 1.0×10^{-7} M as shown in Fig. 4. The electrode response was found reproducible within about 120 d without any deviation in linear range, detection limit and Nernstian slope. After that period of time, the potential response of the

Table 2
K_d values of some metal ions on graphene Th(IV) phosphate column in different solvent systems

	K_d values (mL/g) Solvents									
Metal ions	DMW	10^{-2} M HNO_3	10^{-1} M HNO_3	1 M HNO_3	10^{-2} M $HClO_4$	10^{-1} M $HClO_4$	1 M $HClO_4$	10^{-2} M HCl	10^{-1} M HCl	1 M HCl
Co(II)	135	137	123	115	155	128	117	140	117	104
Ba(II)	110	100	86	71	116	94	81	110	93	79
Pb(II)	560	580	523	470	640	593	548	500	430	380
Hg(II)	380	390	362	284	470	426	377	360	337	246

Table 3
Characterization of ion-exchanger membranes

	Membrane composition				
Membrane	Graphene Th(IV) phosphate (mg)	PVC (mg)	Plasticizer (μL)	Thickness (mm)	Proton conductivity (S cm^{-1})
M-1	200	200	10	0.28	1.30×10^{-4}
M-2	250	200	10	0.30	1.42×10^{-4}
M-3	300	200	10	0.33	1.40×10^{-4}
M-4	350	200	10	0.35	1.40×10^{-4}

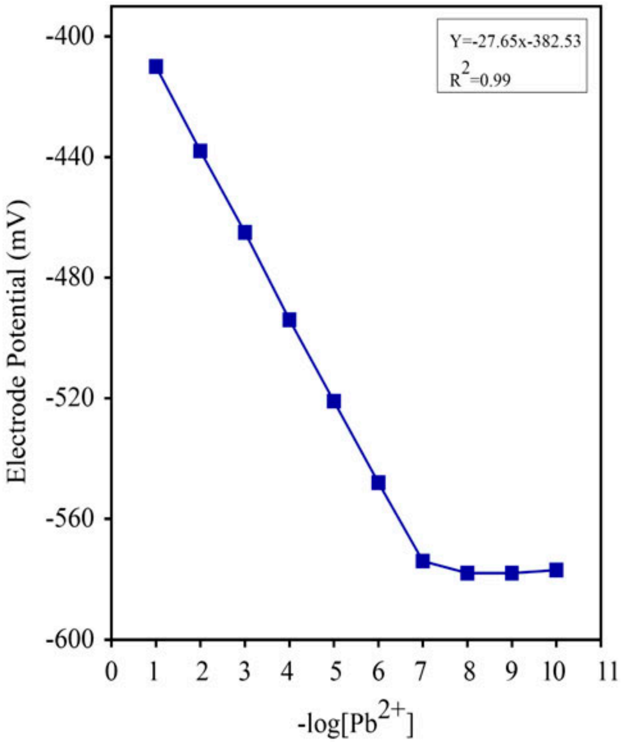

Fig. 4. Calibration curve for Pb^{2+} ion selective membrane electrode.

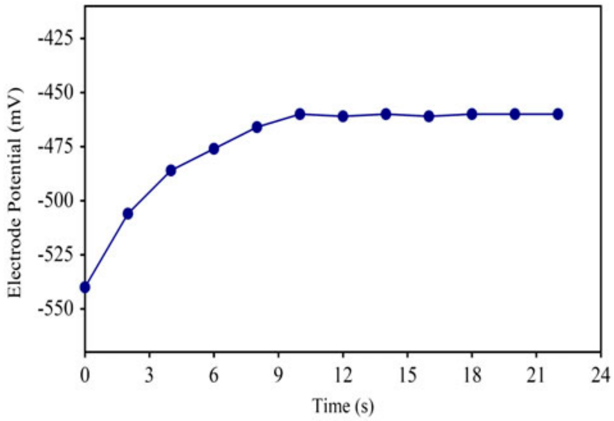

Fig. 5. Response time characteristics of Pb^{2+} ion-selective membrane electrode at different time intervals for 1×10^{-2} M concentration of lead.

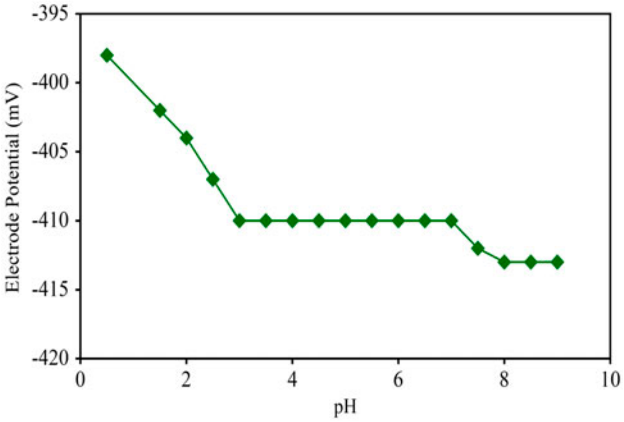

Fig. 6. Effect of pH of the test solution on the potential response of Pb^{2+} ion-selective membrane electrode at 1×10^{-2} M concentration of lead.

electrode gradually deteriorated which may be due to the loss of proton conductivity of membrane and also dehydration as well as the damage of the membrane electroactive material. The dynamic response time of an electrode is considered as the time required to attain steady potential which can be observed after successive addition in a series of solutions each having a 10-fold higher difference. The dynamic potential-time responses of the membrane electrode obtained upon successive addition of 10-fold higher Pb^{2+} ion concentrations from 1.0×10^{-3} to 1.0×10^{-2} M was measured and plotted against time as shown in Fig. 5. It was found that the potential response was steady after 10 s (Fig. 5). Thus, the response time of this electrode is assumed to be 10 s and checked sooner every time before using it for any analytical purpose. The

Table 4
A comparison of previously reported ISMEs with the proposed study

S. no.	Working concentration range (M)	Life time (d)	Response time (s)	pH range	Slope (mV)/decade change in concentration	References
1	1×10^{-5} –1×10^{-1}	90	15	4.0–6.5	43.8	[50]
2	1×10^{-6} –1×10^{-1}	60	<15	3.5–6.5	−29.6	[51]
3	1×10^{-6} –1×10^{-1}	120	20	3.0–6.0	29.3	[52]
4	1×10^{-7} –1×10^{-1}	90	35	4.0–7.0	29.6	[53]
5	1×10^{-6} –1×10^{-1}	60	14	3.0–6.0	28.7	[54]
6	1×10^{-7} –1×10^{-1}	120	10	3.0–7.0	27.65	Proposed assembly

response of this membrane electrode was also significantly affected by pH at the Pb^{2+} ion concentrations of 1.0×10^{-2} M (Fig. 6). Fig. 6 shows that the potential of ISME was independent of pH in the range 3.0–7.0 and thus this was considered as the working pH range of this electrode. However, deviation in response potential after pH 7.0 is considered due to the formation of lead hydroxides and below pH 3.0 is accounted for the competition of H^+ ions with the composite cation-exchanger counter ions. A comparison of response characteristics of this electrode showed that this electrode is comparatively better in response characteristics compared to those already reported in literature [50–54] (Table 4).

The interference of other ions on the selectivity of this ISME was determined at pH 4 by the mixed solution method [39]. The response potentials in the presence of interfering ions were observed and plotted against the logarithms of the molar concentration of Pb^{2+} ions as shown in Fig. 7. It is evident from Fig. 7 that alkali and alkaline metal cations like Na(I), K(I), Ca(II), Mg(II) and Sr(II) would not cause any significant interference in the estimation of Pb^{2+} ions, while divalent and trivalent heavy metal ions like Cu(II), Cd(II), Zn(II), Hg(II), Al(III), Fe(III) and Cr(III) caused a little interference in the estimation of Pb^{2+} over 1.0×10^{-6} M concentration of lead. Thus, this ISME is highly selective for Pb^{2+} ions and there would not be any interference when the interfering ions are present in smaller or comparable amount. The optimized ISME based on graphene Th(IV) phosphate cannot only be used for the determination of Pb^{2+} ions using calibration method, but the analytical utility of this membrane electrode can also be achieved as an indica-

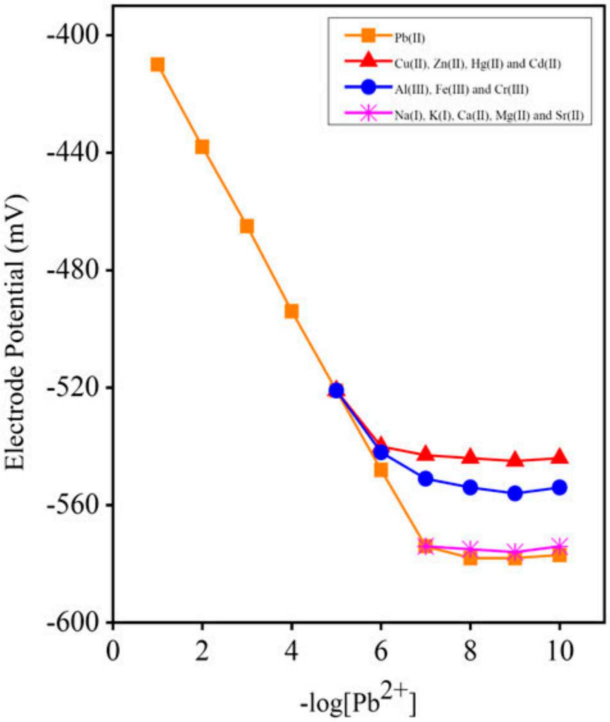

Fig. 7. Response curves of Pb^{2+} ion-selective membrane electrode in presence of interfering metal ions.

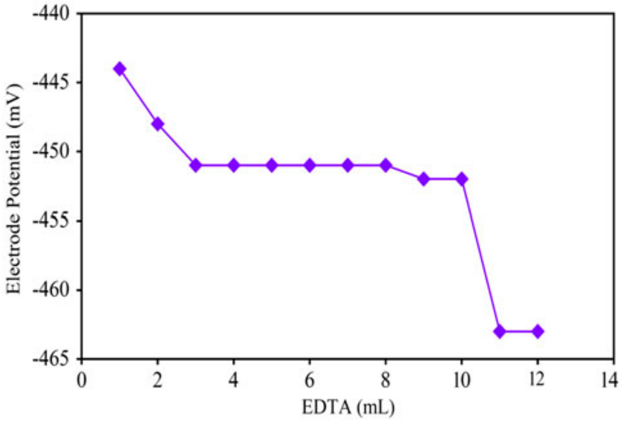

Fig. 8. Potentiometric titration curve of 10 mL of $Pb(NO_3)_2$ solution at 1×10^{-2} M against 1×10^{-2} M EDTA solution.

tor electrode in the potentiometric titration of various concentrations of lead solutions against an EDTA solution as a titrant.

In this study, 10 mL $Pb(NO_3)_2$ solutions at 1.0×10^{-2} M concentrations was titrated against 1.0×10^{-2} M EDTA solution and the electrode potential was measured after each successive addition of 1 mL of EDTA. The necessary adjustment of pH (≈4) was made before adding the titrant. The addition of EDTA causes a decrease in potential as a result of the decrease in free Pb^{2+} ion concentration due to formation of a complex with EDTA (Fig. 8). The amount of Pb^{2+} ions in solutions can be accurately determined from the resulting neat titration curve providing a sharp end point. It is also clear from the figure that the sharp end point at 10 ml of EDTA corresponds to the stoichiometry of Pb^{2+} EDTA complex.

4. Conclusion

In the present study, a Pb^{2+} ion-selective composite cation-exchanger graphene Th(IV) phosphate having an IEC of 1.56 meq dry g^{-1} of exchanger is used to prepare ion-selective membrane electrode. The electrode exhibited a fast response time of 10 s for Pb^{2+} ions with a working concentration range of 1.0×10^{-1} to 1.0×10^{-7} M. The practical utility of the membrane electrode was demonstrated in the titration of Pb^{2+} using ethylenediamine tetraacetic acid as a titrant.

Acknowledgements

The authors are thankful to Department of Applied Chemistry, Z.H. College of Engineering and Technology, A.M.U. (Aligarh) for providing research facilities and University Grants Commission for the financial support [vide F. No. 41-278/2012 (SR) 01/07/2012].

References

[1] B.J. Alloway, D.C. Ayres, Chemical Principles of Environmental Pollution, Blackie Academic and Professional, London, 1993.

[2] S. Klimmek, H.J. Stan, A. Wilke, Comparative analysis of the biosorption of cadmium, lead, nickel, and zinc by algae, Environ. Sci. Technol. 35 (2001) 4283–4288.

[3] D.M. Roundhill, Novel strategies for the removal of toxic metals from soils and waters, J. Chem. Edu. 81 (2004) 275–282.

[4] Q. Zhou, J. Zhang, J. Fu, J. Shi, G. Jiang, Biomonitoring: An appealing tool for assessment of metal pollution in the aquatic ecosystem, Anal. Chim. Acta 606 (2008) 135–150.

[5] L.N. Liang, J.T. Hu, D.Y. Chen, Q.F. Zhou, B. He, G.B. Jiang, Primary investigation of heavy metal contamination status in Molluscs collected from Chinese costal sites, Bull. J. Environ. Contam. Toxicol. 72 (2004) 937–944.

[6] S.D. Wu, H.F. Zhao, The Analytical Methods in the Monitoring of Water and Wastewater, China Environmental Science Press, Beijing, 2006.

[7] P.G.C. Campbell, Cadmium-A priority pollutant, Environ. Chem. 3 (2006) 387–388.

[8] Q. Qu, Q. Gu, Z. Gu, Y. Shen, C. Wang, X. Hu, Efficient removal of heavy metal from aqueous solution by sulfonic acid functionalized nonporous silica microspheres, Colloid. Surf. A Physicochem. Eng. Aspect. 415 (2012) 41–46.

[9] N. Kocak, M. Sahin, S. Kücükkolbasi, Z.O. Erdogan, Synthesis and characterization of novel nano-chitosan schiff base and use of lead (II) sensor, Int. J. Biol. Macromol. 51 (2012) 1159–1166.

[10] J. Richardson, A. Drake, C. Lazo-Miller, J. Hand, T. Morgan, I. Lagadic, Lead detection in environmental water sample using an organoclay film-based attenuated total reflectance sensor, Sensor. Actuator. B Chem. 158 (2011) 271–277.

[11] M.R. Ganjali, N. Motakef-Kazami, F. Faridbod, S. Khoee, P. Norouzi, Determination of Pb^{2+} ions by a modified carbon paste electrode based on multiwalled carbon nanotubes (MWCNTs) and nanosilica, J. Hazard. Mater. 173 (2010) 415–419.

[12] N. Aksuner, Development of a new fluorescent sensor based on a triazolo thiadiazin derivative immobilized in polyvinyl chloride membrane for sensitive detection of lead(II) ions, Sensor. Actuator. B Chem. 157 (2011) 162–168.

[13] Low Level Lead Exposure Harms Children: A Renewed Call for Primary Prevention Report of the Advisory Committee on Childhood Lead Poisoning Prevention of the Centers for Disease Control and Prevention (2012) 1–65.

[14] Drinking Water Specification, IS, second ed., BIS, New Delhi, 2012, p. 10500.

[15] M. Mazloum Ardakani, M. Khayat Kashani, M. Salavati-Niasari, A.A. Ensafi, Lead ion-selective electrode prepared by sol–gel and PVC membrane techniques, Sensor. Actuator. B Chem. 107 (2005) 438–445.

[16] F. Arduini, J.Q. Calvo, A. Amine, G. Palleschi, D. Moscone, Bismuth-modified electrodes for lead detection, Trends Anal. Chem. 29 (2010) 1295–1304.

[17] P. Bühlmann, E. Pretsch, E. Bakker, Carrier-based ion-selective electrodes and bulk optodes. Part 2. Ionophores for potentiometric and optical sensors, Chem. Rev. 98 (1998) 1593–1688.

[18] M.F. Mousavi, M.B. Barzegar, S. Sahari, A PVC-based capric acid membrane potentiometric sensor for lead(II) ions, Sensor. Actuator. B Chem. 73 (2001) 199–204.

[19] L. Guo, S. Hong, X. Lin, Z. Xie, G. Chen, An organically modified sol-gel membrane for detection of lead ion by using 2-hydroxy-1-naphthaldehydene-8 aminoquinoline as fluorescence probe, Sensor. Actuator. B Chem. 130 (2008) 789–794.

[20] X.J. Yuan, R.Y. Wang, C.B. Mao, L. Wu, C.Q. Chu, R. Yao, Z.Y. Gao, B.L. Wu, H.Y. Zhang, New Pb(II)-selective membrane electrode based on a new schiff base complex, Inorg. Chem. Commun. 15 (2012) (2012) 29–32.

[21] P.J. Parsons, W. Slavin, A rapid Zeeman graphite furnace atomic absorption spectrometric method for the determination of lead in blood, Spectrochim. Acta B 48 (1993) 925–939.

[22] J.E. Tahán, V.A. Granadillo, R.A. Romero, Electrothermal atomic absorption spectrometric determination of Al, Cu, Fe, Pb, V and Zn in clinical samples and in certified environmental reference materials, Anal. Chim. Acta 295 (1994) 187–197.

[23] H.W. Liu, S.J. Jiang, S.H. Liu, Determination of cadmium, mercury and lead in seawater by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry, Spectrochim. Acta B 54 (1999) 1367–1375.

[24] R.J. Bowins, R.H. McNutt, Electrothermal isotope dilution inductively coupled plasma mass spectrometry method for the determination of sub ng/ml levels of lead in human plasma, J. Anal. At. Spectrom. 9 (1994) 1233–1236.

[25] M.N. Bui, C.A. Li, K.N. Han, X.H. Pham, G.H. Seong, Electrochemical determination of cadmium and lead on pristine single-walled carbon nanotube electrodes, Anal. Sci. 28 (2012) 699–704.

[26] V.L. Dressler, D. Pozebon, A.J. Curtius, Determination of heavy metals by inductively coupled plasma mass spectrometry after on-line separation and preconcentration, Spectrochim. Acta B (1998) 1527–1539.

[27] S. Anastasova, A. Radu, G. Matzeu, C. Zuliani, U. Mattinen, J. Bobacka, D. Diamond, Disposable solid-contact ion-selective electrodes for environmental monitoring of lead with ppb limit-of-detection, Electrochim. Acta 73 (2012) 93–97.

[28] M. Guziński, G. Lisak, J. Kupis, A. Jasiński, M. Bocheńska, Lead(II)-selective ionophores for ion-selective electrodes: A review, Anal. Chim. Acta 791 (2013) 1–12.

[29] M.R. Huang, X.W. Rao, X.G. Li, Nitrogen-bearing organic compounds as carriers for lead ion-selective electrodes with excellent response, Chin. J. Anal. Chem. 36 (2008) 735–1741.

[30] B. Rezaei, S. Meghdadi, R.F. Zarandi, A fast response cadmium-selective polymeric membrane electrode based on N, N´-(4-methyl-1,2-phenylene)diquinoline 2 carboxamide as a new neutral carrier, J. Hazard. Mater. 153 (2008) 179–186.

[31] K.K. Tiwari, M.C. Chattopadhyaya, Heterogeneous precipitate based Cu(II)-ion selective electrodes and its application in the determination of stability constant of Cu(II) complex with 4-(2-pyridylazo)-resorcinol, Indian J. Chem. 40A (2001) 619–621.

[32] A.P. Gupta, Renuka, studies on araldite based zirconium tungstophoaphate membrane—A lead (II) ion-selective electrode, Indian J. Chem. 36A (1997) 1073–1074.

[33] A.P. Mishra, M. Khare, S.K. Gautam, Precipitate based selective ion sensitive membrane electrodes for dipositive cobalt and copper, J. Electrochem. Soc. India 50 (2001) 119–121.

[34] R.P. Buck, E. Lindner. Recommendations for nomenclature of ionselective electrodes (IUPAC recommendations pure 1994), Appl. Chem. 66 (1994) 2527–2536.

[35] A.A. Khan, Inamuddin, Preparation, physico-chemical characterization, analytical applications and electrical conductivity measurement studies of an ‘organic–inorganic’ composite cation-exchanger: Polyaniline Sn(IV) phosphate, React. Funct. Polym. 66 (2006) 1649–1663.

[36] N.K. Raman, M.T. Anderson, C.J. Brinker, Template-based approaches to the preparation of amorphous, nanoporous silicas, Chem. Mater. 8 (1996) 1682–1701.

[37] T.A. Rangreez, M. Inamuddin, M. Naushad, H. Ali, Synthesis and characterisation of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) Zr(IV) monothiophosphate composite cation exchanger: analytical application in the selective separation of lead metal ions, Int. J. Environ. Anal. Chem. 95 (2015) 556–568.

[38] C.N. Reilley, R.W. Schmid, F.S. Sadek, Chelon approach to analysis (I) survey of theory and application, J. Chem. Edu. 36 (1959) 555–564.

[39] A. Craggs, G.J. Moody, J.D.R. Thomas, PVC matrix membranes ion selective electrodes. Construction and laboratory experiments, J. Chem. Edu. 51 (1974) 541–544.

[40] G.J. Moody, J.R.D. Thomas, Selective Ion Sensitive Electrode, Marrow, Watford, 1971.

[41] S. Kumar, S. Raj, E. Kolanthai, A.K. Sood, S. Sampath, K. Chatterjee, Chemical functionalization of graphene to augment stem cell osteogenesis and inhibit biofilm formation on polymer composites for orthopedic applications, Appl. Mater. Interfaces 7 (2015) 3237–3252.

[42] M. Naebe, J. Wang, A. Amini, H. Khayyam, N. Hameed, L.H. Li, Y. Chen, B. Fox, Mechanical property and structure of covalent functionalised graphene/epoxy nanocomposites, Sci. Rep. 4 (2014) 4375–4381.

[43] P.G. Ren, D.X. Yan, X. Ji, T. Chen, Z.M. Li, Temperature dependence of graphene oxide reduced by hydrazine hydrate, Nanotechnology 22 (2011) 055705–055712.

[44] M. Islam, R. Patel, Polyacrylamide thorium (IV) phosphate as an important lead selective fibrous ion exchanger: Synthesis, characterization and removal study, J. Hazard. Mater. 156 (2008) 509–520.

[45] M. Islam, R. Patel, Removal of lead (II) from aqueous environment by a fibrous ion exchanger: Polycinnamamide thorium (IV) phosphate, J. Hazard. Mater. 172 (2009) 707–715.

[46] C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963, p. 315.

[47] Inamuddin, A. Khan, M. Luqman, Dutta, Kraton based ionic polymer metalcomposite (IPMC) actuator, Sensor. Actuator. A Phys. 216 (2014) 295–300.

[48] Inamuddin, A. Khan, R.K. Jain, M. Naushad, Development of sulfonated poly(vinyl alcohol)/polpyrrole based ionic polymer metal composite (IPMC) actuator and its characterization, Smart Mater. Struct. 24 (2015) 095003 (14 pp).

[49] Inamuddin, A. Khan, R.K. Jain, M. Naushad, Study and preparation of highly water-stable polyacrylonitrile–kraton–graphene composite membrane for bending actuator toward robotic application, J. Intell. Mater. Syst. Struct. 24 (2015), doi: 10.1177/1045389X15596627.

[50] M. Rashid, F. Khan, Lutfullah, R. Wahab, Zirconium (IV) phosphosulphosalicylate-based ion selective membrane electrode for potentiometric determination

of Pb(II) ions, Arabian J. Chem. (2015), doi: j.arabjc.2014.12.013.

[51] L. Chen, J. Zhang, W. Zhao, X. He, Y. Liu, Doublearmed calix[4]arene amide derivatives as ionophores for lead ion-selective electrodes, J. Electroanal. Chem. 589 (2006) 106–111.

[52] R. Bushra, M. Shahadat, M.A. Khan, Inamuddin, R. Adnan, M. Rafatullah, Optimization of polyaniline supported Ti(IV) arsenophosphate composite cation exchanger based ion-selective membrane electrode for the determination of lead, Ind. Eng. Chem. Res. 53 (2014) 19387–19391.

[53] A. Khan, A.M. Asiri, M.A. Rub, N. Azum, A.A.P. Khan, S.B. Khan, M.M. Rahman, I. Khan, Synthesis, characterization of silver nanoparticle embedded polyaniline tungstophosphate-nanocomposite cation exchanger and its application for heavy metal selective membrane, Compos. B Eng. 45 (2013) 1486–1492.

[54] Q.R. Zhang, B.C. Pan, B.J. Pan, W.M. Zhang, K. Jia, Q.X. Zhang, Selective sorption of lead, cadmium and zinc ions by a polymeric cation exchanger containing nano-Zr(HPO_3S)$_2$, Environ. Sci. Technol. 42 (2008) 4140–4145.