Determination of Lead Ion by a Modified Carbon Paste Electrode Based on Multi-Walled Carbon Nanotubes (MWCNTs) and Ligand (N-(4-Hydroxyphenyl) Ethanamide)

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ABSTRACT

The preparation of a new modified carbon paste electrode (CPE) to measure lead ion has been reported in this study. Lead is a highly toxic element which can have a negative impact on the environment. Therefore, measurement of lead in aquatic environments is very important. Although several methods have been developed for determination of lead ion in aquatic environments, there is no a cheap, simple, accurate and rapid method to measure this ion. Aim of this study is to develop a new method to measure the lead based on using multi walls carbon nanotubes (MWCNTs) and Paracetamol as an ionophore for modification of a CPE. The optimum composition of modified CPE was determined as 64% of graphite powder, 20% of paraffin oil, 12% of nanotube and 4% of ionophore. This optimum composition was shown high selectivity, with appropriate Nernestian slope (-29.73 mV/decade), linear range (from $1.0 \times 10{-1}$to $1.0 \times 10{-8}M$), low lead concentration detection limit ($7.5 \times 10{-9}M$) and good response time (equal of 25 sec).The results of this study to introduce a cheap, accurate and simple method for determination of lead ion in aquatic environments.

Introduction

Lead is a toxic heavy metal that is present in a variety of products (e.g. ammunitions, pipes, paints and tin-based welding alloys). Unfortunately a large amount of lead is released into the environment by industries each year. Regardless of the fact that, lead is only slightly hazardous in case of skin contact, but it is highly toxic in case of swallowing. Lead is toxic for every organ system in the human body. Lead is able to inhibit or mimic the actions of calcium which can have a negative effect on the calcium processes. Also, it is able to interact with metabolism of proteins. Some compounds containing lead are soluble in water which can contaminate water resources. Usually, lead exists as an inorganic anion $Pb2+$that has harmful effects on the human and animals health like, renal disease, cardiovascular effects, reproductive toxicity and toxicity for central nervous system[1-2]. Consequently, it is necessary and demanding to develop methods for the determination of lead (II) even in trace amount.

In the past decades, numerous methods have been developed to determine heavy metals, including spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS), electro thermal atomic absorption spectrometry (ETAAS) [3-9].However, the majority of the above techniques require complex devices, training special skills and time consuming operations, which result in high costs.

Electrochemical methods such as potentiometric is one of the most favorable approaches for the determination of heavy metal ions, due to its high sensitivity, ability for portability, low cost and time saving. Also they are able to preconcentrate the analytes on the electrode surface and have ability to analyze element speciation with no or minimum sample change [10-15].

Carbon paste electrodes (CPEs) have gained much attraction as ion selective electrodes of potentiometric mostly due to their benefits over

membrane electrodes such as fixed response, renewability, low Ohmic resistance and no necessity for internal solution [16-19]. Graphite powder usually becomes dispersed in a non-conductive mineral oil, as a binder, to make carbon paste [20].

Newly, CPEs have been chemically modifying to boost the sensitiveness, selectivity, detection limit and other aspects of these electrodes. For example, some matters such as functionalized nanoparticles and appropriate ligands, have been applied within the electrode structure [21-24].

In this area, carbon nanotubes(CNTs), have attractive physicochemical properties that make them favorable for using as electrode modifiers, like ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, ordered structure with high aspect ratio, high surface area and metallic or semi-metallic behavior [25-26].Also, the ability of electron transfer between the electrodes and the electro active species offers great potential for creating electrochemical sensors. These aspects make CNTs unique materials for diverse electrochemical applications [27-29]. The paracetamol, (N-(4-hydroxyphenyl) ethanamide), Fig. 1 has nitrogen and oxygen giving groups that enable it to make complex with the lead cations.
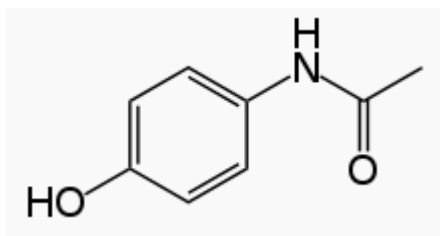

Fig.1: The structure of paracetamol

The main aim of this study is to develop a new method to measure the lead based on using multi walls carbon nanotubes (MWCNTs) and Paracetamol as an ionophore for modification of a CPE.

MATERIALS AND METHODS
1- Apparatus
In this study the potentiometric measurements was performed with a pH/mV meter (ZagShimi, Iran) at 25.0 ± 0.1 °C. The Ag/AgCl electrode (Azar electrode, Iran) was as the reference electrodes. A pH meter (model UK3020) was used for pH measurements. Atomic absorption spectrometer (Shmadzu, AA-760, and Japan) was used to determine metal ions under recommended conditions in the instrument manual.

2- Reagents
The paraffin oil with high purity and the carbon graphite powder with a 1–2 μm particle size were prepared from Fluka, Switzerland. The MWCNTs with purity more than 95% and 20-30nm diameter were purchased from the www.cheap tubes.com.Cationsnitrate salts and chloride salts were bought from Merck and Fluka, respectively. The double distilled water was utilized for preparation of all the aqueous solutions.

3- CPE preparation
Preparation of the used electrode in this study was as follows: At first, the different amounts of the ligand were selected and then each part was mixed by suitable amount of pure graphic powder and MWCNTs. Next, the mixture was blended with tetrahydrofuran (THF) solvent and then, the paraffin oil was added as a binder. The resulted mixture was intermixed well to produce smooth dough.

In the next step, the paste was thrust into a Propylene support. A copper stem was used to establish the electric current. The surface of the electrode was polished by a smooth paper and finally the electrode's tip was submerged in the 0.001 molar lead nitrate solutions for 24 hours. After this time the electrode was prepared to use.

4- Emf measurements
The 100 ml electrochemical glass cell with constant magnet stirring speed was assembled as follows: Ag, AgCl(s), KCl (3M) sample solution CPE. The ion activities were calculated according to the Debye–Huckelprocedure [30].

RESULTS AND DISCUSSION
1- Electrode composition and modification
Table 1 shows the different used CPE compositions and their performances. As the results show, the electrode (No.1) has not demonstrated corrective response in absence of carrier and MWCNTs. In No.3, the electrode has exhibited a Nernestian response as the result of adding ligand to CPE for concentrations from 2.0-5.3. By using both carrier and MWCNTs in the electrode composition, the selectivity and linear range concentration of ion selective electrode from 1.0-8 has risen remarkably in No.4 due to MWCNTs's electrical conductivity, that has improved the dynamic working range and response time.

According to the results of Table 1, the best performance belongs to No 7, which has shown the lowest detection limit (7.5×10^{-9}M) and an excellent Nernestian slope about (-29.43mV/decade). This electrode composition was chosen as the optimum electrode through this study with 4.0 wt. % ligand, 64.0 wt. % graphite powders 20 wt. % Paraffin oil

and 12 wt. % MWCNTs. Also the results show that the modified electrode for other metal cations didn't have a Nernestian slope and a wide linear range of concentration (Fig. 4 & 5). Ghorbani and Ghaemi

reported that their electrode for lead detection has a Nernestian slope equal of 29.2±0.2 mV/decade with linear range from 1.0×10-5 to 1.0×10-1 M) [36] which is not as well as our developed electrode.

**Table.1**: The optimization of the carbon paste ingredients.

Composition (%)				Performances		
No.	GP[a]	PO[b]	MWCNTs[c]	carrier[d]	Slope(mV/dec)	DL(pM)[e]	LR(pM)[f]
1	75	25	-	-	-	-	-
2	70	20	10	-	-17.95	2.1	(1.0-2.1)
3	74	20	-	6	-26.12	5.5	(2.0-5.3)
4	63	20	12	5	-29.10	7.2	(1.0-7.0)
5	63	18	12	7	-28.92	7.9	(1.0-7.7)
6	64	20	12	4	-29.73	8.2	(1.0-8.0)
7	66	20	10	4	-29.0	7.5	(1.0-7.3)
8	62	22	12	4	-28.55	7.0	(1.0-6.8)

[a] Graphite powder, [b] Paraffin oil, [c] Multi wall carbon nano tubes, [d]N-(4-hydroxyphenyl) acetamide, [e] Detection limit, [f] Linear range

*2- pH effect*

For investigating the pH effect on the potential response of the electrode, a fixed concentration of Pb2+ $(1.0\times10-4$mol L−1) with different pH values were used in the potentiometric measurements. The pH of the solution varied from 2 to 10 by addition of 0.01M HNO3 or NaOH solutions.

Fig. 2 shows the potential variation as a function of pH. The composition of the electrode was kept constant during all experiments. As the Fig.2 shows, the electrode response is stable in the pH range of 4.0–7.5that is why the pH of experiments was selected in this range. At higher pH values, there is a drift in the potential of the electrode that could be the result of the formation of some hydroxyl complexes of Pb2+ in the solution. On the other hand, at lower pH values, the potentials increased due to hydrogen ions.
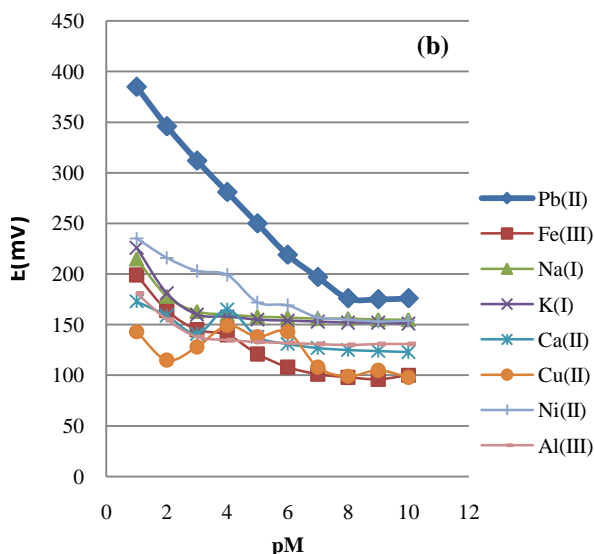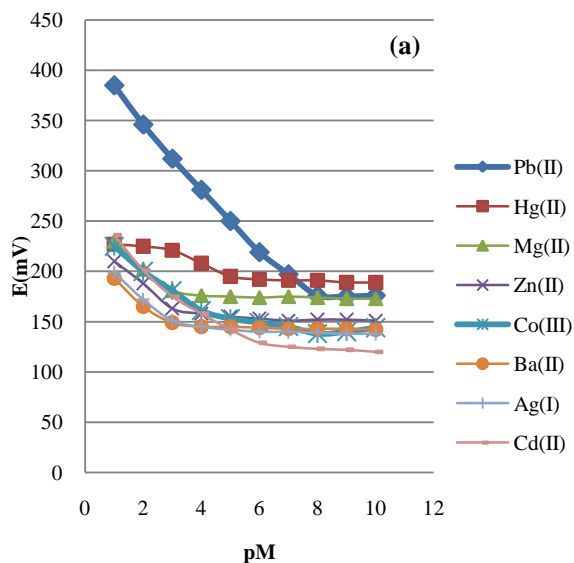

Fig. 2: The potential response of various cations on CPE; (a) for Pb (II), Hg(II), Mg(II), Zn(II) and Co(III); (b) for Fe(III), Na(I), K(I), Ca(II) and Cu(II)
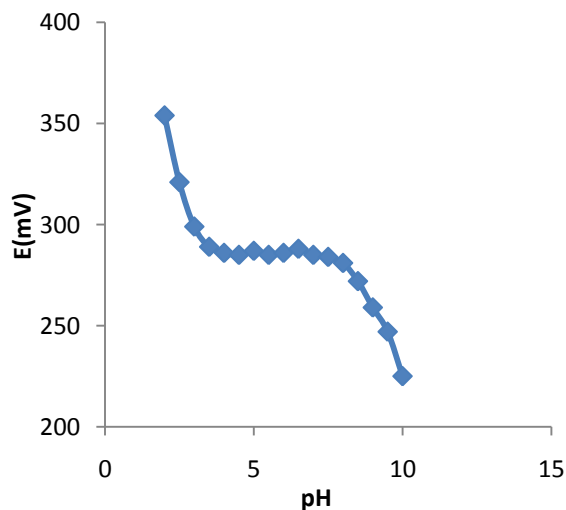
Fig.2: Effect of pH on the potential response 1.0×10^{-4}mol L^{-1} Pb^{2+} solution.

3- Response time

The average response time for an electrode, is defined as the necessary time for achieving the potential of 90% of the final equilibrium value. This time is also an important factor for any analytical application [31]. The obtained potential–time responses for the used electrode in this study have been plotted in Fig. 3.For evaluation response time, the lead ion concentration, in a buffer solution, was changed in the range of 0.1-1.0×10−8 M. Based on the results, potentiometric response time is around 25 sec.
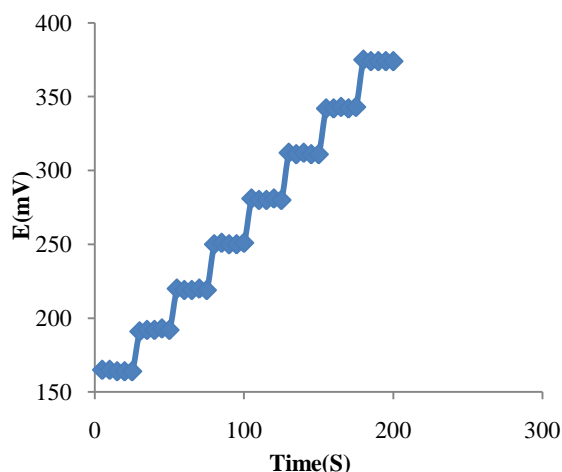
Fig.3: Dynamic response time of the CPE based on MWCNTS and ligand

To evaluate the prepared electrode lifetime, the potentiometric response to Pb2+ ion in buffer solutions has been recalibrated periodically. Since there has been no significant change in the efficiency of the electrode, its lifetime has been about 70 days.

4- Interference studies

The potentiometric selectivity coefficients for each electrode describes the priority of the proposed electrode for an interfering ion, X, with reference to the lead ion, Pb2+. This coefficient can be evaluated by several methods like, separate solution method (SSM), fixed interference method (FIM) and matched potential method (MPM) [32-33]. In this study the fixed interference method was used and selectivity coefficients of the Pb2+ sensor were evaluated graphically with a fixed concentration of the interfering ions (0.1M) and different amounts of the Pb2+ ion (from 1×10-1 to 1×10-8), was calculated by using Nikolsi-Eizenman equation as below:

$$k_{A,B}^{pot} = \frac{a_A}{a_B^{(z_A/z_B)}}$$

In the above equation, aA is activity of the primary ion, aB is constant activity of the interfering ion, z is the charge of ion and k_ (A,B)^pot is the selectivity coefficient. In this study, different ions were applied as interfering ions (see Table 2). Interfering of various ions followed the underlying model. Based on the results shown in Table 2, the studied ions do not interfere in the progress of lead anion determination.

Table.2: The selectivity coefficients of various interfering cations for the electrode no. 8

C^{n+}	$\log k_{Pb,B}^{pot}$	C^{n+}	$\log k_{Pb,B}^{pot}$
Na^+	-5.54	Hg^{+2}	-3.36
K^+	-5.33	Zn^{+2}	-4.18
Cu^{+2}	-4.12	Cd^{+2}	-3.43
Ba^{+2}	-4.96	Co^{+2}	-4.51
Ca^{+2}	-4.78	Al^{+3}	-5.58
Mg^{+2}	-4.83	Ag^{+1}	-4.74
Ni^{+2}	-3.65	Fe^{+3}	-5.65

5- Analytical application

5-1- Titration

Since, the used CPE in this study, could work well under the laboratory conditions, it was used as an indicator electrode in titration of 25.0mL 0.001 M Pb(NO3)2solution with 0.01 M Na2SO4 solution. The resulting titration curve, Fig. 6, shows the CPE is able to monitor the amount of Pb (II) ions in the solutions.
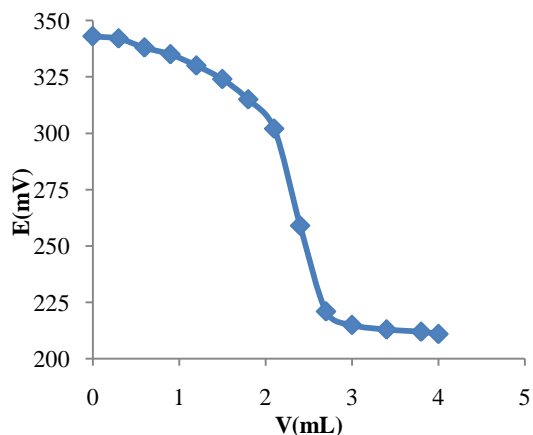
Fig.4: Potentiometric titration plot of a 25 mL 0.001 M Pb(NO3)2 solution with 0.01 M Na2SO4 solution.

5-2- Determination of lead ion in different water samples

Beside the potentiometric titration for studying the electrode performance, it was used for determination of Pb2+ in the Esfahan ZobAhan co wastewater and Esfahan tap water (drinking water of Isfahan city) samples. The obtained results showed that there is no significant difference among the results of the elevation standard; direct Potentiometry using

drawing the calibration curve and atomic absorption spectrometry methods (see Table 3).

Table.3: Determination of lead ion in samples

| NO	sample	Pb^{2+}added(ppm)	Pb^{2+}concentration (ppm)	
			CPE[a]	AAS[a]
2	Tab water	0.5	0.506	0.502
3	Waste water[b]	-	0.045	0.40
4	Waste water[b]	0.5	0.550	0.546

[a] The average of three measurements, [b]ZobAhan co

6- Detection limit

In order to find the limitation of lead concentration measurement by using this method, the calibration curve was plotted at variousPb2+ concentrations from 1.0×10 -1M to 1.0×10-10M. Then, the detection limit was evaluated from the intersection of the two extrapolated sections of the above calibration plot at the lowest portion (Fig.7).Based on this part of the experiment, the detection limit is7.5×10-9M.Ghorbani and Ghaemi reported that their electrode for lead detection has a lead concentration detection limit equal of 6.06×10-6 M [36] which is not as well as our developed electrode.

Also used electrode performance was compared with other modified electrode using other ligands. Table 4 shows this comparison. Babapor *et al*. reported that high level of some heavy metals such as lead has been detected in a large number of revers. According to Babapor *et al.* industrials activities without considering the wastes treatment is the main reason of heavy metals pollution in the rivers [34]. Based on the environmental protection agency (EPA) maximum contaminant levels in drinking water for lead is equal of zero which is due to high toxicity of this element for human body [35]. Various comparisons between our results and results of other researchers are shown in Table 4.
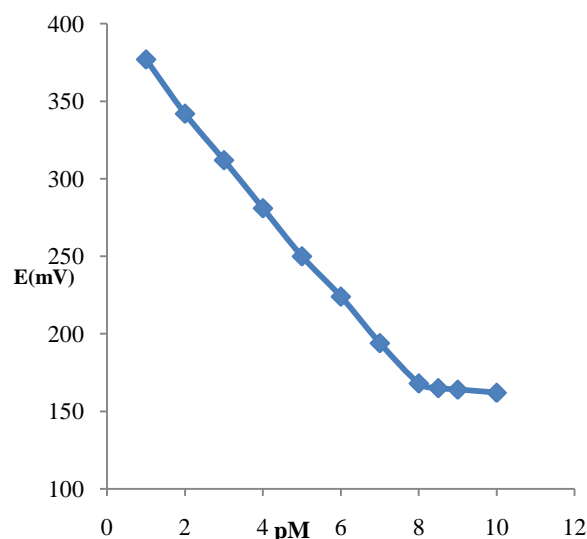
Fig.5: The calibration curve of the CPE at varying Pb2+ concentrations (from 1.0×10-1 to 1.0×10-10 M) in the solution

Table 4: Comparison between the response's characteristics of different Pb2+ ion-selective electrodes

Modifier	slope	LOD(M)	Linear range	Ref
This work	-29.73	7.5×10^{-9}	1.0×10^{-1}-1.0×10^{-8}	-
MWCNTs and nano silica-	29.8 ± 0.2	7.3×10^{-8}	1.0×10^{-2}-1.0×10^{-7}	[37]
-capric acid	29.0 ± 0.5	6.0×10^{-6}	1.0×10^{-2}-1.0×10^{-5}	[38]
- 4-*tert*-butylcalix[6]arene	30.0 ± 0.1	6.0×10^{-7}	1.0×10^{-1}-1.0×10^{-6}	[39]
- poly(vinyl chloride) based on piroxicam	30 ± 0.2	4.0×10^{-6}	1.0×10^{-1}-1.0×10^{-5}	[40]
-1,4,8,11-Tetrathiacyclotetradecane	29.9	2.2×10^{-6}	1.0×10^{-2}-1.0×10^{-5}	[41]
-1, 5-diphenylthiocarbazone	29 ± 2	3.4×10^{-6}	1.0×10^{-2}-5.0×10^{-6}	[42]

CONCLUSION

As conclusion of this study Paracetamol as an ionophore with MWCNTs can be satisfied applied in order to modify the CPE for determination of low concentration of lead. Modified CPE in optimum condition has a few properties such as Nernestian slope, wide linear range, fast response time, rather long lifetime and low determination limit. Also the presence of other ions with significant concentration has no undesirable effects on the electrode performance. The results of this study could introduce a cheap, accurate and simple method for determination of lead ion in aquatic environments. The developed method can also make lead measurement easier for scientists to environmental studies.

COMPETING INTERSTS

Authors of this manuscript declare that we have no significant competing financial, professional or personal interests that might have influenced the performance or presentation of the work described in this manuscript.

AUTHOR CONTRIBUTION

This is to declare that all authors of this manuscript including Marzieh Bagheri, Amirreaza Talaiekhozani and Fatemeh Ahmadvand wrote the main manuscript text. Also all above mentioned authors reviewed the manuscript.

REFERENCES

[1] Jacobs D, Clickner R, Zhou J, The prevalence of lead-based paint hazards in U.S. housing, Environ Health Perspect. 2002; 110(10): A599-06.

[2] Rogan W, Dietrich K, Ware J, The effect of chelation therapy with succimer on neuropsychological development in children exposed to lead. N Engl J Med. 2001; 344(19):1421-26

[3] Longerich HP, Fryer BJ, Strong DF, Determination of lead isotope ratios by inductively coupled plasma-mass spectrometry (ICP-MS), Spectrochimica Acta Part B. 1987; 42(1): 39-48.

[4] Bispo MS, Korn MG, Morte ES, Teixeira LS, Determination of lead in seawater by inductively coupled plasma optical emission spectrometry after separation and pre-concentration with cocrystallized naphthalene alizarin, SpectrochimicaActa Part B. 2002;57(12): 2175-80.

[5] Cho HJ, Myung SW, Determination of Cadmium, Chromium and Lead in Polymers by ICP-OES Using a High Pressure Asher (HPA), Bull. Korean Chem. Soc, 2011; 32(2): 489.

[6] Bagheri H, Afkhami A, Saber-Tehrani M, Khoshsafar H, Prepa-ration and characterization of magnetic nanocomposite of Schiffbase /silica/ magnetite as a preconcentration phase for the trace determination of heavy metal ions in water, food and biological samples using atomic absorption spectrometry, Talanta 2012;97(7): 87-95

[7] Sohrabi MR, Matbouie Z, Asgharinezhad AA, Dehghani A, Solid phase extraction of Cd(II) and Pb(II) using a magnetic metal-organic frame work, and their determination by FAAS, Microchim. Acta, 2013;180 (7-8): 589-97.

[8] Shiri S, Delpisheh A, Haeri A, Poornajaf A,Gol zadeh B, Shiri S, Determination of Trace Amounts of Lead Using the Flotation-spectrophotometric method, Anal Chem Insights. 2011; 6(3): 15–20

[9] Grinberg P, de Campos R, Iridium as permanent modifier in the determination of lead in whole blood and urine by electrothermal atomic absorption spectrometry. Spectrochim Acta Part B. 2001; 56(10): 1831-43.

[10] Munoz E, Palmero S, Determination of heavy metals in milk by potentiometric stripping analysis using a home-made flow cell, Food Control. 2004;15(8): 635-41.

[11] Abbasi S, Bahiraei A, Abbasai F, A highly sensitive method for simultaneous determination of ultra trace levels of copper and cadmium in food and water samples with luminol as a chelating agent by adsorptive stripping voltammetry, Food Chem. 2011;*129*(3): 1274-80.

[12] Cao L, Jia J, Wang Z, Sensitive determination of Cd and Pb by differential pulse stripping voltammetry with in situ bismuth modified zeolite doped carbon paste electrodes. ElectrochimActa.2008; 53(5): 2177-82.

[13] Javanbakht M, Fard SE, Abdouss M, Mohammadi A, Ganjali MR, Norouzi P, Safaraliee L, A biomimetic potentiometric sensor using molecularly imprinted polymer for the cetirizine assay in tablets and biological fluids, Electroanalysis. 2008; *20*(18), 2023-30.

[14] Kaličanin B, Velimirović D, Potentiometric Stripping Analysis of Zinc, Cadmium and Lead in Tobacco Leaves (Nicotian a Tabacum) and Soil Samples, Int. J. Electrochem. Sci.2012; 7(1): 313-23

[15] Gupta VK, Jain AK, Kumar P, PVC-based membranes of N, N_-dibenzyl-1, 4, 10, 13-tetraoxa-7, 16-diazacyclooctadecane as Pb (II)-selective sensor, Sens.Actuators B 2006; 120(1): 259-65.

[16] Guo J, Chai Y, Yuan R, Song Z, Zou Z, Lead (II) carbon paste electrode based on derivatized multi-walled carbonnanotubes: Application to lead content determination in environmental samples, Sens. Actuators B 2011;155(2): 639–45.

[17] Afkhami A, Ghaedi H, Madrakian T, Rezaeivala M, Highly sensitive simultaneous electrochemical determination of trace amounts of Pb(II) and Cd(II) using a carbon paste electrode modified with multiwalled carbon nanotubes and a newly synthesized Schiff base, Electrochimica Acta, 2013;89(2): 377– 86

[18] Shams E, Torabi R, Determination of nanomolar concentrations of cadmium by anodic-stripping voltammetry at carbon paste electrode modified withzirconiumphosphatedmorphous silica, Sens. Actuators B 2006;117(1): 86-92.

[19] Kokkinos C, Economou A, Raptis I, Efstathiou CE., Lithographically fabricated disposable bismuth-film electrodes for the trace determination of Pb(II) and Cd(II) by anodic stripping voltammetry, ElectrochimActa.2008;53(16): 5294-99.

[20] Hu C, Wu K,Dai X, Hu S, Simultaneous determination of lead(II) and cadmium(II) at a diacetyldioxime modified carbon paste electrode by

differential pulse stripping voltammetry. Talanta.2003; 60(1): 17-24.

[21] Ganjali MR, Motakef-Kazami N, Faridbod F,Khoee S, Norouzi P, Determination of Pb^{2+} ions by a modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and nanosilica, J Hazard Mater.2010;173(1): 415-19.

[22] Wang Y, Wei WZ, Liu XY, Zeng XD, Fabrication of a copper nanoparticle/chitosan/carbon nanotube-modified glassy carbon electrode for electrochemical sensing of hydrogen peroxide and glucose, MichrochimicaActa.2008; 160(1-2), 253-60.

[23] Javanbakht M, Ganjali MR, Norouzi P, Hashemi-Nasa A, Badei AR, Carbon paste electrode modified with functionalized nanoporous silica gel as a new sensor for determination of silver ion, Electroanalysis.2007;19(12): 1307-14.

[24] Afkhami A, Ghaedi H, Madrakian T, Rezaeivala M, Highly sensitive simultaneous electrochemical determination of trace amounts of Pb(II) and Cd(II) using a carbon paste electrode modified with multi-walled carbon nanotubes and a newly synthesized Schiff base, ElectrochimicaActa.2013;89(2):377– 86.

[25] Ganjali MR, Motakef-Kazami N, Faridbod F, Khoee S, Norouzi P, Determination of Pb^{2+} ions by a modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and nanosilica, J. Hazard. Mater.2010;173(1):415–19.

[26] Ajayan PM, Nanotubes from carbon, Chem. Rev. 1999; 99 (7):1787–99.

[27] Bianco A, Kostarelos K, Prato M, Applications of carbon nanotubes in drug delivery, Curr. Opin. Chem. Biol. 2005; 9(6): 674-79.

[28] Chou A, Bocking T, Singh NK, Gooding JJ, Demonstration of the importanceof oxygenated species at the ends of carbon nanotubes for their favorable electrochemical properties, Chem. Commun. 2007; 7(6):842–44

[29] Hu C, Wu K, Dai X, Hu S, Simultaneous determination of lead(II) and cadmium(II) at a diacetyldioxime modified carbon paste electrode by differential pulse stripping voltammetry, Talanta. 2003;60(1): 17-24.

[30] Bakker E, Pretsch E, Bühlmann P, Selectivity of potentiometric ion sensors, Anal. Chem.2000; *72*(6): 1127-33.

[31] Macca C, Response time of ion-selective electrodes current usage versus IUPAC recommendations, Anal. Chim.Acta.2004; 512(2): 183-90.

[32] Umezava Y, Bultlmann P, Tohda K, Amemiya S, Potentiometric Selectivity Coefficients of Ion-Selective Electrodes, Pure & Appl. Chem. 2000;72(10): 1851-82.

[33] Bereczki R, Takacs B, Langmaier J, Neely M, Gyurcsanyi RE, Toth K, Nagy G, Lindner E, How To Assess the Limits of Ion-Selective Electrodes: Method for the Determination of the Ultimate Span, Response Range, and Selectivity Coefficients of Neutral Carrier-Based Cation Selective Electrodes, Anal. Chem. 2006; 78(3): 942-50.

[34] BabapourMofrad A, Rostami S, Alanezhad M, Frozanfar M, Khaksar E, Ramezani Z., Determination of some heavy metals in Karoon and Dez rivers , Jentashapir. Sci. Med. J., 2013;3(2): 87-100

[35] Lead Toxicity, What Are the Physiologic Effects of Lead Exposure? EPA website; 2012, [updated 20 August, 2012; cited 06 Jun, 2015]; Available from: http://www.atsdr.cdc.gov/csem/csem.asp?csem=7&po=10.

[36] Ghorbani A, Ghaemi A, Determination of lead in Karron and Dez revers and Persioan Golf by using a lead sensitive potentiometric electrode based on kryptphix22DD, The Second National Conference on Environmental Research, Hamedan, August 07, 2014.

[37] Ganjali MR, Kazami NM, Faridbod F, Khoee S, Norouzi P, Determination of Pb2+ ions by a modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and nanosilica, J. Hazard. Mater, 2010; 173(1): 415-19.

[38] Mousavi MF, Barzegar MB, Sahari S., A PVC-based capric acid membrane potentiometric sensor for lead(II) ions, Sensors and Actuators B, 2001;73(2): 199-04.

[39] Vaishali S, Ijeri SV, Srivastava AK., Coated wire lead(II) selective potentiometric sensor based on 4-tert-butylcalix[6]arene, Sensors and Actuators B, 2004;99(1): 98-05.

[40]- Sadeghi S, Dashti GR, Shamsipur M, Lead-selective poly(vinyl chloride) membrane electrode based on piroxicam as a neutral carrier, Sensors and Actuators B, 2002;81(2): 223-28.

[41] Elmosallamy MF, Ahmed AM, Ghoneim AK., Lead(II) Potentiometric Sensor Based on 1,4,8,11-Tetrathiacyclotetradecane Neutral Carrier and Lipophilic Additives, Electroanalysis, 20098;20(11): 1241-45.

[42] Elsalamouny AR, Elreefy SA, Hassan AM., Lead Ion Selective Electrode Based on 1, 5-diphenylthiocarbazone, Research Journal of Chemical Sciences, 2012;2(6): 38-42.