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Nanocomposite Carbon Paste Sensor for Selective Determination of Lu(III) Ion

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It was found that N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-{[(Z)-1-(2-thienyl)methylidene] amino}benzyl)phenyl] amine (TBPA) can form a selective complex with lutetium ions respect to other lanthanide ions based on our previous study. To have a long-term stable electrode for potentiometric uses, TBPA was applied as an ionophore in preparation of a nanocomposite carbon paste electrode. The pastes were prepared using functionalized multi-walled carbon nanotube (MWCNT-NH_2), nanosilica (NS), graphite, and room temperature ionic liquid (RTIL). The carbon paste electrode composed of 5% MWCNT-NH_2, 1%NS, 25% TBPA, 20% RTIL, and 49% graphite powder showed the best response. Nernstian response of (19.8±0.2 mV decade^{-1}) in the concentration range of 1.0×10^{-6}-1.0×10^{-2} M with a detection limit of 9.5×10^{-7} M was achieved. The response of the electrode was pH independent in the range of 3.5-9.0. The proposed Lu(III) nano-composite carbon paste sensor displayed good selectivity, fast response time and long lifetime.

Keywords: Lutetium, carbon paste, multi-walled carbon nanotubes, ionic liquid, nanosilica sensor, ion selective electrode, potentiometry

1. INTRODUCTION

Lutetium is the last member of lanthanide group usually occurs in association with the element yttrium and is sometimes used in metal alloys and as a catalyst in various chemical reactions. Lanthanide family has an enormous applications ranging from the production of glass and ceramic industry to metallurgy electronics, and agriculture. The main problem in quantitative analysis of this family of elements is the selectivity. Many reagents have been reported for the spectrophotometric determination of lanthanides but they have not been specific and even the most selective requires extractive separation to remove interfering elements. Hence, finding an easy method to measure these elements selectively is of great importance [1].

Application of ion-selective electrodes (ISEs) can offer inexpensive and convenient analyses methods for different anions and cations [2-5] including rare-earth ions, if the used sensors enjoy levels acceptable sensitivity and selectivity. These devices in comparison with other advance electrochemical techniques [6,7] also have the benefits of being simple to use, fast, inexpensive, and capable of producing reliable responses in wide ranges of concentration. A very rough classification of the conventional ISEs divides them into the groups of PVC membrane electrodes, microelectrodes, coated wire electrodes, and carbon paste electrodes, among which carbon paste electrodes (CPEs) have currently attracted a great deal of interest due to their improved renewability, stable response, and low ohmic resistance as compared to the other members of the family [8-15].

CPE-based potentiometric sensors reported are generally based on the incorporation of a sensing material into a carbon paste matrix, which consists of graphite powder dispersed in a non-conductive mineral oil. Because of the structure of this kind of electrodes, they can be easily modified to achieve better responses. Since mineral oils are prepared in petrochemical processes, they have not a pure composition. Thus, the classic CPE suffer some disadvantages caused by the contaminants or matrix components. Room temperature ionic liquids (RTIL), which have a number of interesting properties including their good solvating properties, high conductivity, non-volatility, low toxicity, good electrochemical and chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity have recently been used as binders in the construction of CPEs which seems to have solved the problems of using mineral oils [9-18].

Addition of functionalized multi-walled carbon nanotubes (MWCNT-NH_2) with special physicochemical properties of ultra-low weight, high mechanical strength, high electrical conductivities, high thermal conductivity, metallic or semi-metallic behaviors and high surface areas to CPEs, has also been found to cause improvement in the response of such sensors [19,20]. Nanosilica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical properties of the electrode.

In this work a highly selective modified nano-composite carbon paste sensor based on N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-{[(Z)-1-(2-thienyl)methylidene] amino}benzyl)phenyl] amine (TBPA), Fig. 1, as the sensing material has been developed and tested for the monitoring of Lu(III). Selectivity behavior of this ligand was previously studied [21].

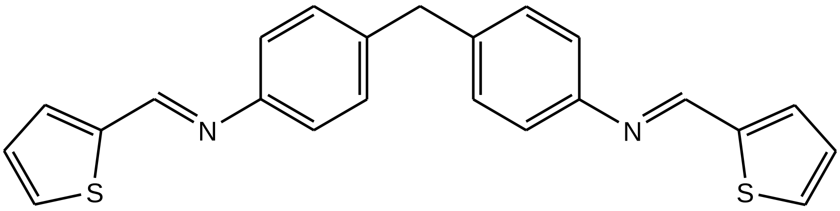

Figure 1. Structure of TBPA

2. EXPERIMENTAL SECTION

2.1. Apparatus

The electrochemical cell used for the determination of potentials, consist of Lu(III) sensor as an indicator electrode and an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode and had a assembly as below:

Nano-composite carbon based sensor | sample solution | Ag/AgCl–KCl (satd.)

2.2. Reagents and materials

Graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for the construction of the carbon pastes. The nanosilica used was purchased from Wacker HDK®H20 and BET of the hydrophilic silica was 170-230 m^2/g. The ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and chloride and nitrate salts of the cations were purchased from Merck Co. and were used without further treatment. The NH_2- functionalized multi-walled carbon nanotube (MWCNT-NH_2) sample used was synthesized as described elsewhere [22]. TBPA was prepared as described elsewhere [21]. Distilled deionized water was used throughout all experiments.

2.4. Electrode Fabrication

The modified CPEs were prepared through a general procedure as follows: Desired amounts of TBPA, graphite powder, nano silica, ionic liquid or the paraffin oil and MWCNT-NH_2 were thoroughly mixed and then transferred into a glass tube (5 mm i.d. and 3 cm in length). To avoid the formation of air gaps in the structure of the CPE, the mixture was then homogenized before being packed into the tube tip. This can help avoid unwanted increases in the electric resistance of the electrodes. Next copper wire was inserted into the opposite end act as an electrical contact and the external surface of the CPE was cleaned with soft abrasive paper, which was repeated prior to any measurement. The electrode was finally rested for 48 h by being soaked in a 1.0×10^{-3} M $LuCl_3$ solution [9-11].

3. RESULTS AND DISCUSSION

3.1. Optimization of the CPEs

The ionophore (here TBPA) is the main ingredient of any ISE which determines the selectivity of such devices [23-30]. Selectivity of TBPA was previously studied [21]. The role of the composite concentration on electrode response was studied by variety of compositions, some of which were modified using the ionic liquid, NS and MWCNT-NH$_2$ according to Table 1. As it can be seen from the data, the CPEs lacking TBPA (compositions no. 1 & 15), did not show any considerable responses of the concentration changes of the target ion. Even changing the amount of the graphite powder as the filler and RTIL as the binder did not significantly affect the potential response.

Table 1. The optimization of the nano-composite based Lu(III) carbon paste ingredients

No.	**Composition (%)**					**Slope (mV decade^{-1})**	**Linear range (M)**
	Graphite	Binder	TBPA	MWCNT-NH$_2$	NS		
1	80	20, RTIL	-	-	-	No response	-
2	60	15, RTIL	25	-	-	14.7 ± 0.4	1.0×10^{-2} - 5.0×10^{-5}
3	55	20, RTIL	25	-	-	16.6 ± 0.3	1.0×10^{-2} - 1.0×10^{-5}
4	50	25, RTIL	25	-	-	16.4 ± 0.2	1.0×10^{-2} - 1.0×10^{-5}
5	55	20, Paraffin	25	-	-	13.1 ± 0.4	5.0×10^{-2} - 5.0×10^{-5}
6	65	20, RTIL	15	-	-	14.2 ± 0.4	4.0×10^{-2} - 5.0×10^{-5}
7	60	20, RTIL	20	-	-	15.5± 0.3	1.0×10^{-2} - 3.0×10^{-5}
8	50	20, RTIL	30	-	-	16.7 ± 0.4	1.0×10^{-2} - 1.0×10^{-5}
9	54	20, RTIL	25	1	-	17.5 ± 0.2	1.0×10^{-2} - 1.0×10^{-5}
10	52	20, RTIL	25	3	-	18.1 ± 0.1	1.0×10^{-2} - 5.0×10^{-6}
11	50	20, RTIL	25	5	-	18.8 ± 0.2	1.0×10^{-2} - 5.0×10^{-6}
12	48	20, RTIL	25	7	-	18.6 ± 0.3	1.0×10^{-2} - 5.0×10^{-6}
13	49	20, RTIL	25	5	1	19.8 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}
14	47	20, RTIL	25	5	3	19.2 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}
15	74	20, RTIL	-	5	1	3.7 ± 0.5	1.0×10^{-2} - 1.0×10^{-3}

Upon the addition of the ionophore, in amounts of 15-30%, to the composition of carbon paste electrodes considerable increases in the potential response of the CP electrodes was observed and presence of 25% of TBPA to CP electrode was found to lead to a very good response behavior. The response was still sub-Nernstian which was not improved by further increase in the amount of the ionophore up to 30% wt. But addition of 1-5% wt of MWCNT-NH$_2$ (Nos. 9-12) was found to improve the potential response to 17.5 ±0.2 and 18.8± 0.2 mV decade^{-1} of Lu(III) activity respectively. There is no need to mention that this was equivalent to reducing the amount of the graphite powder in the composition. This is most probably due to the improvements in the conductivity of the CPEs.

Further addition of 1% and 3% wt of nanosilica (NS) to the CPEs (nos. 13,14) was found to cause increases in the slope from 18.8 to 19.8 mV decade^{-1}.

Eventually, as can be concluded from the data in Table 1 a composition of 25% TBPA, 20% [bmim]BF_4, 49% graphite powder, 5% MWCNT-NH_2 and 1% nanosilica (no. 13) leading to CPEs with a Nernstian slope of 19.8±0.2 mV decade^{-1}, was chosen concluded to be optimum.

3.2. Measuring range and limit of detection

The response of the CPE with the optimum composition (no. 13) was examined in a range of 1.0×10^{-1}-1.0×10^{-7} M and the results are shown in Fig. 2.

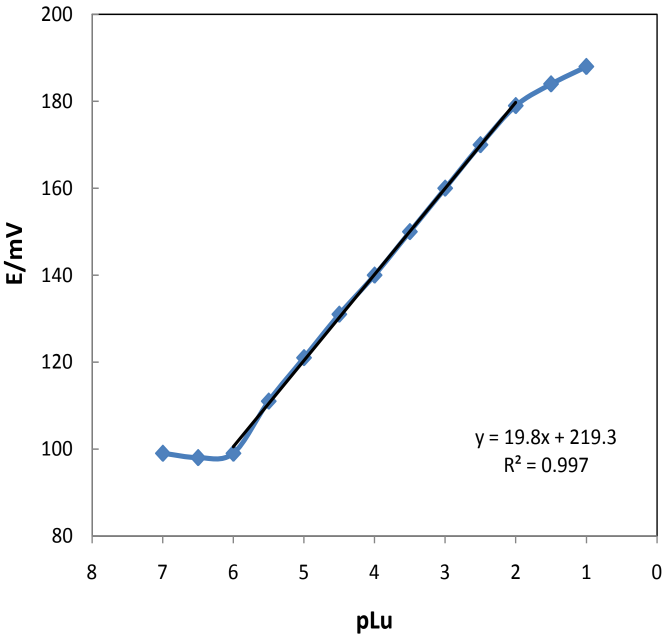

Figure 2. The calibration curve of the Lu(III) nano-composite modified CPE based on TBPA (Electrode no. 13)

The results show that the CPEs have a linear response behavior in the concentration range of 1.0×10^{-2}-1.0×10^{-6} M (Fig. 2). Further, the detection limit of the CPE was evaluated by extrapolating the linear portions of the electrode's calibration curve and was found to be 9.5×10^{-7} M.

3.3. pH effect

pH effect of the test solution on the response behavior of CPEs with the optimum composition was studied by monitoring the potential response of the sensor in 1.0×10^{-4} and 1.0×10^{-3} M Lu(III) solutions while varying the pH values in the range of 1.0-12.0 through adding concentrated HNO_3 or NaOH [31-33].

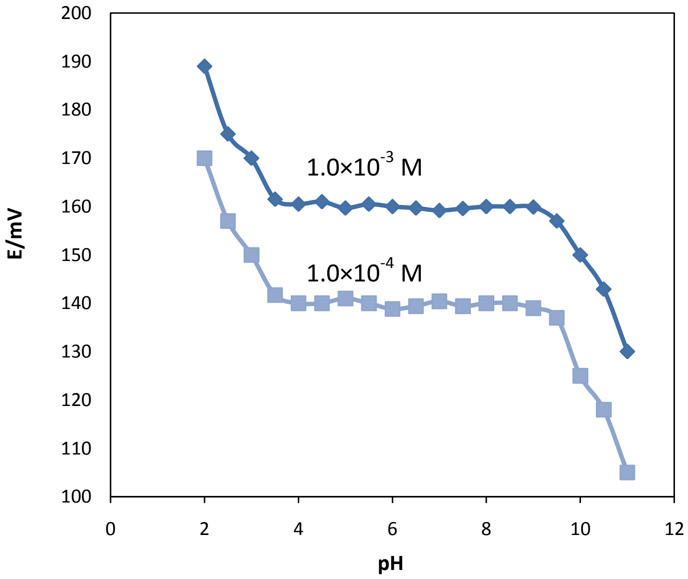

Figure 3. Effect of pH on the potential response of the Lu(III) nano-composite CPE based on (Electrode no. 13) in the test solution of Lu(III) ion (10^{-4} and 10^{-3} M)

The results as depicted in Fig. 3 reveal that the potential response of the Lu(III) CPEs are pH-independent in the range of 3.5-9.0. Potential drifts at higher pH values are attributed to the formation of soluble or insoluble Lu(III) hydroxy complexes and/or precipitates. At pH values less than 3.5 the potential drifts most probably due to the partial protonation of the donor atoms in TBPA.

3.4. Response time and lifetime of the CPEs

The response time of the CPEs was evaluated through studying the average time takes for CPE to produce potential values within ±0.1 mV of their steady-state potentials upon their immersion in a series of solutions of Lu(III), each having a ten-fold difference in concentration [34-46]. Parameters including the temperature, type and speed of stirring, the concentration and composition of each solution, and preconditioning of the electrode are also known to influence the response time the sensors and they were hence kept at constant values throughout the experiments. The tests revealed the response time of the CPEs to be less than 10s in the concentrated solution (10^{-3}-10^{-2} M) and about 20s in diluted solutions (10^{-6}-10^{-4} M).

Lifetime is another very imprtant issue for any sensor. We found that for most ion selective sensors the lifetime values range from 4 to 10 weeks after which the slope and detection limt of the sensor are consinderablly altered.

The lifetime of the proposed Lu(III)-selective CPEs was studied for a period of 15 weeks. In this period, the sensor was used for one hour per day and the changes in its slope and detection limit were recorded (Table 2). As it is seen in Table 2, the CPEs can be used for at least 11 weeks. without significant changes in their slope and detection limits. After this periood, a significant decrease in the slope from 19.8±0.2 to 14.3±0.5 mV decade^{-1} and a gradual increase in the detection limit from

9.5×10^{-7} to 3.7×10^{-5} were observed. This can be attributed to the loss of the RTIL and TBPA from the CPEs as a result of application over time.

Table 2. Lifetime of Lu(III) nano-composite modified CPE

Week	Slope (mV decade^{-1})	DL (M)
1	19.8 ± 0.2	9.5×10^{-7}
2	19.8 ± 0.3	9.7×10^{-7}
3	19.7 ± 0.2	9.9×10^{-7}
4	19.7 ± 0.4	1.0×10^{-6}
5	19.6 ± 0.3	1.2×10^{-6}
6	19.5 ± 0.2	1.4×10^{-6}
7	19.5 ± 0.2	1.5×10^{-6}
8	19.4 ±0.2	1.5×10^{-6}
9	19.2 ± 0.3	1.7×10^{-6}
10	19.1 ± 0.4	1.7×10^{-6}
11	18.6 ± 0.2	2.0×10^{-6}
12	18.0 ± 0.3	5.3×10^{-6}
13	17.1 ± 0.5	8.4×10^{-6}
14	15.2 ± 0.4	1.0×10^{-5}
15	14.3 ± 0.5	3.7×10^{-5}

3.5. Selectivity

As it can be conluded from the name of the devices, selectivity behavior of ion selectyive sensors, is of determining importace. Hence, we included matched potential (MPM) studies of the selectivity coefficients [47-52].

Table 3. The selectivity coefficients of various interfering cations for electrode no. 13; concentration of the reference solution of Lu(III) ion was 1.0×10^{-6} M and the concentration of interfering ions was between 1×10^{-4} to 1.0×10^{-1} M

Cation	Selectivity Coefficient	Cation	Selectivity Coefficient
Na^+	8.3×10^{-5}	Gd^{3+}	3.5×10^{-3}
K^+	6.7×10^{-5}	Yb^{3+}	4.5×10^{-3}
Nd^{3+}	5.0×10^{-3}	Tb^{3+}	6.7×10^{-3}
Ho^{3+}	9.6×10^{-3}	La^{3+}	5.3×10^{-4}
Ca^{2+}	5.4×10^{-4}	Sm^{3+}	5.5×10^{-3}
Cu^{2+}	3.5×10^{-4}	Dy^{3+}	5.2×10^{-3}
Pb^{2+}	5.5×10^{-4}	Pr^{3+}	9.5×10^{-4}
Co^{2+}	3.7×10^{-4}	Eu^{3+}	1.0×10^{-3}
Zn^{2+}	4.2×10^{-4}	Ce^{3+}	6.6×10^{-4}
Tm^{3+}	6.4×10^{-3}	Er^{3+}	7.1×10^{-3}

The results of which are summarized in Table 3 which shows that the selectivity coefficients of CPEs for a number of mono, di and teivalents cations to be in the ranges of 9.6×10^{-3}-3.5×10^{-4}. This indicates that the tested ions do not have considerable interferences with the response of the CPEs.

4. CONCLUSION

A potentiometric carbon paste electrode was constructed for determination of Lu(III). The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 9.5×10^{-7} M and potential responses across the range of 1.0×10^{-6}-1.0×10^{-2} M. 2-{[(6-aminopyridin-2-yl) imino] methyl}-phenol (TBPA) was employed as a sensing element in construction of both electrodes. A nano-composite carbon paste electrode was designed to improve the analytical responses. The carbon paste electrode incorporation of modified multi-walled carbon nano-tube (MWCNT-NH_2) and nano-silica showed a better response especially in term of lifetime and response time. The best nano-composite electrode was composed of 1%NS, 5% MWCNT-NH_2, 25% TBPA, 20% RTIL, and 49% graphite powder. The response of the sensor was found to be stable in the pH range of 3.5-9.0.

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References

1. O.R. Kirk and F.D. Othmer, ‘Encyclopedia of Chemical Technology’ Vol. 19 Wiley, New York p. 851, 1982.
2. V. K. Gupta, R. Mangla and S. Agarwal, *Electroanalysis,* 14 (2002) 1127.
3. F. Faridbod, M. R. Ganjali, R. Dinarvand, and P. Norouzi, *Afr. J. Biotechnol.,* 6 (2007) 2960.
4. V. K. Gupta, A. K. Jain, L. P. Singh and U. Khurana, *Anal. Chim. Acta,* 355 (1997) 33.
5. F. Faridbod, M. R. Ganjali, R. Dinarvand, and P. Norouzi, *Sensors,* 8 (2008) 2331.
6. P. Norouzi, M. R. Ganjali, T. Alizadeh, and P. Daneshgar, *Electroanalysis,* 18 (2006) 947.
7. P. Norouzi, G. R. Nabi Bidhendi, M. R. Ganjali, A. Sepehri, and M. Ghorbani, *Michrochim. Acta,* 152 (2005) 123.
8. M. Javanbakht, A. Badiei, M. R. Ganjali, P. Norouzi, A. Hasheminasab and M. Abdouss, *Anal. Chim. Acta,* 601 (2007) 172
9. P. Norouzi, Z. Rafiei-Sarmazdeh, F. Faridbod, M. Adibi and M. R. Ganjali, *Int. J. Electrochem. Sci.,* 5 (2010) 367.
10. M. R. Ganjali, H. Ganjali, M. Hosseini and P. Norouzi, *Int. J. Electrochem. Sci*., 5 (2010) 967.
11. M. R. Ganjali, M. Rezapour, S. K. Torkestani, H. Rashedi, and P. Norouzi, *Int. J. Electrochem. Sci*., 6 (2011) 2323.
12. H. Yaghoubian, V. Soltani-Nejad and S. Roodsaz, *Int. J. Electrochem. Sci*., 5 (2010) 1411.
13. F. Faridbod, M. R. Ganjali, M. Pirali-Hamedani and P. Norouzi, *Int. J. Electrochem. Sci.,* 5 (2010) 1103.
14. M. V. B. Zanoni, E. I. Rogers, C. Hardacre and R. G. Compton, *Int. J. Electrochem. Sci.,* 4 (2009) 1607.

15. M. R. Ganjali, H. Khoshsafar, A. Shirzadmehr, M. Javanbakht and F. Faridbod, *Int. J. Electrochem. Sci.,* 4 (2009) 435.
16. G. P. Guo, F. Q. Zhao, F. Xiao and B. Z. Zeng, *Int. J. Electrochem. Sci.,* 4 (2009) 1365.
17. A. Safavi, N. Maleki, F. Honarasa, F. Tajabadi, and F. Sedaghatpour, *Electroanalysis* 19 (2007) 582.
18. N. Maleki, A. Safavi, and F. Tajabadi, *Anal. Chem.* 78 (2006) 3820.
19. M. Siswana, K. I. Ozoemena, and T. Nyokong, *Sensors* 8 (2008) 5096.
20. P.M. Ajayan, *Chem. Rev.* 99 (1999) 1787.
21. H. A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M. S. Zabihi, M. R. Ganjali, M. Salavati-Niasari, *Mater. Sci. Eng. C* 30 (2010) 917.
22. J.S. Jeong, S.Y. Jeon, T.Y. Lee, J.H. Park, J.H. Shin, P.S. Alegaonkar, A.S. Berdinsky, J.B. Yoo, *Diamond Relat. Mater.* 15 (2006) 1839.
23. M. R. Ganjali, M. Rezapour, M. R. Pourjavid, and S. Haghgoo, *Anal. Sci.,* 20 (2004) 1007.
24. S. K. Srivastava, V. K. Gupta, and S. Jain, *Anal. Chem.*, 68 (1996) 1272.
25. M. R. Ganjali, A. Daftari, P. Nourozi and M. Salavati-Niasari, *Anal. Lett*., 36 (2003) 1511.
26. H. A. Zamani, M. R. Ganjali and M.J. Pooyamanesh, *J. Brazil. Chem. Soc.,* 17 (2006) 149.
27. M. R. Ganjali, Z. Memari, F. Faridbod, R. Dinarvand and P. Norouzi, *Electroanalysis*, 20 (2008) 2663.
28. H. A. Zamani, G. Rajabzadeh, M. R. Ganjali and P. Norouzi, *Anal. Chim. Acta*, 598 (2007) 51.
29. V. K. Gupta, R. Mangla, U. Khurana, P. Kumar, *Electroanalysis*, 11 (1999) 573.
30. V. K. Gupta, A. K. Singh and B. Gupta, *Anal. Chim. Acta*, 575 (2006) 198.
31. H. A. Zamani, M. R. Ganjali, P. Norouzi, and S. Meghdadi, *J. Appl. Electrochem.*, 37 (2007) 853.
32. H. A. Zamani, G. Rajabzadeh and M. R. Ganjali, *J. Brazil. Chem. Soc.,* 17 (2006) 1297.
33. M.R. Ganjali, H.A. Zamani, P. Norouzi, M. Adib, and M. Accedy, *Acta Chim. Slov.*, 52 (2005) 309.
34. S. K. Srivastava, V. K. Gupta and S. Jain, *Anal. Chem.,* 68 (1996) 1272.
35. A. K. Jain, V. K. Gupta, L. P. Singh, P. Srivastava and J. R. Raisoni, *Talanta*, 65 (2005) 716.
36. R. Prasad, V. K. Gupta, and A. Kumar, *Anal. Chim. Acta*, 508 (2004) 61.
37. A. K. Jain, V. K. Gupta, U. Khurana and L. P. Singh, *Electroanalysis*, 9 (1997) 857.
38. V. K. Gupta, R. N. Goyal, and R. A. Sharma, *Int. J. Electrochem. Sci.*, 4 (2009) 156.
39. H. A. Zamani, A. Imani, A. Arvinfar, F. Rahimi, M. R. Ganjali, F. Faridbod and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 588.
40. F. Faridbod, M. R. Ganjali, B. Larijani, M. Hosseini and P. Norouzi, *Mater. Sci. Eng. C*, 30 (2010) 555.
41. A. K. Singh, V. K. Gupta and B. Gupta, *Anal. Chim. Acta*, 585 (2007) 171.
42. A. S. Al Attas, *Int. J. Electrochem. Sci.*, 4 (2009) 9.
43. A. K. Jain, V. K. Gupta, and L. P. Singh, *Analytical Proceedings Including Analytical Communication*, 32 (1995) 263.
44. V. K. Gupta, A. K. Singh and B. Gupta, *Anal. Chim. Acta*, 575 (2006) 198.
45. M. R. Ganjali, N. Davarkhah, H. Ganjali, B. Larijani, P. Norouzi and M. Hossieni, *Int. J. Electrochem. Sci.,* 4 (2009) 762.
46. H. A. Zamani, M. S. Zabihi, M. Rohani, A. Zangeneh-Asadabadi, M. R. Ganjali, F. Faridbod and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 409.
47. P. R. Buck, and E. Lindneri, *Pure Appl. Chem.*, 66 (1994) 2527.
48. M. R. Ganjali, R. Nemati, F. Faridbod, P. Norouzi, F. Darviche, *Int. J. Electrochem. Sci.*, 3 (2008) 1288.
49. M. R. Ganjali, S. Rasoolipour, M. Rezapour, P. Norouzi, A. Tajarodi, Y. Hanifehpour, *Electroanalysis*, 17 (2005) 1534.
50. H. Behmadi, H. A. Zamani, M. R. Ganjali, P. Norouzi, *Electrochim. Acta*, 53 (2007) 1870.
51. M. R. Ganjali, H. Shams, F. Faridbod, L. Hajiaghababaei, and P. Norouzi, *Mater. Sci. Eng. C* 29 (2009) 1380

52. M. R. Ganjali, P. Norouzi, A. Atrian, F. Faridbod, S. Meghdadi, and M. Giahi, *Mater. Sci. Eng. C*, 29 (2009) 205