

Samarium (III) PVC-Membrane Sensor based on 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl] acetic acid

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2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid (CSAA) was employed as a lipophilic ionophore to form a selective complexation with Sm^{+3} ions in preparation of a novel Sm^{+3} ion selective electrode with polymeric matrix. To achieve the most acceptable potential response, type and amount of membrane composition was optimized. The electrode with membrane composition (w/w) of PVC: 30% (0.030 gr), CSAA: 2% (0.002gr), NaTPB: 2% (0.002gr) and NB: 66% (0.066 gr) demonstrated the Nernstian behavior in wide concentration range of 1.0×10^{-7} and 1.0×10^{-2} M with the slope of 20.8 ± 0.4 mV/decade and the lower detection limit of 7.4×10^{-8} M. The performance pH range of designed electrode was 2.4 – 8.2 with the fast response time of ~ 5.0s. According to selectivity coefficients which were obtained by K^{MPM} (matched potential method); the electrode in presence of other interfering cation has an acceptable sensitivity toward Sm^{+3} ions. In case of analytical application such as both potentiometric titration and designation of Sm^{+3} ions in blend of disparate ions, this samarium electrode could be applied successfully as an indicator electrode.

Keywords: PVC Membrane Sensor, Ion Selective Electrode (ISE), Samarium (III), Potentiometry

1. INTRODUCTION

The rare earth elements have wide variety of applications by using in manufactured goods [1]. Samarium is the Sixth element in the lanthanide series with atomic number 62. Because of its wide application in various fields such as use in industry as an appropriate absorber and in CaF_2 crystals as a doping element in order to manufacture of optical masers and lasers, and etc.; therefore, it is sincerely important to choose such a method which including good sensitivity and selectivity, accuracy, fast working time, and affordable [1, 2]. Among Different techniques which have been proposed to determine the samarium ion in aqueous solutions the potentiometric technique based on ion selective

electrodes due to its excellences including selectivity, working fast and simple, economical, the accuracy response in widish working ranges and etc. are frequently used as admissible analytical method [3-8].

In accordance to reports there are some researches on lanthanide ion selective electrode [9-34].

A new ion selective electrode has been introduced for samarium ion in present work. Due to potentiometric studies because of selective interaction of 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid (CSAA) (Fig. 1), with samarium ions, it can be a good active material for applying as carrier ion in a new samarium ion selective electrode.

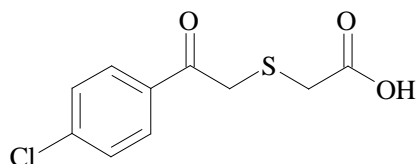


Figure 1. Molecular structure of CSAA.

2. EXPERIMENTAL

2.1. Reagents

The reagent grades of high relative molecular weight PVC, sodium tetraphenyl borate (NaTPB), nitrobenzene (NB), acetophenone (AP), dibutyl phthalate, (DBP), benzyl acetate (BA), tetrahydrofuran (THF) and Nitrate and chloride salts of all cations were purchased from Merck Chemical Co. and used without any further modification. Moreover, deionized distilled water was used during all experiments.

2.2. Synthesis of 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid (CSAA)

In order to synthesize the 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid first, a mixture of 2-thiole acetic acid (0.005 mol) and sodium hydrogen carbonate (0.012 mol) in acetone 10 mL, was added to a solution of 2-bromo(p-chloro)acetophenone(p-chloro phenacyl bromide) (0.005 mol) in acetone 5 ml slowly. Then, the result mixture was stirred at room temperature for 2 h, during this time the residue solid NaBr was formed. Next, the resulting solid was filtered and the solution was adjusted to pH 6-7 with acetic acid, and concentrated in vacuum. Finally, the residue solid material was filtered and washed with water and recrystallized from ethanol to produce pure compound CSAA. Yield: 76%; [Found: C, 48.95; H, 3.69; S, 12.89%. $C_{10}H_9ClO_3S$ requires C, 49.08; H, 3.71; S, 13.10%]; $\nu_{max}(KBr)$ 3495, 3036, 1695, 1626, 1336, 1321 cm^{-1} ; $\delta_H(ppm)(CDCl_3)$ 3.31 (2H, s, CH_2), 3.58 (2H, s, CH_2), 7.35-7.74 (4H, dd, C_6H_4), 10.21 (1H, s, OH); MS(m/z) M^+ , 244 (100%), $(M+2)^+$, 246 (31%).

2.3. Electrode preparation

The sufficient amount of membrane ingredients containing plasticizer as a solvent mediator, CSAA as a sensing element, NaTPB as an ionic additive, PVC as a polymeric matrix in order to preparation of the PVC membrane electrode were blended and dissolved in 3-4 mL of THF. The resulting mixture was evaporated slowly to obtain an oily concentrated blend. In order to form a transparent membrane of about 0.3 mm in thickness a Pyrex tube (3–5 mm i.d.) was dipped into the membrane solution for about 5 s. after removing the tube from the solution, it was kept at room temperature for at least 12 h. then, it was filled with internal filling solution ($1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ SmCl}_3$) and conditioned for 24 h by soaking in $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ SmCl}_3$ solution. A silver/silver chloride coated wire electrode was applied as an internal reference electrode [35-68].

2.4. EMF measurements

In order to electromotive force (emf) measurements the following cell assembly was applied:

Ag–AgCl | $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ SmCl}_3$ | PVC membrane: test solution | Hg–Hg₂Cl₂, KCl (satd).

A Corning ion analyzer 250 pH/mVmeter was employed for the potential measurements at 25.0 °C. Activities were calculated according to the modified Debye–Hückel approximation equation (1):

$$\log \gamma = -0.511z^2 \left[\frac{\mu^{1/2}}{1+1.5\mu^{1/2}} - 0.2\mu \right] \quad (1)$$

3. RESULTS AND DISCUSSION

Choosing the best selective ionophore is the major problem in the field of lanthanide potentiometric membrane sensors. Although the lanthanide series are rather similar, but due to their different radii of the lanthanum ions (1.02 to 0.80 Å from Ce³⁺ to Lu³⁺) they show the different properties, such as charge densities and hydration energy over the range of 3370 to 3760 kJmol⁻¹ from Ce³⁺ to Lu³⁺ [69]. However, using the ionophore with the properties such as high flexibility, and containing semi cavity, heteroatoms (N, O and S as donor atoms) is the reasonable way to design a selective electrode for the different lanthanide ions which would be able to form a template with reference easily to the size of the cation [70]. Additionally, these material that use as an ionophores, could form complexation with one of the lanthanides than the other ones with the optimum free energies. This event can be ascribing to various items such as flexibility; number, type and site of its donor atoms; size and the charge density of the lanthanides. Due to presence of oxygen and sulfur atoms in the molecular structure of CSAA, it was expected to enhance both the permanence and selectivity of its complexes with transition and heavy metal ions (especially with lanthanide ions). To assessment the role of CSAA as a selector material for diverse metal ions, it was employed as ionophore to make ready a several PVC-membrane ion-selective electrode for a large number of metal ions. In accordance to the results, except for Sm³⁺ ions, in all other cases the Nernstian slopes of the

sensor are much lower than the expected. This observation is most probably due to the proper size of Sm^{3+} ion to the semi cavity of flexible CSAA.

3.1. The membrane composition influence

In consideration of the fact that the nature and amount of the membrane ingredients such as ionophore, plasticizer, ionic additive, and polymeric matrix have consequential impress in the electrode responses [71–90], the effect of membrane components were investigated on the response of Sm^{3+} ion selective electrode. Due to the obtained results, among four different plasticizers, nitrobenzene (NB) owing to efficacy of its dielectric constant on the membrane phase which help to movement of ionophore and better extraction of the samarium ions, show the best potential response and near Nernstian slope. Moreover, the suitable amount of lipophilic anions additive such as NaTPB in cation selective electrode leads to step down the ohmic resistance and rapid extraction of Sm^{3+} ions from the watery solution to the membrane phase. According to Table 1 the membrane composition of PVC: 30%, CSAA: 2%, NaTPB: 2% and NB: 66% (no. 1) show the best Nernstian behavior of electrode.

Table 1. Membrane compositions optimization

No.	Composition (w/w, %)				Slope (mV decade ⁻¹)	Dynamic Linear range (M)
	CSAA	Plasticizer	NaTPB	PVC		
1	2	NB, 66	2	30	20.8 ± 0.4	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻²
2	2	AP, 66	2	30	18.4 ± 0.3	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻²
3	2	BA, 66	2	30	17.3 ± 0.2	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻²
4	2	DBP, 66	2	30	16.7 ± 0.3	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻²
5	2	NB, 68	0	30	13.6 ± 0.6	1.0 × 10 ⁻⁶ -5.0 × 10 ⁻²
6	2	NB, 67	1	30	17.5 ± 0.5	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻²
7	2	NB, 65	3	30	18.3 ± 0.4	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻²
8	1	NB, 67	2	30	17.2 ± 0.3	1.0 × 10 ⁻² -1.0 × 10 ⁻⁷
9	3	NB, 65	2	30	18.9 ± 0.5	1.0 × 10 ⁻² -1.0 × 10 ⁻⁷

3.2. Calibration graph

The optimized Sm^{3+} electrode displays potentiometric behavior over a rectilinear range from 1.0×10^{-7} to 1.0×10^{-2} M with the calibration curve slope equal 20.8 ± 0.4 mV/decade of Sm^{3+} ions concentration (fig. 2). The detection limit of the electrode, where the electrode starts to lose sensitivity toward the primary ion and deviate considerably from a Nernstian behavior and that was determined by intersection of the two extrapolated linear calibration graph, was 7.4×10^{-8} M.

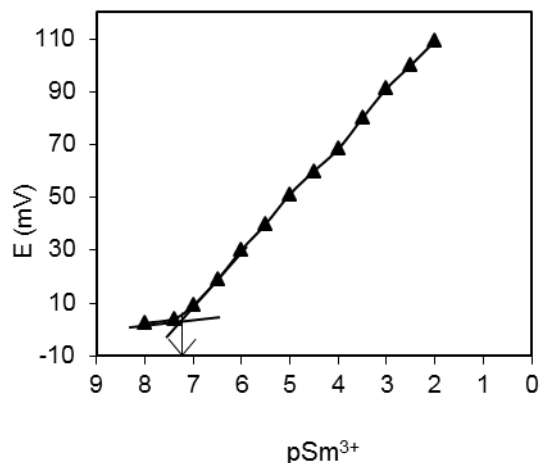


Figure 2. Calibration curves of the CSAA -based samarium electrode.

3.3. The pH effect

The potential response of Sm^{+3} electrode was studied for different pH values to determine the applicable pH range in which the potential remains constant. In order to do this, the potential was measured by adding the amount of HCl and NaOH in $1.0 \times 10^{-3}\text{M}$ of samarium solution during the pH range of 1-11. According to given results which are shown in Fig. 3 the designed electrode can work independently from the activity Changes of H_3O^+ ion in the widish pH range of 2.4 – 8.2. The observed drift in potential behavior of electrode at pH higher than 8.2 is attributed to the formation of some hydroxyl complexes of Sm^{3+} ions and diminish the free concentration of the Sm^{3+} ions in the solution which lead to decrease the response of the sensor. On the other hand, by decrease the pH values to less than 2.4 the increase in potential response was observed. This phenomenon due to protonate the heteroatoms of ionophore and reduce the sensitivity of electrode toward Sm^{+3} ion which cause to responds to the H_3O^+ ion in the solution.

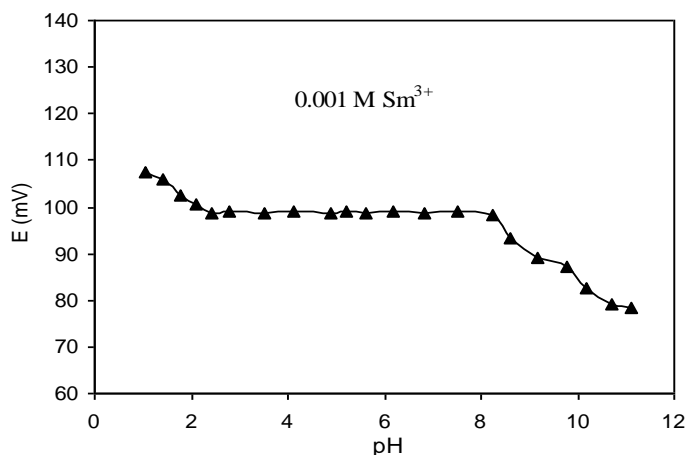


Figure 3. the effect of pH on the potential response of the Sm^{3+} sensor.

3.4. Dynamic response time

In order to calculate the dynamic response time, the mean of demanded time to attain a potential within ± 0.1 mV of the final steady-state potential was measured by applying the various concentrations of Sm^{3+} solutions from the lower ($1.0 \times 10^{-7} \text{ mol L}^{-1}$) to the higher ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) concentration. Conforming to Fig. 4, which is shown the actual potential versus time, electrode responds within about 5 s.

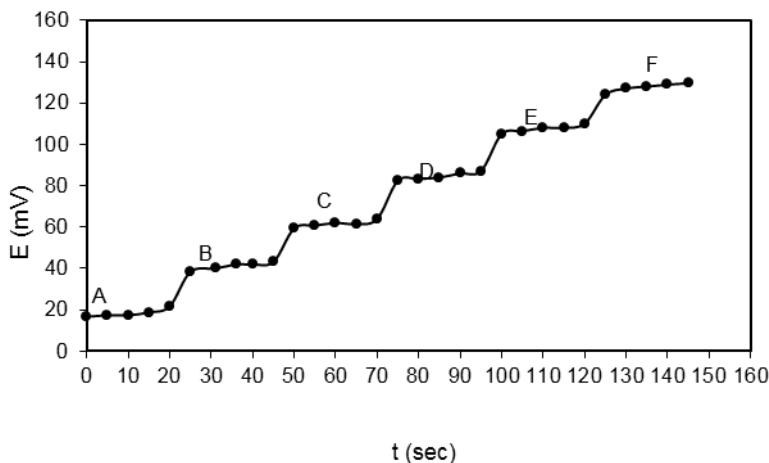


Figure 4. Dynamic response time of the samarium electrode for step changes in the Sm^{3+} concentration: A) 1.0×10^{-7} M, B) 1.0×10^{-6} M, C) 1.0×10^{-5} M, D) 1.0×10^{-4} M, E) 1.0×10^{-3} M, F) 1.0×10^{-2} M.

3.5. The sensor selectivity

Table 2. Selectivity coefficients of the developed Sm^{3+} electrode

Ion	K^{MPM}	Ion	K^{MPM}
Dy^{3+}	5.4×10^{-4}	Pb^{2+}	5.7×10^{-4}
Lu^{3+}	2.2×10^{-3}	Hg^{2+}	2.1×10^{-4}
Yb^{3+}	3.5×10^{-3}	Ni^{2+}	3.2×10^{-4}
Er^{3+}	5.7×10^{-4}	Co^{2+}	1.0×10^{-4}
Gd^{3+}	6.3×10^{-4}	Cd^{2+}	7.1×10^{-4}
Ho^{3+}	2.5×10^{-3}	Zn^{2+}	1.0×10^{-3}
Tm^{3+}	5.8×10^{-3}	Ca^{2+}	3.0×10^{-3}
La^{3+}	3.2×10^{-3}	Ba^{2+}	2.2×10^{-3}
Nd^{3+}	2.8×10^{-3}	Na^{+}	7.5×10^{-4}
Cr^{3+}	4.7×10^{-3}	K^{+}	8.8×10^{-4}
Fe^{3+}	5.4×10^{-4}	—	—

To investigate the sensitivity of proposed electrode toward Sm^{+3} ion, the selectivity coefficients of the sensor into variety of cations were studied by Matched potential method (MPM) [91-114]. The matched potential method selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{\text{MPM}} = a_A/a_B$, where a_A is the initial primary ion (A) activity and a_B the activity of interfering ion (B).

As seen in Table. 2 the obtained K^{MPM} for monovalent, divalent, and trivalent cations are relatively small, which indicate the high selectivity of developed electrode toward samarium ions.

Table 3 shows the analogy of the K^{MPM} , lower detection limit, linear range, and response time of the proposed Sm^{3+} sensor with those of the previously reported samarium sensors. It is obvious, the selectivity coefficients of the electrode for majority of cations is superior to those reported for the samarium ion-selective membrane electrodes [5, 6].

Table 3. Comparison of various samarium electrodes

Parameter	Ref. 5	Ref. 6	This work
LR (M)	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-5} - 1.0×10^{-1}	1.0×10^{-7} - 1.0×10^{-2}
DL (M)	6.0×10^{-7}	3.1×10^{-6}	7.4×10^{-7}
Response time (s)	<10	~20	~5
pH range	4.0-8.0	4.0-7.0	2.4-8.2
Slope (mV/decade)	19.8	19.4	20.8
Log $K_{\text{sel}} > -2$	-	Gd, Ce, La, Cu, Pb Mg, Zn, Cd, Ni, Co, Ag	-

3.6. Analytical application

In accordance with the titration curve which is shown in Fig. 5 the samarium electrode illustrated the acceptable role as an indicator electrode to monitoring the amount of samarium ions in the potentiometric titration of SmCl_3 solution (1.0×10^{-4} M) with EDTA (1.0×10^{-2} M).

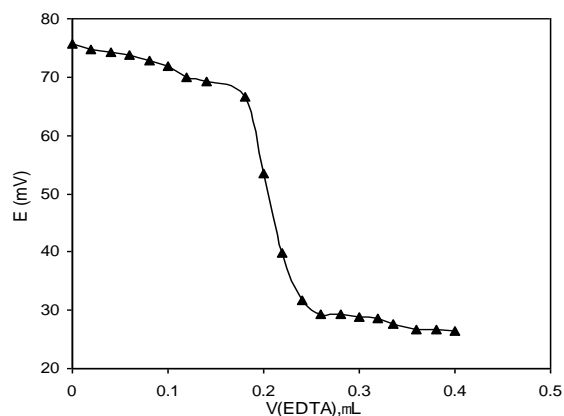


Figure 5. Potential titration curves of 20.0 mL Sm(III) solution (1.0×10^{-4} M) with EDTA (1.0×10^{-2} M).

This electrode was also applied to the determination of the fluoride ions in mouth wash solutions. The resulting data in Table 4 indicate that the accuracy of the Sm^{3+} ions detection in different sample solutions is almost quantitative.

Table 4. Determination of fluoride ions in mouth wash solutions

Sample	Labeled (mg mL^{-1})	Found ISE ^a (mg mL^{-1})
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1.35	$(1.39^b \pm 0.04)$
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1.45	$(1.47^b \pm 0.03)$

a. Proposed Sm^{3+} sensor

b. Results are based on three measurements

4. CONCLUSION

Due to tendency of 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid (CSAA) to form complexation with Sm^{+3} ions in comparison of many other cations, CSAA was used as a selective ionophore for Sm^{+3} ions to fabricate a new potentiometric ion selective electrode. The electrode could apply over the wide linear range of 1.0×10^{-7} to 1.0×10^{-2} M. The designed electrode showed independent potential behavior toward the changes of H_3O^+ ions activity in pH range of 2.4–8.2. Moreover, the dynamic response time was estimated circa 5 s. according to the selectivity coefficients of electrode for various cations which was investigated by match potential method, the influence of interfering ions to the Sm^{+3} electrode response is negligible. Eventually, the proposed electrode was used as an indicator electrode in determination of Sm (III) ion to show the Accuracy of the electrode.

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References

1. O.R. Kirk, and F.D. Othmer, Encyclopedia of Chemical Technology, Wiley, New York, 1982.
2. U. Oesch, D. Amman, and W. Simon, *Clin. Chem.* 32 (1986) 1448.

3. H. A. Zamani, M. Masrournia, M. Rostame-Faroge, M. R. Ganjali, and H. Behmadi, *Sensor Lett.* 6 (2008) 759.
4. M. Pooyamanesh, H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, and P. Norouzi, *Anal. Lett.* 40 (2007) 1596.
5. M.R. Ganjali, M.R. Pourjavid, M. Rezapour, and S. Haghgoo, *Sens. Actuators B* 89 (2003) 21.
6. M. Shamsipur, M. Hosseini, K. Alizadeh, M.M. Eskandari, H. Sharghi, M.F. Mousavi, and M.R. Ganjali, *Anal. Chim. Acta* 486 (2003) 93.
7. H. A. Zamani, G. Rajabzadeh, and M. R. Ganjali, *Bull. Chem. Soc. Jpn* 80 (2007) 172.
8. S.K. Mittal, H.K. Sharma, and A.S.K. Kumar, *Sensors* 4 (2004) 125.
9. M.J. Gismera, D. Hueso, J.R. Procopio, M.T. Sevilla, *Analytica Chimica Acta* 524 (2004) 347.
10. M.R.Abedi, H. A. Zamani, M. R. Ganjali, and P. Norouzi, *Sensor Lett.* 5 (2007) 516.
11. H. A. Zamani, M. R. Ganjali, and M. Adib, *J. Braz. Chem. Soc.* 18 (2007) 215.
12. H. A. Zamani, G. Rajabzadeh, A. Firouz, and M. R. Ganjali, *J. Anal. Chem.* 62 (2007) 1080.
13. V.K. Gupta, A.K. Jain, S. Agarwal, and G. Maheshwari, *Talanta* 71 (2007) 1964.
14. H. A. Zamani, M. R. Ganjali, P. Norouzi, and M. Adib, *Sensor Lett.* 5 (2007) 522.
15. A. Sil, V.S. Ijeri, and A.K. Srivastava, *Sens. Actuators B* 106 (2005) 648.
16. C.E. Koenig, and E.W. Granber, *Electroanalysis* 7 (1995) 1090.
17. H. A. Zamani, M. R. Ganjali, and N. Seifi, *Collect. Czech. Chem. Commun.* 72 (2007) 1189.
18. H. A. Zamani, M. T. Hamed-Mosavian, E. Aminzadeh, M. R. Ganjali, M. Ghaemy, H. Behmadi, and F. Faridbod, *Desalination* 250 (2010) 56.
19. H. A. Zamani, M. T. Hamed-Mosavian, E. Hamidfar, M. R. Ganjali, and P. Norouzi, *Mater. Sci. Eng. C* 28 (2008) 1551.
20. M. R. Abedi, and H. A. Zamani, *Anal. Lett.* 41 (2008) 2251.
21. M. R. Ganjali, P. Norouzi, F. Faridbod, S. Riahi, J. Ravanshad, J. Tashkhourian, M. Salavati-Niasari and M. Javaheri, *Ieee Sensors J.* 7 (2007) 544.
22. H. A. Zamani, M. R. Ganjali, P. Norouzi, A. Tajarodi, and Y. Hanifehpour, *J. Chil. Chem. Soc.* 52 (2007) 1332.
23. M. R. Ganjali, P. Norouzi, F. S. Mirnaghi, S. Riahi and F. Faridbod, *Ieee Sensors J.* 7 (2007) 1138.
24. M. R. Ganjali, N. Motakef-Kazami, F. Faridbod, S. Khoee and P. Norouzi, *J. Hazard Mater.* 173 (2010) 415.
25. H. A. Zamani, J. Abedini-Torghabeh, and M. R. Ganjali, *Bull. Korean Chem. Soc.* 27 (2006) 835.
26. P. Norouzi, M.R. Ganjali, F. Faridbod, S.J. Shahtaheri, and H. A. Zamani, *Int. J. Electrochem. Sci.* 7 (2012) 2633.
27. H. A. Zamani, A. Imani, A. Arvinfar, F. Rahimi, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 588.
28. M. R. Abedi, H. A. Zamani, M. R. Ganjali, and P. Norouzi, *Intern. J. Environ. Anal. Chem.* 88 (2008) 353.
29. H. A. Zamani, *Anal. Lett.* 41 (2008) 1850.
30. K. Alizadeh, R. Parooi, P. Hashemi, B. Rezaei and M. R. Ganjali, *J. Hazard. Mater.* 186 (2011) 1794.
31. V. K. Gupta, R. N. Goyal, M. K. Pal, and R. A. Sharma, *Anal. Chim. Acta* 653 (2009) 161.
32. H.A. Zamani, G. Rajabzadeh, and M.R. Ganjali, *Sensor Lett.* 7 (2009) 114.
33. H. A. Zamani, M. Nekoei, M. Mohammadhosseini, M. R. Ganjali, *Mater. Sci. Eng. C* 30 (2010) 480.
34. H. A. Zamani, M. Mohammadhossieni, M. Nekoei, and M. R. Ganjali, *Sensor Lett.* 8 (2010) 303.
35. H.A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M.S. Zabihi, M.R. Ganjali, and M. Salavati-Niasari, *Mater. Sci. Eng. C* 30 (2010) 917.
36. H. A. Zamani, M. Masrournia, S. Sahebhasagh, and M. R. Ganjali, *Anal. Lett.* 42 (2009) 555.

37. H. Khani, M.K. Rofouei, P. Arab, V. Kumar Gupta, Z. Vafaeia, *Journal of Hazardous Materials* 183 (2010) 402.
38. M. Mohammadhossieni, H. A. Zamani, and M. Nekoei, *Anal. Lett.* 42 (2009) 298.
39. H. A. Zamani, G. Rajabzadeh, A. Firouz, and A. A. Ariaii-Rad, *J. Braz. Chem. Soc.* 16 (2005) 1061.
40. S. K. Mittal, S. K. A. Kumar, and H. K. Sharma, *Talanta* 62 (2004) 801.
41. M. Nekoei, H. A. Zamani, and M. Mohammadhossieni, *Anal. Lett.* 42 (2009) 284.
42. H. A. Zamani, *Anal. Lett.* 42 (2009) 615.
43. A. K. Singh, R. P. Singh, and P. Saxena, *Sens. Actuators B* 114 (2006) 578.
44. P. J. Milham, A. S. Awad, R. E. Paull, and J. H. Bull, *Analyst* 95 (1970) 751.
45. F. J. Sáez de Viteri, and D. Diamond, *Analyst* 119 (1994) 749.
46. Tom Lindfors, Ari Ivaska, *Analytica Chimica Acta* 437 (2001) 171.
47. 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.
48. H.K. Sharma, and N. Sharma, *E-J. Chem.* 6 (2009) 1139.
49. H.A. Zamani, M.R. Ganjali, H. Behmadi, and M.A. Behnajady, *Mater. Sci. Eng. C* 29 (2009) 1535.
50. R. Zare-Dorabei, P. Norouzi and M. R. Ganjali, *J. Hazard. Mater.* 171 (2009) 601.
51. H. A. Zamani, G. Rajabzadeh, M. Masrornia, A. Dejbord, and M. R. Ganjali, *Desalination* 249 (2009) 560.
52. K. Srinivasan, G. A. Rechnitz, *Anal. Chem.* 41 (1969) 1203.
53. J. Růžička, E.H. Hansen, J.C. Tjell, *Analytica Chimica Acta* 67 (1973) 155.
54. H. A. Zamani, M. R. Ganjali, P. Norouzi, and M. Adib, *Mater. Sci. Eng. C* 28 (2008) 157.
55. S.R. Sheen, and J.S. Shih, *Analyst* 117 (1992) 1691.
56. H. A. Zamani, M. R. Ganjali, P. Norouzi, and S. Meghdadi, *Anal. Lett.* 41 (2008) 902.
57. M. Javanbakht, M. R. Ganjali, P. Norouzi, A. Badiei, A. Hasheminasab and M. Abdouss, *Electroanalysis* 19 (2007) 1307.
58. P. Anker, E. Wieland, D. Ammann, R.E. Dohner, R. Asper, W. Simon, *Anal. Chem.* 53 (1981) 1970.
59. H.A. Zamani, M.R. Ganjali, F. Faridbod, and M. Salavati-Niasari, *Mater. Sci. Eng. C* 32 (2012) 564.
60. P.J.S. Smith, K. Hammar, D.M. Porterfield, R.H. Sanger, and J.R. Trimarchi, *Microscopy Research and Technique* 46 (1999) 348.
61. W.T. Bresnahan, C.L. Grant, J.H. Weber, *Anal. Chem.* 50 (1978) 1675.
62. S. Kamata, A. Bhale, Y. Fukunaga, and A. Murata, *Anal. Chem.* 60 (1998) 2464.
63. H. A. Zamani, M. Masrournia, H. Mohamadzadeh, M. R. Ganjali, M. Rahimizadeh, and P. Ziaei, *Mater. Sci. Engin. C* 29 (2009) 976.
64. M. Javanbakht, S. E. Fard, A. Mohammadi, M. Abdouss, M. R. Ganjali, P. Norouzi and L. Safaraliev, *Anal. Chim. Acta* 612 (2008) 65.
65. R.A. Saar, J.H. Weber, *Anal. Chem.* 52 (1980) 2095.
66. P. Bühlmann, E. Pretsch, and E. Bakker, *Chem. Rev.* 98 (1998) 1593.
67. V.P.Y Gadzekpo1, G.D Christian, *Analytica Chimica Acta* 164 (1984) 279.
68. U. Fiedler, J. Růžička, *Analytica Chimica Acta* 67 (1973) 179.
69. L. Liu, L. Wang, H. Yin, Y. Li, and X. He, *Analytical Letters* 39 (2006) 879.
70. N. N. Greenwood, A. Earnshaw, *Chemistry of the elements*, Pergamon (1984).
71. M. R. Ganjali, M. Tavakoli, F. Faridbod, S. Riahi, P. Norouzi, M. Salavati-Niassari, *Int. J. Electrochem. Sci.* 3 (2008) 1559.
72. H. A. Zamani, R. Kamjoo, M. Mohammadhossieni, M. Zaferoni, Z. Rafati, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 32 (2012) 447.

73. E. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Pungor, *Anal. Chim. Acta* 171 (1985) 119.
74. H. A. Zamani, M. Mohammadhossieni, Saeed Haji-Mohammadrezazadeh, F. Faridbod, M. R. Ganjali, S. Meghdadi, and A. Davoodnia, *Mater. Sci. Eng. C* 32 (2012) 712.
75. R. De Marco, G. Clarke, and B. Pejic, *Electroanalysis* 19 (2007) 1987.
76. J.E. Harwood, *Water Research*. 3 (1969) 273.
77. R.K Mahajan, I. Kaur, T.S. Lobana, *Talanta*. 59 (2003) 101.
78. H. A. Zamani, M. Rohani, M. Mohammadhosseini, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Sensor Lett.* 9 (2011) 1745.
79. J.S. Kim, A. Ohki, R. Ueki, T. Ishizuka, T. Shimotashiro, and S. Maeda, *Talanta* 48 (1999) 705
80. R.J. Levins, *Anal. Chem.* 43 (1971) 1045.
81. U. Schaller, E. Bakker, U.E. Spichiger, E. Pretsch, *Anal. Chem.* 66 (1994) 391.
82. H. A. Zamani, B. Feizyadeh, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 9 (2011) 1767.
83. E. Naddaf, and H. A. Zamani, *Anal. Lett.* 42 (2009) 2838.
84. M. Masrournia, H.A. Zamani, H.A. Mirrashid, M.R. Ganjali, and F. Faridbod, *Mater. Sci. Eng. C* 31 (2011) 574.
85. H. Yu Qin, S. Peper, and E. Bakker, *Electroanalysis* 14 (2002) 1375.
86. J.D.R. Thomas, *Analytica Chimica Acta* 180 (1986) 289.
87. H. A. Zamani, B. Feizyadeh, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 31 (2011) 1379.
88. K. Suzuki, H. Yamada, K. Sato, K. Watanabe, H. Hisamoto, Y. Tobe, K. Kobiro, *Anal. Chem.*, 65 (1993) 3404.
89. R.Y. Tsien, T.J. Rink, *Biochimica et Biophysica Acta (BBA) - Biomembranes.* 599 (1980) 623.
90. H. A. Zamani, A. Arvinfar, F. Rahimi, A. Imani, M. R. Ganjali, and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 307.
91. A. Craggs, L. Keil, G.J. Moody, J.D.R. Thomas, *Talanta* 22 (1975) 907.
92. H. A. Zamani, Fatemeh Naghavi-Reyabbi, M. Mohammadhossieni, Babak Feizyadeh, M. R. Abedi, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 10 (2012) 112.
93. H. A. Zamani, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 33 (2013) 608.
94. Sokalski, A. Ceresa, T. Zwickl, and E. Pretsch, *J. Am. Chem. Soc.* 119 (1997) 11347.
95. H. A. Zamani, F. Naghavi-Reyabbi, F. Faridbod, M. Mohammadhosseini, M. R. Ganjali, A. Tadjarodi, and M. Rad, *Mater. Sci. Eng. C* 33 (2013) 870.
96. H.A. Zamani, A. Zanganeh-Asadabadi, M. Rohani, M. S. Zabihi, J. Fadaee, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 33 (2013) 984.
97. R. W. Cattrall, H. Freiser, *Anal. Chem.* 43 (1971) 1905.
98. H. A. Zamani, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 33 (2014) 488.
99. J. F. Coetzee, W. K. Istone, *Anal. Chem.* 52 (1980) 53.
100. H. A. Zamani, and F. Faridbod, *J. Anal. Chem.* 69 (2014) 1073.
101. F. Mohammadabadi, H.A. Zamani, F. Joz-Yarmohammadi, and M.R. Abedi, *Int. J. Electrochem. Sci.* 10 (2015) 2791
102. R. W. Cattrall, P. Chin-Poh, *Anal. Chem.* 47 (1975) 93.
103. H.A. Zamani, M. Ranjkesh, and M.R. Abedi, *Int. J. Electrochem. Sci.* 9 (2014) 8435.
104. E. Bakker, P. Bühlmann, and E. Pretsch, *Chem. Rev.* 97 (1997) 3083.
105. A. Fitch, F.J. Stevenson, Y. Chen, *Organic Geochemistry* 9 (1986) 109.
106. A. Dehnavi, and H.A. Zamani, *Int. J. Electrochem. Sci.* 9 (2014) 8273.
107. E. Hatami, H.A. Zamani, and R. Sanavi-Khoshnod, *Int. J. Electrochem. Sci.* 9 (2014) 8263.
108. S. Matysik, F. M. Matysik, J. Mattusch, and W. D. Einicke, *Electroanalysis* 10 (1998) 57.
109. A. Craggs, G. J. Moody, and J. D. R. Thomas, *J. Chem. Educ.* 51 (1974) 541.
110. M.R. Abedi, and H. A. Zamani, *E-J. Chem.* 8 (2011) S467.
111. S. Karimian, H. A. Zamani, and M. Vahdani, *Int. J. Electrochem. Sci.* 8 (2013) 2710.
112. S.L. Belli, A. Zirino, *Anal. Chem.* 65 (1993) 2583.

- 113.M. Vahdani, H. A. Zamani, and S. Karimian, *Int. J. Electrochem. Sci.* 8 (2013) 2734.
114.Y. Umezawa, K. Umezawa, and H. Sato, *Pure Appl. Chem.* 67 (1995) 507.

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