Evaluation of a wide rim phosphorylated calix[4]arene's properties as a sensory molecule in an Er(III)-PVC membrane sensor

Abbas Ali ZAMANI[1], **Massoumeh PARINEJAD**[1], **Fataneh JAMALI**[1],
Mohammad Reza YAFTIAN[1,*], **Dominique MATT**[2]

[1]*Phase Equilibria Research Laboratory, Department of Chemistry, Faculty of Science,*
University of Zanjan, Zanjan–IRAN
e-mail: yaftian@znu.ac.ir
[2]*Laboratory of Inorganic Molecular Chemistry, Louis Pasteur University,*
Strasbourg–FRANCE

This study concerns the evaluation of ionophoric properties of a functionalized calix[4]arene, named 5,17-bis(diphenylphosphinoyl)-25,26,27,28-tetrapropoxycalix[4]arene (*Calix*), by its application as a sensing material in an erbium(III)-PVC membrane potentiometric sensor. A membrane formed by 30% PVC, 65% dioctyl phthalate (DOP) as plasticizing solvent mediator, 2% sodium tetraphenyl borate (NaTPB) as ion excluder, and 3% of *Calix* as ionophore shows the best performance of the sensor. The prepared sensor presents a nearly Nernstian response (a slope of 20.0 ± 0.5 mV/decade) over a concentration range of 1×10^{-7}–1×10^{-3} M of erbium ions, with a limit of detection of 3.8×10^{-8} M. Its potential response was independent of pH variation in the relatively wide range 4.5–6.5. The dynamic response time of the electrode to achieve a steady potential was found to be about 7 s. The selectivity of the sensor towards erbium ions with respect to several mono-, di-, tri-, and tetravalent metal ions was examined. The prepared sensor can be used for 3 months without considerable divergences in potential response. The performance of the sensor was examined as an indicator electrode for complexometric titration of erbium solutions by EDTA.

Key Words: Phospha-calix[4]arene, ion binding properties, Er(III), potentiometric sensor

Introduction

Calixarenes are a group of macrocyclic compounds formed via phenol-formaldehyde condensation. They are important ion receptors due to their ease of synthesis and multiple sites for functionalization giving access to

---

*Corresponding author

a wide variety of multifunctional ligands suitable in host–guest chemistry studies, preparation of homogeneous catalysis, and also in their applications as phase transfer agents.[1]

Among the methods applied for evaluation of the ion binding properties of macrocyclic ionophores are their uses as sensing materials in membrane potentiometric sensors.[2] These analytical tools are important because they are powerful, versatile, rapid, simple, and low cost for application in clinical and environmental analysis.[3] Both non-functionalized and functionalized calixarenes have been used as potent ionophores for preparation of ion-selective sensors.[4−10]

It is well known that phosphoryl groups are suitable for complexation of lanthanides and actinides.[11] Particular interest has been devoted to the use of calixarenes bearing phosphine oxide functionalities that create a pseudo-cavity suitable for metal ion complexation.[12−20] A comparative study on the binding properties of a phosphorylated calixarene and tri-n-octylphosphine oxide shows the significant effect of the macrocyclic platform on the selectivity presented by the ligands.[14] It is noteworthy that calixarenes with P^V-containing substituents have been used in the fabrication of various ion-selective electrodes.[21,22]

The toxicity of erbium is not verified in detail, but it shows low to moderate toxicity. While erbium stimulates metabolism, it does not play a biological role.[23−25] Nevertheless, erbium and other rare earths are fission products and therefore their monitoring and determination are important. Various methods and techniques such as voltammetry,[26] spectrophotometric method,[27] secondary ion mass spectrometry,[28] Rutherford back-scattering technique,[29] and spectrofluorometric method[30] have been investigated for the determination of erbium(III) ions.

Although a great number of lanthanide sensors have been designed and fabricated and their applicability has been investigated,[31−42] there are few reports on the preparation of erbium(III) ion-selective sensor and the first one was published in 2006.[43−48]

Following our studies on the ion binding properties of phosphorylated calixarenes towards lanthanides and actinides[14−20] and their use as sensory molecules in ion-selective electrodes,[49−52] the present work verifies the applicability of a wide rim phosphorylated calix[4]arene (Figure 1) named 5,17-bis(diphenylphosphinoyl)-25,26,27,28-tetrapropoxycalix[4]arene (*Calix*). To the best of our knowledge the present work is the first report on the application of a calix[4]arene for fabrication of an Er(III) potentiometric sensor.
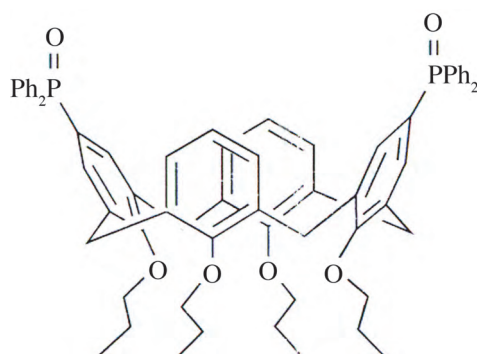

Figure 1. 5,17-Bis(diphenylphosphinoyl)-25,26,27,28-tetrapropoxycalix[4]arene (*Calix*).

Experimental

Reagents

5,17-Bis(diphenylphosphinoyl)-25,26,27,28-tetrapropoxycalix[4]arene (*Calix*) was synthesized according to the procedure report previously.[53] Benzylacetate (BA), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), acetophenone (AP), dioctyl phthalate (DOP), 1,2-dichloroethane, and high relative molecular weight polyvinyl chloride (PVC), *ortho*-nitrophenyloctyl ether (NPOE), and metal nitrate salts were analytical reagent grade (Merck or Fluka) and were used as received.

Extraction procedure

Extraction experiments were carried out in stoppered glass tubes immersed in a thermostated water bath (25.0 $\pm$ 0.1 °C) using equal volumes (10 mL) of organic and aqueous phases. The extraction equilibrium was reached after 30 min under continuous magnetic stirring. Then the 2 phases were separated with the aid of centrifugation. The organic phase was stripped with a 0.025 M aqueous solution of nitric acid. It is noteworthy that X-ray fluorescence analysis on the evaporated stripped organic phase showed that the stripping is quantitative under these conditions. Rare earth ion concentrations were analyzed using a Varian-Liberty 200ICP/AES instrument.

Electrode preparation and potential measurements

The general procedure for preparing the membranes involved mixing the optimized quantity of membrane constituents, including PVC powder, ionophore (*Calix*), plasticizer, and anion excluder in 5 mL of THF. This mixture was mixed well and it was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s. A transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. It was then filled with the internal solution (erbium nitrate, 1×10^{-3} M). The prepared membrane was finally conditioned for 48 h by soaking in a 1×10^{-3} M solution of $Er(NO_3)_3$. A pH-meter (Metrohm, model 780) was used for potential and pH measurements. All pH adjustments were made with nitric acid and sodium hydroxide solutions. A silver/silver chloride reference electrode was used for potential measurements at 25.0 $\pm$ 0.1 °C. All potential measurements were performed using the following assembly:

Ag, AgCl (sat'd)/internal soln. (Er(III), 1×10^{-3} M)/PVC membrane/test soln./Ag, AgCl (sat'd.)

Results and discussion

Solvent extraction experiments

As there was no report on the binding ability of the studied calixarene towards rare earth metal ions, in a preliminary experiment liquid–liquid extraction of 11 rare earth ions, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}, and Y^{3+} (1×10^{-3} M of each of the cations), from nitrate solution (1 M, $Al(NO_3)_3$)

into a 1,2-dichloroethane solution of *Calix* (2×10^{-3} M) was performed. The results (Figure 2) show a suitable binding ability of the calix[4]arene towards heavier lanthanides with respect to lighter lanthanides. However, the selectivity presented by *Calix* among the heavier lanthanides Dy^{3+}, Ho^{3+}, Er^{3+}, and Yb^{3+} is significantly better for erbium ions. It is well known that, except for the ionophore properties of an ion sensing material, constituents can improve the selectivity presented by a potentiometric sensor. This motivates us to investigate the applicability of the studied calixarene as a sensing molecule in an Er(III) ion-selective electrode.
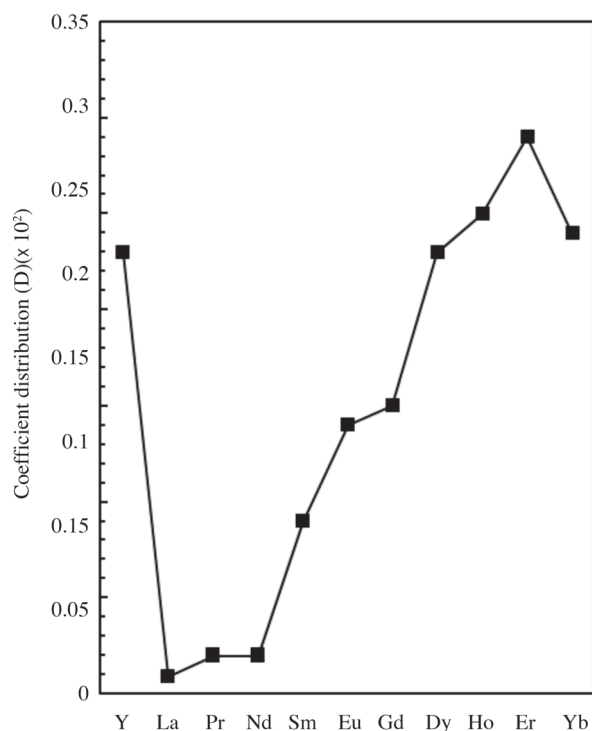

Figure 2. Results of competitive solvent extraction of 11 rare earth ions from aluminum nitrate aqueous solution (1 M) into a 1,2-dichloroethane solution of *Calix* (2×10^{-3} M) at 25 °C.

Membrane composition

Fifteen electrodes were prepared by using various amounts of PVC, plasticizer (AP, BA, DOP, and NPOE), ionophore (*Calix*), and additive (NaTPB). The potential variation as a function of the logarithm of the erbium concentration between 1×10^{-9} and 1×10^{-2} M was investigated. The studied compositions with the corresponding slopes, found for the linear part of the curves, are given in Table 1.

As an example, Figure 3 shows the potential response of the membrane (composition 7) at various concentration of Er(III) ions. The membrane with a composition of 30% PVC, 65% DOP, 3% *Calix*, and 2% NaTPB indicates a rectilinear range in 1×10^{-7} to 1×10^{-3} M. The slopes of the calibration curves were 20.0 ± 0.5 mV per decade of Er(III) concentration (for 4 electrodes). This composition was used throughout the work. The detection limit as determined from the intersection of 2 extrapolated segments of the calibration graph was found as 3.8×10^{-8} M.

Table 1. Examined ingredients composition of the membrane.[a]

| No. | PVC | Plasticizer[b] | | Calix | NaTPB[c] | Slope | Linear range |
		Amount	Type[b]			(mV decade^{-1})	(M)
1	30	55	NPOE	10	5	59.0	10^{-5}–10^{-3}
2	30	60	NPOE	5	5	60.1	10^{-5}–10^{-3}
3	30	63	NPOE	5	2	46.2	10^{-5}–10^{-3}
4	30	65	NPOE	5	0	41.1	10^{-4}–10^{-2}
5	33	66	NPOE	2	0	40.4	10^{-4}–10^{-2}
6	30	65	NPOE	3	2	17.9	10^{-7}–10^{-3}
7	30	65	DOP	3	2	20.4	10^{-7}–10^{-3}
8	30	62	DOP	5	3	27.1	10^{-4}–10^{-2}
9	30	60	DOP	8	2	25.1	10^{-4}–10^{-2}
10	30	62	DOP	5	3	25.0	10^{-4}–10^{-2}
11	30	65	DOP	3	3	41.0	10^{-4}–10^{-2}
12	30	66	DOP	2	2	16.3	10^{-4}–10^{-2}
13	30	65	AP	5	0	14.4	10^{-4}–10^{-2}
14	30	65	BA	5	0	12.3	10^{-4}–10^{-2}
15	30	65	DBP	3	2	26.0	10^{-4}–10^{-2}

[a] Values in percent (%) , [b] NPOE: *O*-nitrophenyloctyl ether, AP: acetophenone, BA: benzylacetate, DOP: dioctyl phthalate, DBP: dibutylphetalate, [c] NaTPB: sodium tetraphenylborate. The membrane conditions are the same as those of composition 7 in Table 1.

Effect of pH

Potential response dependency of the sensor on pH of the solution containing 1×10^{-5} M of erbium(III) ion in the range of 2–11 was investigated (Figure 4).

The potential is independent of pH in the range 4.5–6.5. The decrease in potential values out of this range can be attributed to the formation of erbium hydroxide at the higher pHs, while at the values lower than 4.5 the potential decreases. The latter may be due to the dissolution of the electrode surface in such media.

Dynamic response time

One of the important factors showing the performance of a potentiomeric sensor is its dynamic response time. For evaluating the response time of the prepared electrode, the potential of a stirred solution with an initial Er(III) concentration of 1×10^{-7} M as a function of time by a stepwise change of the metal ion concentration up to 1×10^{-3} M was determined (Figure 5). The response time of the steps varies between 5 and 8 s, depending on the concentration of the test solution.
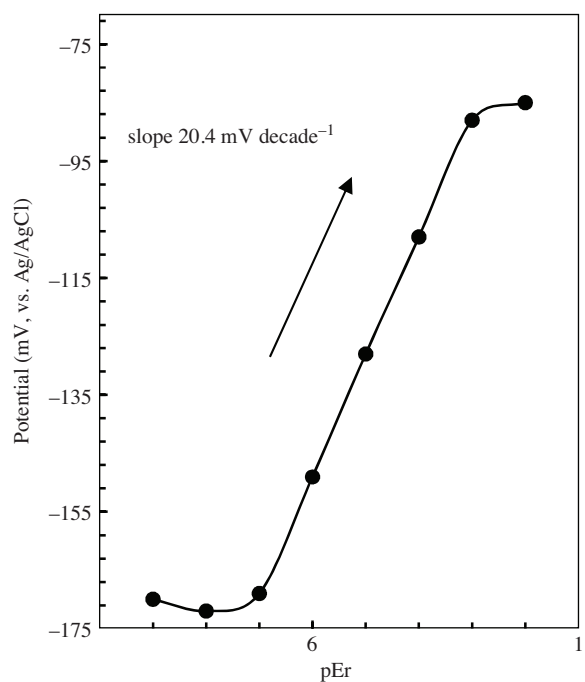
Figure 3. Potential response of the electrode prepared with a composition including 30% PVC, 65% DOP, 2% NaTPB, and 3% of *Calix* (composition 7 in Table 1).
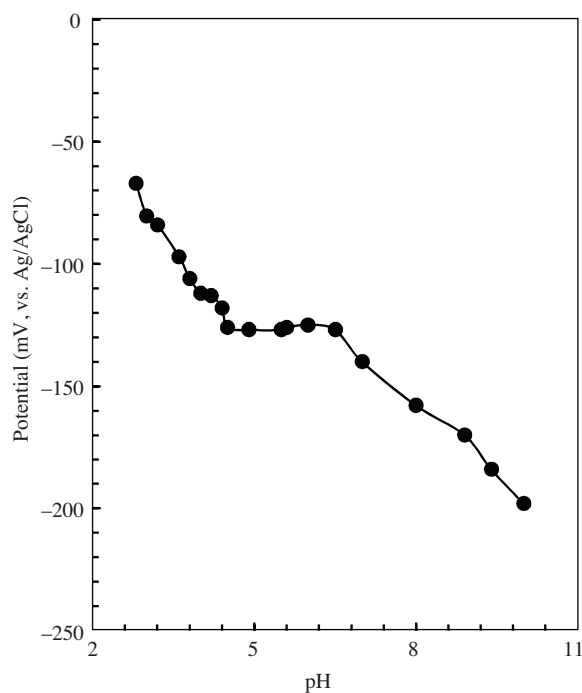
Figure 4. Potential response of the prepared Er(III)-ISE as a function of the pH of sample solutions (1×10^{-5} M of Er(III)). The membrane conditions are the same as those shown in Figure 3.

Lifetime of the electrode

The electrode's lifetime was studied by periodical re-calibration of the electrode response versus log[Er(III)] over the concentration range 1×10^{-7}–1×10^{-3} M of Er(NO$_3$)$_3$, each week over 3 months. The slope remained nearly constant (20.1 $\pm$ 1.5 mV per decade), indicating adequate stability. The electrode was stored in air and re-conditioned with 0.001 M erbium nitrate solution for about 48 h before use. The average response time was calculated to be less than 7 s.

Selectivity of the electrode

Selectivity of the electrode towards erbium ions over some mono-, di-, tri-, and tetravalent ions was tested using the match potential method.[54] In this method a specified amount of the analyte (here Er(III)) is added to a reference solution with a given concentration (25 mL of 1×10^{-4} M Er(NO$_3$)$_3$) and the potential is measured. In other experiments a quantity of the interfering ion (M^{n+}) is gradually introduced to an identical reference solution of Er(III), as before, until the potential equals the potential of the preceding solution. The selectivity coefficient ($K_{Er,M}^{MPM}$) can be obtained as the added Er(III) over added M^{n+} concentrations to the reference solution. Monovalent (Li$^+$, Na$^+$, K$^+$, Ag$^+$, and NH$_4^+$), divalent (Sr^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, and Fe^{2+}), trivalent (Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+},

Dy^{3+}, Ho^{3+}, and Y^{3+}), and tetravalent (Th^{4+}) ions were tested as interfering ions. The resulting selectivity coefficients are presented in Table 2.

Table 2. Selectivity coefficient of the sensor measured using the match potential method.[a]

M^{n+}	$K_{Er,M}^{MPM}$	M^{n+}	$K_{Er,M}^{MPM}$	M^{n+}	$K_{Er,M}^{MPM}$
Li^+	1.04×10^{-3}	Co^{2+}	2.88×10^{-3}	Pr^{3+}	2.78×10^{-3}
Na^+	1.12×10^{-3}	Ni^{2+}	2.19×10^{-3}	Nd^{3+}	3.42×10^{-3}
K^+	0.87×10^{-3}	Cu^{2+}	2.36×10^{-3}	Sm^{3+}	7.32×10^{-3}
Ag^+	0.91×10^{-3}	Zn^{2+}	1.96×10^{-3}	Eu^{3+}	1.05×10^{-2}
NH_4^+	1.17×10^{-3}	Cd^{2+}	0.94×10^{-3}	Gd^{3+}	1.30×10^{-2}
Sr^{2+}	1.38×10^{-3}	Mn^{2+}	2.42×10^{-3}	Dy^{3+}	3.25×10^{-2}
Ca^{2+}	2.21×10^{-3}	Fe^{2+}	2.83×10^{-3}	Ho^{3+}	2.96×10^{-2}
Mg^{2+}	1.23×10^{-3}	Y^{3+}	2.88×10^{-2}	Yb^{3+}	3.18×10^{-2}
Ba^{2+}	0.89×10^{-3}	La^{3+}	3.36×10^{-3}	Th^{4+}	4.17×10^{-3}

[a]The membrane conditions are the same as those of composition 7 in Table 1.
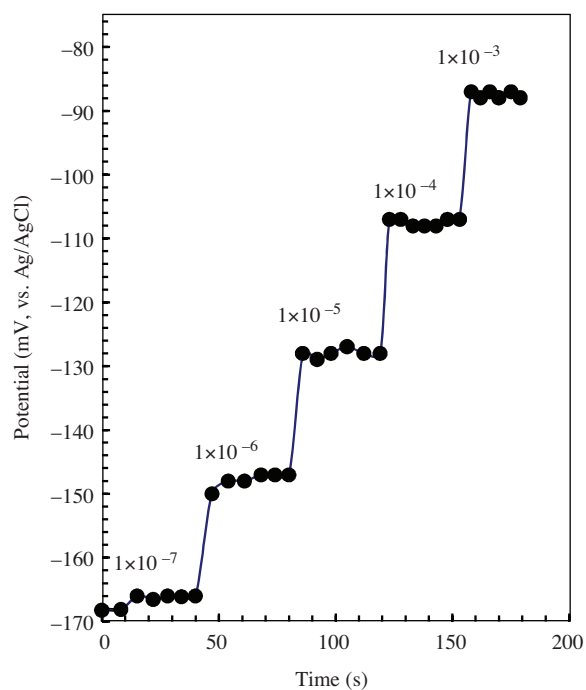

Figure 5. Dynamic response time of the prepared Er(III)-ISE by stepwise addition of the concentration of Er(III). The membrane conditions are the same as those shown in Figure 3.
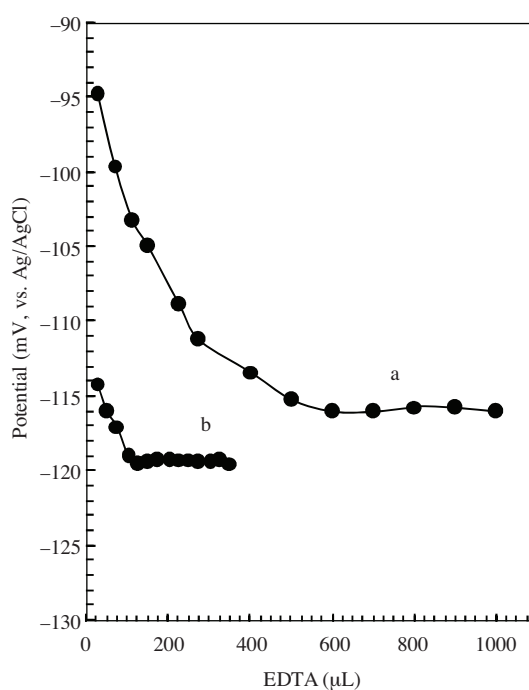

Figure 6. Application of the sensor as an indicator for potentiometric titration of a Er(III) ion solution ((a) 10 mL of 5×10^{-4} M, (b) 25 mL of 5×10^{-5} M) with a solution of EDTA (0.01 M) at pH 5. The membrane conditions are the same as those of composition 7 in Table 1.

Based on the results presented in Table 2, the sensor shows suitable selectivity towards the examined ions. The selectivity coefficients are of the order 10^{-3}, revealing that the Er^{3+} ions can be determined in the presence of most common metal ions. As expected, the selectivity of the electrode towards erbium ions was less pronounced with respect to some examined lanthanides.

Analytical application of the electrode

The prepared sensor was used as indicator electrode for potentiometric titration of erbium solutions (10 mL of 5×10^{-4} M and 25 mL of 5×10^{-5} M $Er(NO_3)_3$) by standard solution of EDTA (0.01 M). The potentiometric curves are presented in Figure 6. The curves show that the electrodes can be used successfully for determination of erbium ions in such complexometric titrations.

Conclusions

This study shows a further ability of phosphoryl substituted calixarenes towards rare earth ions. The examined calixarene 5,17-bis(diphenylphosphinoyl)-25, 26, 27, 28-tetrapropoxycalix[4]arene (*Calix*) shows a good tendency to bind erbium ions, allowing its use as a sensory molecule for fabricating an Er(III) potentiometric sensor. The prepared electrode demonstrates a good selectivity towards erbium ions over some mono-, di-, tri-, and tetravalent metal ions. The excellent stability of the prepared sensor (more than 3 months) can be attributed to the highly lipophilic nature of the ionophore. The electrode is used successfully as an indicator electrode in the complexometric titration of erbium ion solutions with EDTA.

References

1. Sliwa, W.; Kozlowski, C. *Calixarenes and Resorcinarenes: Synthesis, Properties and Applications*, Wiley-VCH, Weinheim, 2009.

2. Zolotov, Y. A. *Macrocyclic Compounds in Analytical Chemistry*, Wiley, New York, 1997.

3. Bakker, E.; Bühlmann, P.; Pretsch, E. *Chem. Rev.* **1998**, *98*, 1593–1687.

4. Kimura, K.; Matsuo, M.; Chono, T. *Chem. Lett.* **1988**, 615–617.

5. Kimura, K.; Miura, T.; Matsuo, M.; Shono, T. *Anal. Chem.* **1990**, *62*, 1510–1513.

6. O'Connor, K. M.; Cherry, M.; Svehla, G.; Harris, S. J.; McKervey, M. A. *Talanta* **1994**, *41*, 1207–1217.

7. Cadogan, F.; Kane, P.; McKervey, M. A.; Diamond, D. *Anal. Chem.* **1999**, *71*, 5544–5550.

8. Kim, J. S.; Ohaki, A.; Ueki, R.; Ishizuka, T.; Shimotashiro, T.; Kaeda, S. *Talanta* **1999**, *48*, 705–710.

9. Ramkumar, J.; Matti, B. *Sens. Actuators B* **2003**, *96*, 527–532.

10. Lu, J.; Chen, R.; He, X. *J. Electroanal. Chem.* **2002**, *528*, 33–38.

11. Horwitz, E. P.; Chiarizia, R. *Separation Techniques in Nuclear Waste Management*; Chipmen, N. A.; Wai, C. M. (Eds.), CRC, Boca Raton, FL, 1996.

12. Harrowfield, J. M.; Mocerino, M.; Peachey, B. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc. Dalton Trans.* **1996**, 1687–1699.

13. Arnaud-Neu, F.; Browne, J. K.; Byrne, D.; Marrs, D. J.; McKervey, M. A.; O'Hagan, P.; Schwing-Weill, M. J.; Walker, A. *Chem. Eur. J.* **1999**, *5*, 175–186.

14. Yaftian, M. R.; Burgard, M.; Matt, D.; Dieleman, C. B.; Rastegar, F. *Solvent Extr. Ion Exch.* **1997**, *15*, 975–989.

15. Yaftian, M. R.; Burgard, M.; Wieser, C.; Dieleman, C. B.; Matt, D. *Solvent Extr. Ion Exch.* **1998**, *16*, 1131–1149.

16. Yaftian, M. R.; Burgard, M.; Dieleman, C. B.; Matt, D. *J. Membr. Sci.* **1998**, *144*, 57–64.

17. Yaftian, M. R.; Vahedpour, M.; Burgard, M.; Matt, D. *Iran. J. Chem. Chem. Eng.* **2000**, *19*, 60–64.

18. Yatian, M. R.; Taheri, R.; Matt, D. *Phosphorus, Sulfur and Silicon* **2003**, *178*, 1225–1230.

19. Yaftian, M. R.; Vahedpour, M. *Phosphorus, Sulfur and Silicon* **2001**, *174*, 93–100.

20. Yaftian, M. R.; Razipour, M. R.; Matt, D. *J. Radioanal. Nucl. Chem.* **2006**, *270*, 357–361.

21. McKittrick, T.; Diamond, D.; Marrs, D. J.; O'Hagan, P.; McKervey, M. A. *Talanta* **1996**, *43*, 1145–1148.

22. Cadogan, F.; Kane, P.; McKervey, M. A.; Diamond, D. *Anal. Chem.* **1999**, *71*, 5544–5550.

23. www.lentech.com/periodic/elements

24. www.environmentalchemistry.com/yogi/periodic

25. www.en.wikipedia.org/wiki/erbium

26. Zakharov, M. S.; Vorobeva, E. V. *Zh. Anal. Khim.* **1994**, *49*, 875–878.

27. Wang, N. X.; Si, Z. K.; Yang, W.; Liang, W. A.; Li, G. Y.; Du, G. Y.; Zhang, G. *Michrochim. Acta* **1997**, *127*, 71–75.

28. Holzbrecher, H.; Brever, U.; Gastel, M.; Becker, J. S.; Dietze, H. J.; Beckers, I.; Bauer, S.; Elenster, M.; Zander, W.; Schubeat, J.; Buehar, C. *Fresenius J. Anal. Chem.* **1995**, *383*, 785–788.

29. Perina, V.; Vaick, J.; Hnatowicz, V.; Cerena, J.; Kolarova, P.; Spirkova-Heradilova, J.; Schrofel, *J. Nucl. Instrum. Methods Phys. Res.* **1998**, *139*, 208–212.

30. Biju, V. M.; Rao, T. P. *Anal. Sci.* **2001**, *17*, 1343–1347.

31. Grady, T.; Maskula, S.; Diamond, D.; Marrs, D. J.; McKervey, M.; O'Hagan, P. *Anal. Proc.* **1995**, *32*, 471–473.

32. Gupta, V. K.; Jain, S.; Chandra, S. *Anal. Chim. Acta* **2003**, *486*, 199–207.

33. Ito, T.; Goto, C.; Noguchi, K. *Anal. Chim. Acta* **2001**, *443*, 41–51.

34. Shamsipur, M.; Yousefi, M.; Hosseini, M.; Ganjali, M. R. *Anal. Chem.* **2002**, *74*, 5538–5543.

35. Khalil, S. *Anal. Lett.* **2003**, *36*, 1335.

36. Ganjali, M. R.; Ravanshad, J.; Hosseini, M.; Salavati-Niasari, M. R.; Pourjavid, M. R.; Baezzat, M. R. *Electroanalysis* **2004**, *16*, 1771–1776.

37. Ganjali, M. R.; Rasoolipour, S.; Rezapour, M.; Norouzi, P.; Tajarodi, Y. *Electroanalysis* **2005**, *17*, 1534–1539.

38. Ganjali, M. R.; Rasoolipour, S.; Rezapour, M.; Norouzi, P.; Amirnasr, M.; Meghdadi, S. *Sens. Actuators B* **2006**, *119*, 89–93.

39. Behmadi, H.; Zamani, H. A.; Ganjali, M. R.; Norouzi, P. *Electrochim. Acta* **2007**, *53*, 1870–1876.

40. Ganjali, M. R.; Shams, H.; Faridbod, F.; Hajiaghababaei, L.; Norouzi, P. *Mater. Sci. Eng. C* **2009**, *29*, 1380–1385.

41. Zamani, H. A.; Nekoei, M.; Mohammadhosseini, M.; Ganjali, M. R. *Mater. Sci. Eng. C* **2010**, *30*, 480–483.

42. Zamani, H. A.; Feizyzadeh, B.; Faridbod, F.; Ganjali, M. R. *Mater. Sci. Eng. C* **2011**, *31*, 1379–1382.

43. Ganjali, M. R.; Faridbod, F.; Norouzi, P.; Adib, M. *Sens. Actuators B* **2006**, *120*, 119–124.

44. Ganjali, M. R.; Rezapour, M.; Rasoolipour, S.; Norouzi, P.; Adib, M. *J. Braz. Chem. Soc.* **2007**, *18*, 352–358.

45. Faridbod, F.; Ganjali, M. R.; Lrijani, B.; Norouzi, P.; Riahi, S.; Mirnaghi, F. S. *Sensors* **2007**, *7*, 3119–3135.

46. Nekoei, M.; Zamani, H. A.; Mohammadhosseini, M. *Anal. Lett.* **2009**, *42*, 284–293.

47. Farbod, F.; Ganjali, M. R.; Larijani, B.; Norouzi, P. *Electrochim. Acta* **2009**, *55*, 234–239.

48. Zamani, H. A.; Mohammadhosseini, M.; Haj-Mohammadrezazadeh. S.; Faridbod, F.; Ganjali, M. R.; Meghdadi, S.; Davoodnia, A. *Mater. Sci. Eng. C* **2012**, *32*, 712–717.

49. Yaftian, M. R.; Rayati, S.; Emadi, D.; Matt, D. *Anal. Sci.* **2006**, *22*, 1075–1079.

50. Hassanzadeh, P.; Yaftian, M. R.; Bahari, Z.; Matt, D. *J. Chin. Chem. Soc.* **2006**, *53*, 1113–1118.

51. Parsa, M.; Yaftian, M. R.; Matt, D. *J. Chin. Chem. Soc.* **2007**, *54*, 1529–1534.

52. Yaftian, M. R.; Parinejad, M.; Matt, D. *J. Chin. Chem. Soc.* **2007**, *54*, 1535–1542.

53. Wiser-Jeunesse, C.; Matt, D.; De Cian, A. *Angew. Chem.* **1998**, *37*, 2861–2864.

54. Umezawa, Y.; Umezawa, K.; Sato, H. *Pure Appl. Chem.* **1995**, *67*, 507–518.