Electrochemical behaviours of Eu(III)/E(II) and Ce(IV)/Ce(III) in H_3PO_4-H_2O media : solvation and complexation reactions

B. Belqat[1,2] and S. Belcadi[2]

[1] Laboratoire de Chimie Appliquée des Matériaux, Université Mohammed V, Faculté des Sciences, Rabat, Morocco
[2] Laboratoire d'électrochimie et Chimie Analytique, Université Mohammed V, Faculté des Sciences, Rabat, Morocco

Abstract. Many kinds of rare earth elements (REE) such as europium and cerium have been make them essential elements in many high-tech components. The electrochemical studies can be presented as an interesting indication for europium and cerium extraction from phosphoric solutions, including solvation and complexation reactions. The normal redox potentials of Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} systems have been determined in H_3PO_4-H_2O media with various phosphoric acid concentration. The solvation of these elements in phosphoric media is characterized by their transfer activity coefficients "f" calculated from the corresponding normal redox potentials. The corresponding solvation increases with increasing the H_3PO_4 concentration. For each REE, the electrochemical properties depend on its number of charges and on its basic properties. Results suggest that solvation and complexation of REE phosphates are important in controlling REE concentration.

1 Introduction

Rare earth elements (REE) are particularly important to emerging technologies in green energy, defense and electronic industries [1-3]. Generally, they are present in sedimentary phosphate deposits, consequently in phosphoric acid. Various phosphoric acid solutions are produced from phosphate ores before fertilizer-grade phosphoric acid using an industrial processing and contain valuable quantities of rare earths elements; hence, it is considered as secondary source for rare-earth elements [4-6]. Only a small proportion of REE deposits are of sufficient size and concentration that they can be exploited economically using existing technology [7]. Rare earth elements exist in phosphorite deposits, which should be extracted using various methods [8-11]. Systematic solvent extraction of rare earths from phosphoric acid by specific reagents aiming to form strong soluble complexes was reported in the literature [12-14]. However, their chemical properties depend not only on their atomic structure, but also on their size and charge.

For the development of a process to extract europium and cerium from phosphoric acid with high current efficiency, it is necessary to understand their electrochemical behavior in produced various phosphoric solutions, which are less developed [15-17]. The acidity function $R_0(H)$ allows to anticipate the thermodynamic constant evolution in phosphoric solutions, involving evening out a concentration gradient and evenly distributing the solute within the water and phosphoric solvents. The improvement of the successive stages in the industrial process to extract europium and cerium from phosphoric solution is possible if the thermodynamic properties such as water activity and solvation properties are known [18-19]. For resolving the solvation properties of Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} systems in phosphoric media, the electrochemical study of various concentrations of H_3PO_4 solutions containing the europium and cerium was carried out to determine the reactivity of these species and their solvation in phosphoric acid. This study intends to highlight the most important characteristics of europium and cerium controlling its behavior in H_3PO_4-H_2O media and so closely connected to its electrochemical properties.

2 Theoretical aspects

The solvation transfer coefficients characterize the changes of REE ion reactivity in phosphoric acid-water and consequently help to extract them. Variations of solute solvation are characterized by means of the solvation transfer activity coefficients "f" [20-22].

When f > 1 (or log f > 0) signifies that the REE ion is less solvated in H_3PO_4-H_2O than in pure water; but when f < 1 (or log f < 0) the REE specie is more solvated in the phosphoric solution. The coefficients "f" are calculated from standard potential values of the corresponding redox systems according to the equations (1) and (2):

$$M^{n+}/M \; : \quad \log f\left(M^{n+}\right) = \frac{n\left(E_o^A - E_o^W\right)}{0.058} \qquad (1)$$

$M^{n+}/M^{(n-m)+}$: $\log f\left(M^{n+}/M^{(n-m)+}\right) = \dfrac{m\,(E_o^A - E_o^W)}{0.058}$ (2)

Where: E_0^w represents the normal potential of the considered redox system in water, E_0^A is its value in a phosphoric medium characterized by the acidity function $R_0(H)$ and the water activity a_{H2O} [22-23], M the metal, M^{n+} the metal cation and n the number of electrons exchanged in the redox reaction. Both are referred to the Ferrocene (Fc^+/Fc) as reference system.

3 Experimental

Different H_3PO_4-H_2O solutions are prepared using phosphoric acid (85%) (Riedel De Haen, pure for Analysis). Europium and Cerium ions are introduced in each phosphoric solution by the dissolution of their pure Eu_2O_3 and Ce_2O_3 oxides. Ce^{4+}/Ce^{3+} and Eu^{3+}/Eu^{2+} ions are studied by cyclic voltammetric (potentiostat galvanostat Tacussel type PGS201T**)** and polarographic method (polaroprocesseur type Pol 150 Polarographic Analyser). The dough of carbon electrode allows covering a large potential area until 2.6 V from -1,0V to 1,6V for large H_3PO_4 concentrations.

To avoid chloride diffusion between the reference electrode and the solution cell, the saturated calomel electrode was connected to the work cell by a capillary, which contained 0.1 M H_3PO_4. During experiments, bubbling of nitrogen was maintained through the solution to avoid the presence of dissolved oxygen. The manufacturing of dough of carbon electrode is made as follows: a known amount of the studied compound was mixed with the graphite powder and the ligand conductor. A mixture of 0.4 - 1.0 mg as electroactif compound, 50 mg of carbon and 40 mg of electrolyte is compressed into glass tube, in which the bottom of vitreous carbon insures the electrical contact. The whole is covered with a fine silica layer or a sintered glass to avoid the dispersion of the dough.

The normal potentials of Eu^{3+}/Eu^{2+}, Ce^{4+}/Ce^{3+} and Fc^+/Fc systems were measured at 25°C by reference to the SCE electrode in a separate compartment containing 0.1M H_3PO_4, where the redox potentials were reported versus Fc^+/Fc electrode at 25°C.

The normal potential values of Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} systems were determined directly by using a cyclic voltammetry and polarographic methods respectively as a function of phosphoric concentration (from 0.1 to 14.8 M). The values of acidity function $R_0(H)$ are calculated on the basis of measurements of the hydrogen electrode potential versus the Fc^+/Fc system.

4 Results

Oxidation and reduction processes play a main role in Eu and Ce rare earth elements chemistry requiring many chemical reactions. Their redox potentials can be used to predict the ionic distribution into solution, which may

interact with the transfer of electrons. Normal and half-wave potentials of the both redox couples are considered equal, while the diffusion coefficients of cations are similar in the solution and amalgam accompanied with rapid reactions with the transfer number equals to 1. Figure 1 shows a typical cyclic voltammograms for the reversible oxidation and reduction of Ce(IV)/Ce(III) system using gold and carbon electrodes.
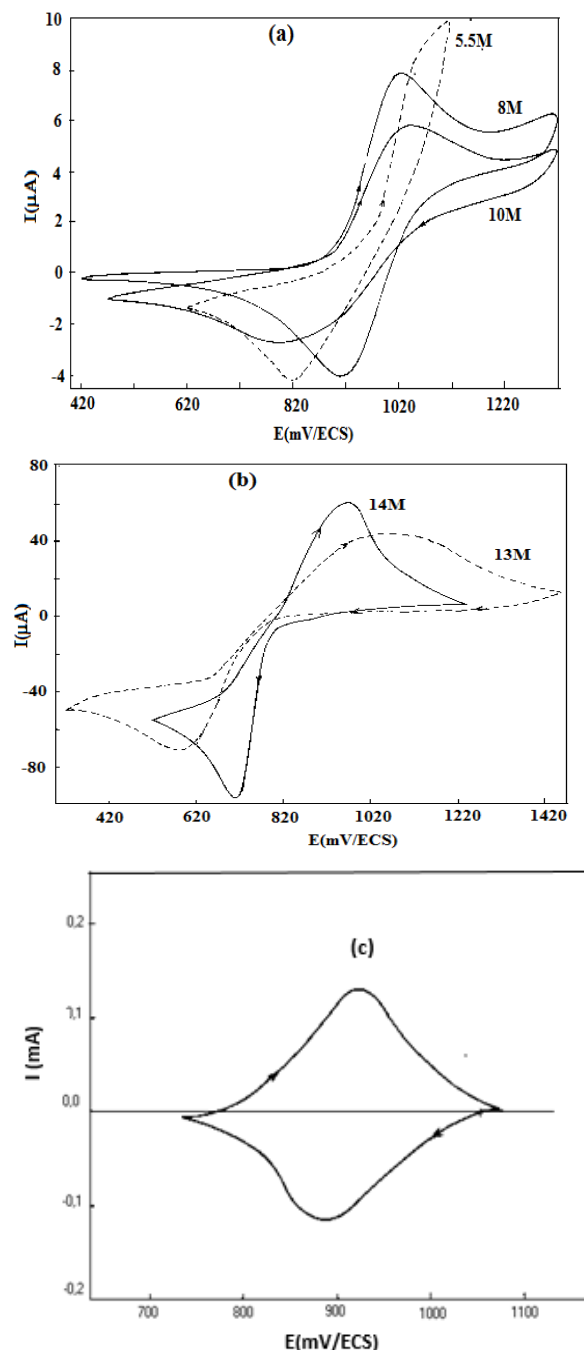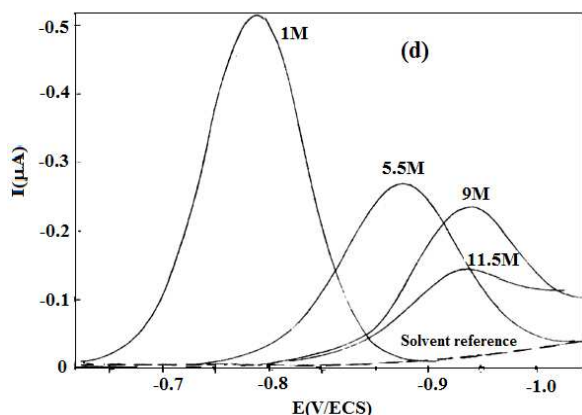
Fig.1. A typical cyclic voltammograms of current verses potential for Ce(IV)/Ce(III) system in (a) medium H_3PO_4 concentration (gold electrode, $[Ce^{3+}]=5.10^{-3}M$, V=20mV/s, initial potential ≈790 mV), (b) high H_3PO_4 concentration (gold electrode, $[Ce^{3+}]=5.10^{-3}M$, V=20mV/s, initial potential ≈790 mV), (c) 8M H_3PO_4 with carbon paste electrode, V=0,5 mV/s and the initial potential of 1050 mV and (d) Pulse polarograms for Eu(III)/Eu(II) system in H_3PO_4 media ($C_{Eu(III)} = 10^{-3}$ M and V = 10 mV/s).

The change in electrochemical behavior of Eu(III)/Eu(II) and Ce(IV)/Ce(III) in the function of H_3PO_4 concentration or with $R_0(H)$ are plotted in figure 2. The potential of each reaction depends upon the relative phosphoric concentration and of oxidized/reduced forms. A small change of the normal potential of Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} redox systems is observed with the phosphoric acid concentration and a significant variation between the both redox systems, showing a variation in acidity and solvation of REE species. Two factors intervening antagonistic manner: the water activity and "REE-phosphate" complexation, which the last approach becomes significant only in the most phosphoric concentration.
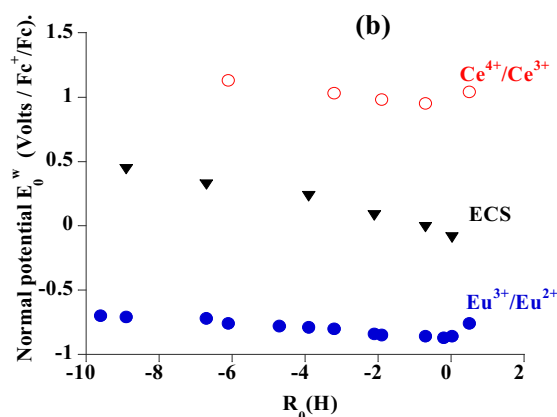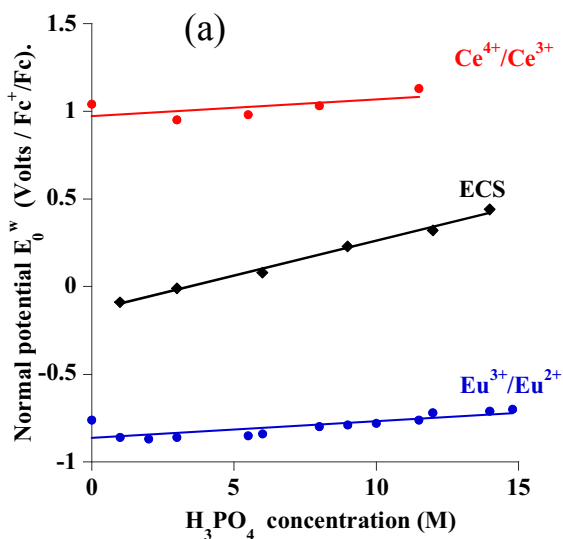
Fig. 2. Normal potential of different redox systems in phosphoric media

LOUIS and al. [24] have studied the relationship between complexation and solvation of some metal elements in various mineral acids (hydrochloric, perchloric, sulfuric) using acidity function $R_0(H)$ and solvation-transfer activity coefficients. In addition, the electrochemical behaviour of Fe(II) and Fe(III) ions on a gold electrode in H_3PO_4-H_2O solutions has already studied in our previous work [25]. In current study, the transfer activity coefficients "f" were calculated from the normal potential values of redox systems (Figure 2). The thermodynamic data lead to the calculation of the coefficients of solvation transfer activity for Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} systems (Figure 3).
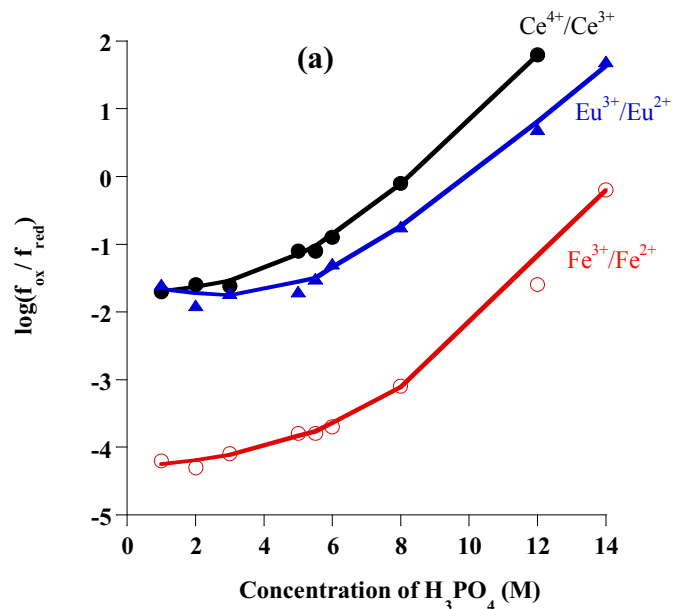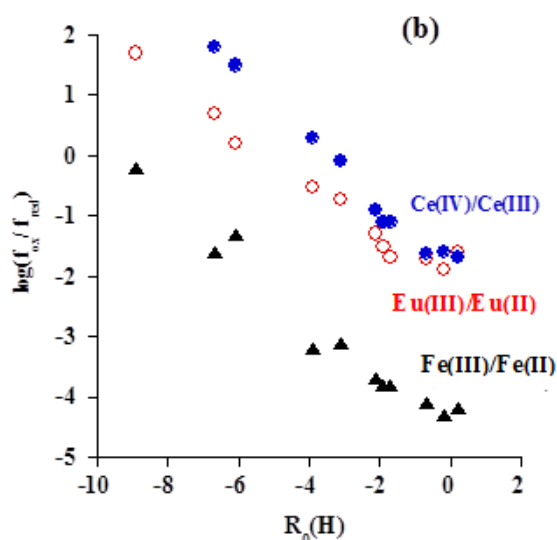
Fig.3. Solvation characteristics $\log(f_{ox}/f_{red})$ of species in H_2O-H_3PO_4 media in a function of (a) H_3PO_4 concentrations and (b) $R_0(H)$.

From figure 2, electrochemical characteristics of Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} show a comparable curves shape to that of Fe^{3+}/Fe^{2+} but having a dissimilar solvation character ($\log f$). The behaviour of these cations in H_3PO_4-H_2O media are studied with increasing of the H_3PO_4 concentration ($\log f$). Thus, they are less solvated and more reactive in the high concentration of phosphoric acid. Therefore, $\log(f_{Eu}^{3+}/f_{Eu}^{2+})$ and $\log(f_{Ce}^{4+}/f_{Ce}^{3+})$ values are negative, except for those in high concentrated H_3PO_4 acid [>11M], noting that the decomplexation of Eu^{3+} ions by phosphate groups is more important than that of Eu^{2+} ions. The increase of H_3PO_4 concentration favours a decomplexation of cations by a decrease of their solvation and consequently accelerates their reactivity. In 1 M H_3PO_4, the $\log(f_{Eu}^{3+}/f_{Eu}^{2+})$ =-1.64, as $\log(f_{Ce}^{4+}/f_{Ce}^{3+})$ = -1.63 expresses that the Eu^{2+} and Ce^{3+} cations are more solvated by the water while Eu^{3+} ions and Ce^{4+} are complexed by phosphate species ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}). This association becomes less at least relevant when the phosphoric concentration increases. When the H_3PO_4 concentration increases until 11 M ($R_0(H)$ = -5.5), the REE-phosphate interactions diminish rapidly and proved by the increase of the normal potential of their redox systems. In addition, the power oxidizing of the Eu^{3+} ions is comparable in water using 11 M H_3PO_4, e.g $\log(f_{red}/f_{ox}) > 0$, indicating that Eu^{3+} and Ce^{4+} cations are less solvated than Eu^{2+} and Ce^{3+} ions respectively, and so their reactivity increases. Similar results found for power oxidizing of Ce^{4+} ions in 8 M H_3PO_4 medium ($\log(f_{Ce}^{4+}/f_{Ce}^{3+})$ = -0,02). In diluted phosphoric acid, the Ce^{4+} ions {pK ($3Ce^{4+}/4PO_4^{3-}$) = 90.1} are more complexed than Ce^{3+} ions {pK (Ce^{3+}/PO_4^{3-}) = 2}. The analogous phenomenon has been observed for Fe^{3+}/Fe^{2+} and V^{3+}/V^{2+} systems in phosphoric acid media, but Eu^{3+} ions are more complexed {pK(Eu^{3+}) = 8.03} than Fe^{3+} {pK(Fe^{3+}) = 2.2} [26]. This behavior indicates the complexation of Eu^{3+} by means of OH^- groups, which are increasingly formed from the dissociation of water. Bilal and Langer [27] have shown that the formation of

hydrolysed species of the lanthanides occurs in solutions having pH = 3.6 at T > 333 °K, even if these solutions contain complexing ligands. They thus propose, the following unique set of hydrolysis constants for the mentioned trivalent ions [28]:

$$M^{3+} + n\, H_2O \rightarrow M(OH)_n^{3-n} + n\, H^+ . \qquad (3)$$
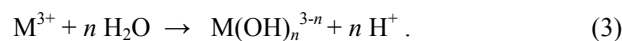
The inorganic speciation of M^{3+} cation (M: Eu and Ce) in H_2O-H_3PO_4 media were evaluated primarily to assess the relative importance chelating phosphate {$MH_2PO_4^{2+}$, $MHPO_4^+$, $M(HPO_4)_2^-$ and MPO_4^0}. In comparing the chemical characteristics of Eu^{3+} and Ce^{4+} cations, the desolvation of Ce^{4+} ions {$pK_sCe(OH)_4$ = 50.5} is greater than the Eu^{3+} ions {$pK_sEu(OH)_3$) = 24.5}. However, the existence of the formation of insoluble phosphate containing REE indicates that REE cations are more complexed with phosphates than hydroxide anions. By comparison of the complexation constants of Ce(III) in different acidic media (H_2O-HF, H_2O-HCl, H_2O-H_2SO_4), Ce(III) forms of more stable complexes in H_3PO_4 {pK(Ce^{3+}/PO_4^{3-}) = 23) than in other acids such as in H_2SO_4 {pK(Ce^{3+}/SO_4^{2-}} = 3.6), in HF {pK(Ce^{3+}/F^-) = 4} and in HCl {pK(Ce^{3+}/Cl^-) = 0.5} [29]. Therefore, Ce^{4+} cations form a more stable complexes in H_3PO_4 {pK($3Ce^{4+}/4PO_4^{3-}$) = 90.1} than in H_2SO_4 {pK(Ce^{4+}/SO_4^{2-}) = 4.6} . It has been concluded that the power oxidizing depends therefore of the nature of chelating anions.

Consequently, REE-phosphate complexes tend to dominate the speciation of the REEs in H_3PO_4-H_2O media. Our results indicate that Eu and Ce extraction from the produced phosphoric acid is important in diluted H_3PO_4 concentration. More specifically, elevated phosphate concentration tends to enhance the REE complexation through the formation of stable REE-phosphate complexes and consequently to remove the REE elements from water by the formation of REE-phosphate precipitate.

5 Conclusion

The electrochemical properties of Eu^{3+}/Eu^{2+} and Ce^{4+}/Ce^{3+} are studied in various phosphoric acid concentrations, showing the hydrolysis and the complexation behaviours of studied rare earth elements. These systems are characterized by an equal $R_0(H)$ acidity level and different redox and complexing properties. The relationship between the $R_0(H)$ acidity function, solvation properties and the water activity in phosphoric acid concentrated solutions has demonstrated. These confirm that it is possible to prepare a specific phosphoric acid concentration for extracting europium and cerium metals using a systematic solvent extraction and different classes of cation exchangers.

Acknowledgements

References

1. F. Xie, T. A. Zhang, D. Dreisinger, F. Doyle, Minerals Engineering, **56**, 18 (2014)
2. X. Huang, Z. Long, H. Li, W Ying, G.Zhang, X. Xue, Journal of Rare Earth, **23**, 4 (2005)
3. A. Jordens, Y. P. Cheng, K.E Waters, Minerals Engineering, **41**, 17 (2013)
4. D. N. Trifonov, *Terres rares* (Ed. Scientifique, Bucarest, 1963)
5. A. Leveque, J. Helgorski, *Techniques de l'ingénieur, Terres rares* J 6020-2353-1.
6. B. Marmodée, J.S. de Klerk, F. Ariese, C. Gooijer, M.U. Kumke, Anal. Chim. Acta, **652** (2009)
7. P. Moreau, S. Colette-Maatouk, P. Vitorge, P. Gareil, P. E. Reiller, Inorganica Chimica Acta, **1**, 7 **(**2015)
8. J. S. Wu, C. Liao, C Yan, Journal of Rare Earths, **5**, 8 (2004)
9. M. J .Hudson, Hydrometallurgy, **9**, 20 (1982)
10. J. Lu, Z. Wei, D. Li, G. Ma, Z. Jiang, Hydrometallurgy, **50**, 11 (1998)
11. J. S. Preston, A. C. Preez, Journal of Chemical Technology and Biotechnology, **65**, 9 (1996)
12. J. S. Preston, P. M. Cole Preez, A. C. M.H Fox, A. M. Fleming, Part II. Hydrometallurgy, **41**, 24 (1996)
13. D.F. Peppard, G. W. Wason, Kleber, E.V. (Ed.), *Rare Earth Research*. The Macmillan Company, New York, **14** (1961)
14. A. Barkleit, M. Acker, G. Bernhard, Inorganica Chimica Acta, **394**, 6 (2013)
15. C. Louis, J. Bessière. J. Chem. Eng. Data, **31**, 3 (1986)
16. M. Wang, Chem. Abstr, **116** (1989)
17. A. Rollar, Procedia Engineering, **138**, 8 (2016)
18. N. Tahani, Thesis, University of Nançy I, France, (1991)
19. P. A. H. Wyatt, Faraday Discuss. Chem. Soc, **24**, 9 (1957)
20. Z. El Abbassi, S. Belcadi, J. J. Rameau, Electrochimica Acta , **31**, 6 (1986)
21. C. Louis, J. Bessière. Can. J. Chem. **64** (1986)
22. D. Babale. Thesis, University of Yaounde, Cameroun, (1987)
23. F. Coussemant, M. Hellin, B.Torch, *Gordon and Breach* : Paris, London, New York, (1969)
24. C. Louis, A. Bebbaa, ND J. Bessière, Can. J. Chem., **66** (1988)
25. B. Belqat, A. Laghzizil, K. El Kacemi, S. Belcadi. Journal of Fluorine Chemistry, **105**, 5 (2000)
26. B. A. Bilal, Zeitschrift für Naturforschung A, **46**, 9 (1991)
27. B. A. Bilal, P. Langer, Lanthanide and Actinide Research, **3** (1989)
28. V. Neck, J.I. Kim, Radiochim. Acta, **89**, 17 (2001)
29. B. A. Bilal, E. Muller, Zeitschrift für Naturforschung A, **47**, 11 (1992)