

The extraction of Zn(II) in aqueous PEG (1550) – (NH₄)₂SO₄ two-phase system using Cl⁻ ions as extracting agent

LAURA BULGARIU^{1*} and DUMITRU BULGARIU²

¹Department of Management and Environmental Engineering, Faculty of Chemical Engineering, Technical University "Gh. Asachi", 700050 Iasi and ²Department of Geology and Geochemistry, Faculty of Geography and Geology, "Al. I. Cuza" University, 700050 Iasi, Romania
(e-mail: lbulg@ch.tuiasi.ro)

(Received 25 November 2005)

Abstract: The extraction of Zn(II) in an aqueous PEG (1550) – (NH₄)₂SO₄ two-phase system as a function of several experimental parameters was studied. PEG-based aqueous two-phase systems are composed of two immiscible phases: a polymer-rich phase and a salt-rich phase, which can be used for extraction experiments. In the absence of a suitable extracting agent, for the system consisting of a mixture of equal volumes of 40 mass % PEG and 40 mass % (NH₄)₂SO₄ aqueous solutions, Zn(II) remained predominantly in the salt-rich phase. Variation of the pH of the salt stock solution did not change very much the extraction efficiency. By adding chloride ions, an enhancement of the Zn(II) extraction was observed. The Zn(II) extraction efficiency in presence of Cl⁻ depends on the acidity of the salt stock solution and on the concentration of chloride ions added into the system.

Keywords: aqueous two-phase system, Zn(II) extraction, polyethylene glycol, (NH₄)₂SO₄, chloride ions.

INTRODUCTION

Extraction processes are ubiquitous in many fields and the systems employed in liquid–liquid separations frequently involve the use of toxic, inflammable and volatile organic compounds.

Aqueous two-phase systems formed when a water soluble polymer is mixed with a certain inorganic salt (*e.g.* (NH₄)₂SO₄, Na₂SO₄, Na₂CO₃, K₂HPO₄), may represent an alternative for metal ions extraction processes in industrial separation, as well as environmental remediation applications.^{1–4}

Although many different water soluble polymers may be utilized to form aqueous two-phase systems, poly(ethylene glycol)(PEG) is exclusively used because it is non-toxic, non-flammable and non-volatile. For this reason, aqueous two-phase systems are considered an economical avenue for "clean" separation techniques.⁵

* Corresponding author.

Roger *et al.* classified metal ion extraction in aqueous two-phase systems into three categories: (1) extraction in the PEG-rich phase alone, without an extracting agent; (2) extraction of metal ions as chelates using water-soluble chelating extractants and (3) extraction of metal ions as complexes with inorganic anions.⁶

From these three categories, the last type of metal extraction finds wide application in the case of soft metal ions, which form anionic complexes with halides ions and which can be extracted into the PEG-rich phase by an ion-pair extraction mechanism, similar to the extraction of metal halide complexes with ethers or ketones.^{5,6} Thus, it has been shown that iodide ions are useful for the extraction of several metal ions, such as Cd(II), Hg(II), Bi(III), Tl(I).⁷⁻¹⁰

In this study, the extraction of Zn(II) in aqueous PEG(1550)-(NH₄)₂SO₄ two-phase system, using chloride ions as the extracting agent, was investigated. The experiments were performed in the absence and in the presence (0.01–0.07 mol/L) of chloride ions, at a given initial concentration of Zn(II) in the extraction system. The effect of the pH of the stock solution of salt on the efficiency of extraction of Zn(II) was also investigated. The obtained results are discussed on the basis of the stability of the chemical species formed by Zn(II) with both Cl⁻ and SO₄²⁻ ions.

EXPERIMENTAL

The poly(ethylene glycol) (PEG) used in this study, with an average molecular mass 1550, was purchased from Serva Feimbiochema GmbH & Co., and used without purification. The (NH₄)₂SO₄ and NaCl salts, from Aldrich, were analytical grade reagents and were used as received.

Stock solution of 40 mass % PEG was prepared by dissolving solid poly(ethylene glycol) in a certain mass of water. Similarly, the 40 mass % of (NH₄)₂SO₄ stock solution was prepared and the four different pH values were obtained by adding small volumes of concentrated H₂SO₄ or NH₃ solution (Reactivul Bucharest), which was taking into account in the total mass of the solution.

The 1 mol/L chloride ion solution was obtained by dilution of a sodium chloride salt to the volume with salt stock solution. This approach provides a net decrease in the concentration of the phase-forming salt present in the uptake experiments.

A stock solution of 695 µg Zn(II)/mL was prepared by dissolving zinc sulphate (Fluka) in distilled water, followed by solution standardization.¹¹

The Zn(II) distribution studies were carried out as follow: for each determination an aqueous two-phase systems was prepared by mixing equal volumes of the stock solutions of PEG (1550) and (NH₄)₂SO₄, with a different pH value in a glass centrifuge tube. The pH value of the (NH₄)₂SO₄ salt stock solution was measured with a Radelkis pH/ion-meter type OK-271, equipped with a combined glass electrode. 0.7 mL of Zn(II) stock solution and 1 mol/L NaCl solution (0.1–0.7 mL) were added. The system was shaken for 5 min, followed by 10 min of centrifugation at 2000 rpm. Just before analysis, the two immiscible phases were carefully separated with Pasteur pipettes and placed into separated tubes. Equal volumes (1.0 mL) from each phase were measured for Zn(II) spectrophotometric analysis using xylenol orange.¹² The absorbance of the pink-red complex was measured at 570 nm, with a Digital S 104D spectrophotometer in a 1 cm glass cell against distilled water. The Zn(II) content in each phase was determined in duplicate, using a prepared calibration graph. The extraction parameters: distribution coefficients (D_{Zn}) and percent extraction (E_{Zn} %) were calculated according to the relations:

$$D_{Zn} = \frac{[Zn^{2+}]_{PEG-rich\ phase}}{[Zn^{2+}]_{salt-rich\ phase}}; \quad E_{Zn} \% = D_{Zn} \frac{100}{D_{Zn} + \nu} \quad (1)$$

where: ν - is the volumes ratio of the salt-rich phase and PEG-rich phase.

The chloride ion concentration in the PEG-rich phase was determined by conductometric titration with AgNO_3 , using a Radelkis OK-109 conductometer.

RESULTS AND DISCUSSIONS

Generally, the formation of aqueous two-phase system of PEG and a certain inorganic salt can be explained on the basis of the competition for hydration between the two components.¹³ The addition of an inorganic salt increases the dehydration of the polymer chains, due to the salting-out effect and phase separation. Thus, two immiscible aqueous phases are obtained: an upper one – rich in PEG, having the same role as the organic phase in traditional extraction systems, and a lower one, rich in the inorganic salt (Fig. 1).

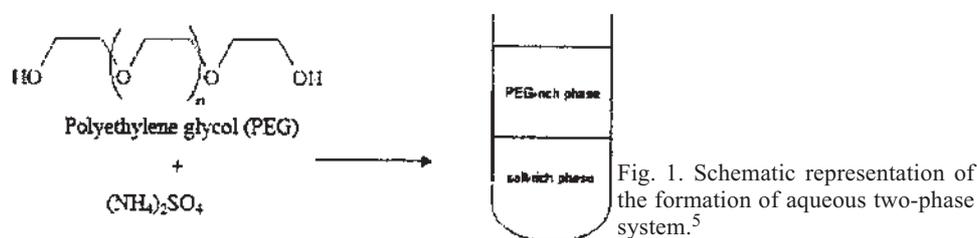


Fig. 1. Schematic representation of the formation of aqueous two-phase system.⁵

According to the literature, the partitioning of the solute in such an aqueous two-phase system depends both on the characteristics of the formed system (nature and concentration of the inorganic salt, molecular mass and concentration of the polymer) and the hydration properties of the solute (the solute extraction increase with decreasing of the solute hydration).^{5,6,14}

The concentrations of the phase forming components were selected according to the phase diagram of the system, that the system remains two-phased throughout all experiments and the difference in the concentration of the two components between the two phases is large.²

In the absence of extracting agent, the experimental results indicate that Zn(II) remains predominantly in the salt-rich phase of the extraction system, and variation of the pH of the salt stock did not enhance the extraction efficiency (Table I).

TABLE I. The E_{Zn} % values obtained in the absence of extracting agent, in the aqueous PEG(1550) – $(\text{NH}_4)_2\text{SO}_4$ two-phase system ($n = 3$; Zn(II) initial concentration = 49 $\mu\text{g}/\text{mL}$; $t = 25^\circ\text{C}$)

	pH 2.05	pH 3.12	pH 4.53	pH 7.12
$E_{\text{Zn}}/\%$	10.29	11.85	25.56	13.78

This means that in the extraction of Zn(II), chemical interactions between the metal ion and the PEG molecules are not involved. The preference of Zn(II) for the salt-rich phase is due to its high negative hydration Gibbs energy ($\Delta G_{\text{hyd}} = -1880 \text{ kJ}/\text{mol}$).¹⁵

On the other hand, under the conditions of the aqueous two-phase preparation, where the SO_4^{2-} concentration is $\approx 3.5 \text{ mol}/\text{L}$, calculation of the distribution of the Zn(II) species shows that the anionic sulphates ($\alpha_{\text{Zn}(\text{SO}_4)_2^{2-}} = 0.892$; $\log \beta_{\text{Zn}(\text{SO}_4)_2^{2-}}$

= 2.57) are dominant; the mol fraction of ZnSO_4 is $\alpha_{\text{Zn}(\text{SO}_4)_2^{2-}} = 0.107$ ($\log \beta_{\text{Zn}(\text{SO}_4)_2^{2-}} = 2.19$) and free Zn^{2+} ions are practically non-existent ($\alpha_{\text{Zn}^{2+}} = 2.019 \cdot 10^{-4}$).¹⁶ Thus, the anionic sulphates ($\text{Zn}(\text{SO}_4)_2^{2-}$) formed from the metal ion with a high ΔG_{hyd} and the anion with a strong salting-out effect have a lower affinity for the PEG-rich phase of the extraction system. Under these conditions, the extraction efficiency, can be changed by changing the nature of the Zn(II) species by using an extracting agent with lower hydration, which will improve the selectivity of the extraction process.

Chloride ions can be used as extracting agents in such aqueous two-phase systems, because they have a high solubility in water,¹⁷ a lower hydration Gibbs energy ($\Delta G_{\text{hyd}} = -270 \text{ kJ/mol}$)¹⁵ and in the absence of metal ion are significant by partitioned in the PEG-rich phase (Table II).

TABLE II. The E_{Cl^-} % values in the absence of metal ions, in the aqueous PEG(1550) – $(\text{NH}_4)_2\text{SO}_4$ two-phase system ($[\text{Cl}^-] = 0.05 \text{ mol/L}$; $t = 25 \text{ }^\circ\text{C}$)

	pH 2.05	pH 3.12	pH 4.53	pH 7.12
E_{Cl^-} %	50.09	49.53	52.36	51.53

In addition, Zn(II) can form neutral molecules (ZnCl_2) with Cl^- ions which are more stable than the anionic complexes (ZnCl_3^- and ZnCl_4^{2-}).¹⁶ Thus, enhancement of Zn(II) extractability in presence of chloride ions can be attributed to the formation of such extractable species.

The use of Cl^- as the extracting agent was investigated by studying the partitioning of the Zn(II) as a function of several experimental parameters: the initial concentration of Zn(II) in the extracton system, the pH of the stock solution of salt and the concentration of chloride ions added to the extraction system.

The initial concentration of Zn(II) in the extraction system was studied in the concentration range between 30 and 65 $\mu\text{g/mL}$ (Fig. 2).

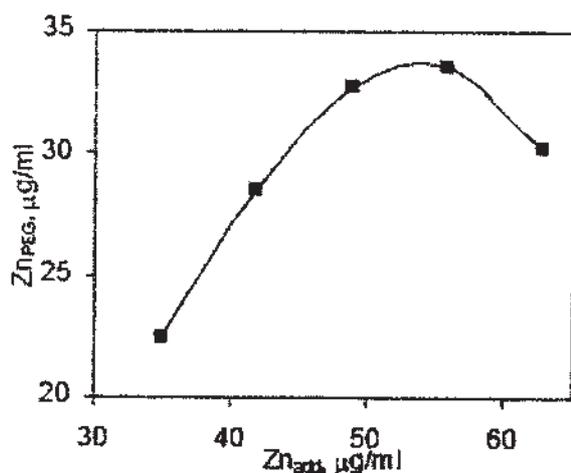


Fig. 2. The influence initial concentration of Zn(II) on its extraction in the presence of Cl^- , in the considered aqueous two-phase system ($[\text{Cl}^-] = 0.05 \text{ mol/L}$; salt stock solution pH 4.53; temperature $25 \text{ }^\circ\text{C}$).

As can be seen from Fig. 2, the Zn(II) concentration extracted in presence of 0.05 mol Cl⁻/L increased with increasing of metal ion concentration up to 55 µg/mL. At higher values of the initial concentration of Zn(II), the extraction efficiency decreased. On the base of this observation and taking into account the limits of analysis method used for the Zn(II) determination, an initial concentration of 49 µg Zn(II)/mL was selected for the further distribution studies.

The influence of the pH of the salt stock solution on the extraction of Zn(II) in presence of chloride ions was studied in the pH range 2 to 7. Li *et al.* showed that the pH variation in this domain has an insignificant effect on the formation and the separation of the two aqueous phases, because the phase forming components (PEG, NH₄⁺, SO₄²⁻) are practically not involved in secondary processes.¹⁸

The experimental results (Fig. 3) indicate that the Zn(II) extraction efficiency in presence of chloride ions increases with the increasing acidity of the salt stock solution.

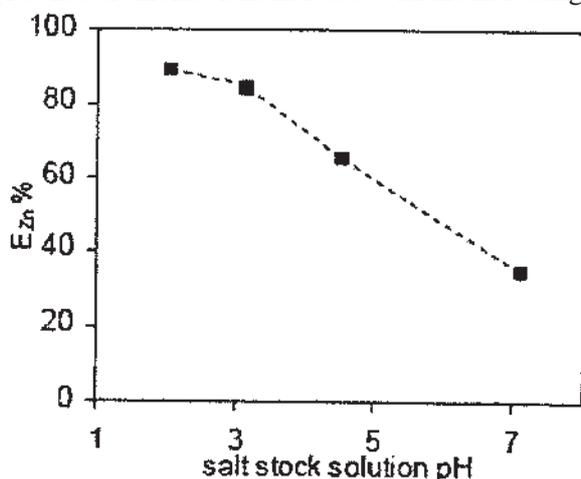


Fig. 3. E_{Zn} % vs pH value of the salt stock solution. (The initial concentration of Zn(II) in the extraction system was 49 µg/mL; temperature 25 °C).

In general, decreasing the pH of the salt stock solution has the effect of increasing the hydrophobicity of the PEG-rich phase and, thus, enhancement of the efficiency of metal ion extraction.^{5,6} However, because this dependence is not a linear one, the nature and the stability of the extractable species, play an important role in the extraction process.

Under the present conditions, increasing the extraction efficiency of Zn(II) by decreasing the pH of the salt stock solution is due to an increase of both, the hydrophobicity of the PEG-rich phase, which in our opinion is a kinetic factor of control, and the accessibility of Zn(II) for the extracting anions, which defines the nature and the stability of the extracted species.

The variations of the percent Zn(II) extracted as a function of the concentration of Cl⁻ added to the system, for all four studied pH values of the salt stock solution, are shown in Fig. 4.

The extraction of Zn(II) into the PEG-rich phase increased with increasing of concentration Cl⁻ ions in the 0.01–0.05 mol/L range, after which it decreased. As

can be seen from Fig. 4, the presence of H_2SO_4 (extraction systems with salt stock solution pH 2.05 and 3.12) resulted in a significant enhancement of Zn(II) extraction, with an extraction maximum of 84–88 %, obtained with 0.05 mol Cl^-/L .

In the absence of H_2SO_4 (extraction system with a salt stock solution pH 4.53), the variation of the percent Zn(II) extracted had the same tendency as above, only with the difference that the extraction maximum obtained with 0.05 mol Cl^-/L was lower (65 %) and the decrease of the Zn(II) extraction efficiency at higher concentration of Cl^- ions was more accentuated.

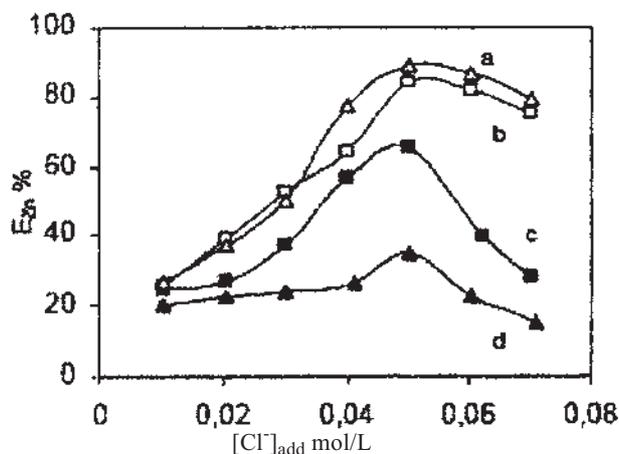


Fig. 4. E_{Zn} % in dependence on the concentration of added Cl^- with a pH of the salt stock solution of: (a) 2.05; (b) 3.12; (c) 4.53; (d) 7.12. (The initial concentration of Zn(II) in the extraction system was 49 $\mu\text{g}/\text{mL}$ temperature 25 °C).

In case of the system with pH 7.12 (obtained by NH_3 addition), practically Zn(II) extraction into the PEG-rich phase was independent of the Cl^- ion concentration, although a slight intensification was obtained with a concentration of 0.05 mol Cl^-/L . Thus, the values of the percent extraction are lower and comparable with those calculated for Zn(II) extraction in absence of extracting agents. This behaviour can be due to the fact that in presence of ammonia, the zinc ions form ammonia complexes with a higher stability and higher degree of hydration than the zinc-chloride complexes, which will prefer to remain in the salt-rich phase of the extraction system.

The different extraction behaviour of Zn(II) in the presence of chloride ions as a function of experimental conditions can be due to the extraction of some different species. The number of chloride ions associated with Zn(II) in the extractable species was determined from the slope of $\log D_{\text{Zn}}$ vs. $\log [\text{Cl}^-]_{\text{PEG}}$ dependences, for the three lower values of the pH of the salt stock solution (Fig. 5).

Thus, in case of systems prepared with addition of H_2SO_4 (salt stock solution pH 2.05 and 3.12), the main extracted species are neutral molecules (ZnCl_2), while in absence of H_2SO_4 (the extraction system with pH 4.53), Zn(II) is extracted predominantly as the cationic complex (ZnCl^+), and the extraction efficiency is lower.

Analysis of the obtained experimental results indicate that for the realization of metal ion extraction in aqueous two-phase systems, the follow two conditions must be satisfied: (1) the formation of a stable extractable species between the metal

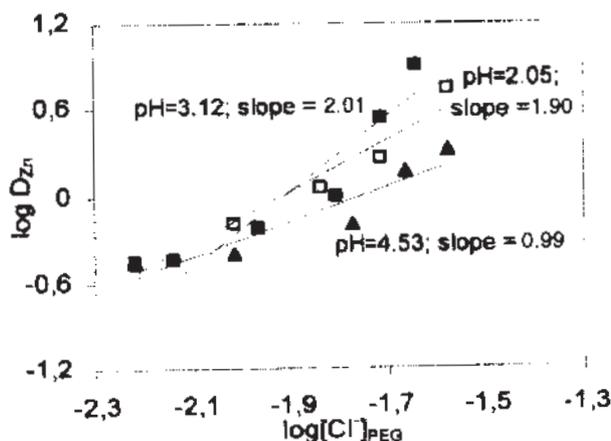


Fig. 5. The dependence of $\log D_{Zn}$ against $\log [Cl^-]_{PEG}$ in the considered aqueous two-phase system. (The initial concentration of Zn(II) in the extraction system was 49 $\mu\text{g/mL}$; temperature 25 $^{\circ}\text{C}$).

ion and the extracting agent in the extraction system and (2) the extractability of the formed species should have a low degree of hydration.

The increase of the extraction percent of Zn(II) in the 0.01 – 0.05 mol Cl^- /L range shows that in this domain Zn(II) forms a stable species in presence of chloride ions, with a lower degree of hydration than $Zn(SO_4)_2^{2-}$. These species are extracted into the PEG-rich phase. Increasing the chloride ion concentration above 0.05 mol/L resulted in a decrease in the extraction efficiency of Zn(II), due to the formation of less stable species. This observation become evident when the values of the stability constants of zinc-chloride complexes are compared, *i.e.*, they follow the order: $ZnCl^+ < ZnCl_2 > ZnCl_3^- > ZnCl_4^{2-}$.¹⁶ Thus, the formation of some anionic complexes ($ZnCl_3^-$, $ZnCl_4^{2-}$) at higher chloride ions concentration, which have a lower hydration, did not improve the extraction efficiency due to the instability of these species.

CONCLUSIONS

The partition behaviour of Zn(II) in aqueous PEG(1550) – $(NH_4)_2SO_4$ two-phase system was investigated as a function of the concentration of the added chloride ions and the pH of the salt stock solution, for a given initial concentration of Zn(II) in the extraction system.

In the absence of chloride ions as an extracting agent, Zn(II) prefer to remain in the salt-rich phase, due to the formation of $Zn(SO_4)_2^{2-}$ species with a high degree of hydration, and a poor extraction was observed for all four studied pH values of the salt stock solution.

The addition of chloride ions in the 0.01 – 0.05 mol/L concentration range resulted in an enhancement of Zn(II) extraction efficiency. At higher values of the Cl^- concentration, a decrease of the Zn(II) partition of the PEG-rich phase was observed. The Zn(II) extraction is more effective in the presence of H_2SO_4 (salt stock solution with pH 2.05 and 3.12) when neutral molecules ($ZnCl_2$) are extracted than

in absence of H_2SO_4 (salt stock solution with pH 4.53), where the predominant extracted species are ZnCl^+ . In case of system with pH 7.12 (obtained by NH_3 addition), the values of the percent extraction were lower and comparable with those obtained in the absence of extracting agents.

On the basis of the experimental results, it can be stated that for the realization of metal ion extraction in aqueous two-phase systems two conditions must be satisfied: (1) a stable species between the metal ion and the extracting agent in extraction system should be formed and (2) the formed species should have a low degree of hydration. Under, the present conditions, the anionic Zn(II) complexes formed at higher chloride ions concentration, which have a lower hydration, were not extracted into the PEG-rich phase due to their instability.

ИЗВОД

ЕКСТРАКЦИЈА Zn(II) У ВОДЕНОМ ДВОФАЗНОМ СИСТЕМУ
 $\text{PEG(1550)-(NH}_4)_2\text{SO}_4$ СА Cl^- КАО ЕКСТРАХУЈУЋИМ АГЕНСОМ

LAURA BULGARIU¹ и DUMITRU BULGARIU²

¹Department of Management and Environmental Engineering, Faculty of Chemical Engineering, Technical University "Gh. Asachi", 700050 Iasi и ²Department of Geology and Geochemistry, Faculty of Geography and Geology, "Al. I. Cuza", University, 700060, Iasi, Romania

Екстракција Zn(II) у воденом $\text{PEG(1550)-(NH}_4)_2\text{SO}_4$ двофазном систему испитивана је као функција неколико експерименталних параметара. Водене PEG двофазне системе чине две фазе које се не мешају: фаза богата полимером и фаза богата сољу, која се може користити за екстракционе експерименте. У одсутности погодног екстракционог агенса, за систем који чини меша једнаких запремина 40 % мас. PEG и 40 % мас $(\text{NH}_4)_2\text{SO}_4$ (водени раствори), Zn(II) доминантно остаје у фази богатој сољу. Варирање рН вредности раствора соли није значајно утицало на ефикасност екстракције. Примећено је да додавање хлоридних јона интензивира екстракцију Zn(II) . У присуству Cl^- ефикасност екстракције зависи од киселости раствора и концентрације Cl^- унете у систем.

(Примљено 25. новембра 2005)

REFERENCES

1. I. V. Ho-Butierrez, E. L. Cheluget, J. H. Vera, M. E. Weber, *J. Chem. Eng. Data* **39** (1994) 245
2. Y. T. Wu, Z. Q. Zhu, D. Q. Liu, M. Li, *Fluid Phase Equilib.* **154** (1999) 109
3. L. H. Meller da Silva, J. S. R. Coimbra, A. J. da A. Meirelles, *J. Chem. Eng. Data* **42** (1997) 398
4. K. Mishima, K. Matsuyama, M. Ezowa, Y. Taruta, S. Takarabe, M. Nagatani, *J. Chromatogr. B* **711** (1998) 313
5. A. E. Visser, S. T. Griffin, C. C. Ingenito, D. H. Hartman, J. G. Huddleston, R. D. Rogers, *Metal Sep. Technol. Beyond* (2000) 119
6. R. D. Regers, A. H. Bond, C. B. Bauer, J. Zhang, S. T. Griffin, *J. Chromatogr. B* **680** (1996) 221
7. L. Bulgariu, I. Sarghie, *Anal. St. Univ. "Al. I. Cuza" s. chemistry*, tom **XIII** (2005) 27
8. R. D. Rogers, S. T. Griffin, *J. Chromatogr. B* **711** (1998) 277
9. M. Shibukawa, N. Nakayama, T. Hayashi, D. Shibuya, Y. Endo, S. Kuwamura, *Anal. Chim. Acta* **427** (2001) 293
10. R. D. Rogers, A. H. Bond, C. B. Bauer, *Solv. Extr. In Proc. Ind.* **3** (1993) 1641

11. J. A. Dean, *Analytical Handbook*, McGraw-Hill, New York, 1995, p. 3; 104
12. A. H. Flsska, A. J. Barnard, *Chelates in Analytical Chemistry*, Marcel Dekker Inc., New York, 1967, p. 15
13. H. Cabezas, Jr., *J. Chromatogr. B* **680** (1996) 3
14. B. Yu. Zaslavsky, N. D. Gulaeva, S. Djafarov, E. A. Masimov, L. M. Miheeva, *J. Coll. Interface Sci.* **137** (1991) 147
15. Y. Marcus, *J. Chem. Soc., Faraday Trans.* **87** (1991) 2995
16. J. Lurie, *Handbook of Analytical Chemistry*, Mir Publisher, Moscow, 1975, p. 283
17. D. I. Seracu, *Indreptar de chimie analitica*, Ed. Tehnica, Bucharest, 1989, p. 64
18. L. Ci, C. Y. He, S. H. Li, F. Liu, S. Su, X. X. Kong, K. A. Li, *Chin. J. Chem.* **22** (2004) 1313.