

Solvent extraction with organophosphorus extractants in environmental samples: determination of cadmium(II) in natural water

Research Article

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Abstract: In this work, Cd(II) extraction in natural waters by organophosphorus extractants as organic phase, as well as its back-extraction in an acidic media, has been studied. Cadmium extraction behavior at natural waters' pH conditions (values in the range 7-8) was studied with two different extractants and co-ions, obtaining the highest extraction efficiency when using 0.1M Cyanex 272 in kerosene as organic phase and 0.1 M NO₃⁻ as co-ion. Once they were selected, the effect on the extraction efficiency of sample pH, buffer concentration, extraction time, Cyanex 272 concentration as well as back-extractant concentration, was studied. The presence of the main inorganic and organic ligands in the sample was also studied, observing that extraction efficiency was affected most significantly when chlorides were present, with a decrease of about 14%, proving negligible for the others. Under the selected conditions, spiked real samples were successfully analyzed.

Keywords: Solvent extraction • Cadmium • Cyanex • Natural waters • Nitrate co-ion
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1. Introduction

The presence of heavy metals in aquatic ecosystems can be due to both natural and anthropogenic sources. Examples of the latter are industrial effluents from mining activities, smelting, agricultural processes, etc., closely related with metal accumulation and its deleterious effect on the environment.

Cadmium is among the most toxic metals in the environment, as it is reflected in the list of priority pollutants of the United States Environmental Protection Agency (USEPA) [1]. A search in the literature [2] reveals that cadmium extraction applications have been mainly focused on its recovery from metallic solutions from the hydrometallurgical industry and, therefore, its extraction from solutions such as sulfate, chloride, nitrate and phosphate (which could have been generated in the processing of this trace metal while bearing other materials) has extensively been studied [3].

Several non-commercial reagents, such as pyridine-carboxamides [4] or pyridyl ketoximes [5] have been assayed to separate cadmium from other metallic species present in chloride solutions. Cd(II) has been extracted from acidic, neutral and basic media as well as different natural matrices [6-10], such as seawater collected from the coast of Spain [11]. In order to enhance the selectivity, different methods have been developed employing mixtures of extractants based on the synergic effect for the recovery of the metal ion [12-14]. Although non-commercial reagents showed to be a good alternative, there is no doubt that commercial extractants fill most applications, being organophosphorus derivatives (phosphoric, phosphonic and phosphinic acids) widely used.

Szilassy *et al.* [15] reported for the first time the use of Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) for the separation of cadmium from nickel from the electrode materials of worn-out Ni-Cd batteries

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scraps. This reagent has also been employed for the extraction of several metal ions from different solutions [16-21]. Other compounds of this series, such as Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid), Cyanex 302 (bis(2,4,4-trimethylpentyl thiophosphinic acid) and Cyanex 923 (mixture of four trialkylphosphine oxides) have also been applied for the removal of cadmium from chloride solutions [22,23].

Some studies on natural waters (such as city lake waters) have used Cyanex extractants in a solid phase extraction method [24]. Nevertheless, Cd(II) solvent extraction has extensively been studied but very few examples may be found in the literature concerning saline samples, most of them based on the extraction of the metal using the classical method of dithiocarbamates [25,26]. To the best of our knowledge, there is no method developed for the extraction of cadmium at natural waters' pH conditions with organophosphorus extractants.

In the present study, a solvent extraction method for the separation and determination of cadmium ions in natural waters is presented. It is based on the use of commercial organophosphorus extractant (Cyanex 272 in kerosene) for its extraction from natural waters and its back-extraction into an acidic solution (HNO₃). The main chemical and physical parameters affecting the extraction system were evaluated in order to maximize the recovery of the ion from the samples. To be successfully used in natural waters, the effect of the main organic and inorganic ligands usually present in these samples was also studied. Finally, the developed method was successfully applied to the determination of cadmium from spiked real samples under the selected conditions.

2. Experimental procedure

2.1. Reagents and solutions

Aqueous cadmium solutions were prepared from a 1000 mg L⁻¹ standard solution (Merck, Darmstadt, Germany). Buffer solutions were prepared from 2-hydroxyethyl piperazine-N'-(2-ethanesulphonic acid) (HEPES) supplied by Biochemical (Barcelona, Spain). Potassium bromide, sodium sulphate (Merck, Darmstadt, Germany) and sodium hydroxide (Scharlab, Barcelona, Spain) were of analytical reagent grade. Sodium chloride was supplied by Qemical (Quality Chemicals). Nitric acid (63%), as well as humic acid (di-sodium salt), was obtained from Sigma-Aldrich (Steinheim, Germany). All aqueous solutions were prepared with Milli-Q deionised water (Millipore, USA). The organic extractants Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) and Cyanex 923 (a mixture of four trialkyl-phosphine

oxides) were obtained from CYTEC (New Jersey, USA). Kerosene (Sigma-Aldrich, Steinheim, Germany) was used as solvent without further purification. The organic phases were obtained by dissolving the appropriate amounts of the extractants in kerosene.

2.2. Instruments

Liquid-liquid extraction (LLE) experiments were performed in 10 mL glass end-cap tubes and mixed by a Reax 2 overhead mixer (Heidolph, Germany). In some cases, turbidity was observed in the aqueous phase and so an ultrasounds bath (J.P. Selecta, Barcelona, Spain) was used to eliminate its effect. A Perkin Elmer AAnalyst 200 atomic absorption Spectrometer (AAS) (Massachusetts, USA) was used to determine metal ion concentration in the different aqueous phases obtained after L-L extraction was performed. Aqueous solution pH was monitored by a combined glass Ag/AgCl electrode pH-meter (Crison, Spain).

2.3. Preliminary studies

Experiments were carried out by mixing in glass end-cap tubes, at a volume ratio 1:1, synthetic aqueous solutions containing 1 mg L⁻¹ Cd(II) at different acidities (controlled by the addition of appropriate volumes of HNO₃ or NaOH) with the organic solutions obtained from the organophosphorus extractants dissolved in kerosene. The tubes were agitated at 40 rpm during 30 min. After agitation, phase separation was allowed for approximately 5 min. Finally, the aqueous solution was analyzed for metal values by FAAS. The efficiency of the process was assessed by Eq. 1, being C_o and C_f the initial and final cadmium concentration in the aqueous solution, respectively. Three extraction replicates for each experiment were performed and their mean and standard deviation values calculated.

$$\% \text{Extraction} = \frac{C_o - C_f}{C_o} \cdot 100 \quad (1)$$

2.4. Selection of the extracting agent and co-ion

Preliminary studies showed the necessity to previously buffer the aqueous samples to maintain constant the pH value (around 6.5) during the extraction process. In this sense, 2-hydroxyethyl piperazine-N'-(2-ethanesulphonic acid) (HEPES) was selected to this purpose. On the other hand, the addition of ion-pairing reagents such as chloride or nitrate facilitates cadmium co-transport and, hence, an improvement in the extraction efficiency could be obtained. As a consequence, chlorides or nitrates (0.1 M final concentration) were added to the aqueous samples as feasible co-ions for cadmium extraction.

Organic phases of each of the reagents dissolved in kerosene were prepared with a final concentration 0.1 M. After LLE experiments were carried out, extraction efficiencies were calculated and the co-ion and extractant agent leading to the best results selected.

2.5. Optimization of the extraction method

The optimization of the method was carried out employing a univariate methodology in which the chemical variables affecting the extraction system were varied accordingly. In all the experiments aqueous solutions were prepared containing 1 mg L⁻¹ Cd(II) and the required reagents for the study. The effect of pH on the extraction efficiency was studied in the range 5-8 by the addition of HEPES and aliquots of NaOH to the aqueous solution. Next, in order to maintain the pH of the aqueous solution, buffer concentration was varied in the range 0.05-0.2 M. Finally, the effect of increasing the extracting agent concentration in the range 0.005-0.1 M on the extraction efficiency was evaluated. Once chemical variables were optimized the extraction time was varied between 1-60 min.

2.6. Effect of the presence of ligands in the aqueous solution

To be applied to natural waters, it was necessary to study the effect on the extraction efficiency of the main organic and inorganic ligands present in these samples. In this sense, chlorides (0.08-0.60 M), bicarbonates (0.1-10 mM), bromides (1-10 mM) and sulphates (0.5-4 mM), as inorganic ligands, and humic acids (15-100 mg L⁻¹) as organic ligands were added to the aqueous solution and its effect on the extraction efficiency was studied under the optimized chemical and physical conditions.

2.7. Back-extraction

Back extraction from organic phase was also studied with nitric acid concentration varying in the range 0.1-1M. These acidic solutions were mixed for 15 min with the organic phases (1:1 v/v), previously loaded with the metal ion, in glass end-cap tubes. Once the extraction was completed, the remaining aqueous solutions were measured for cadmium values by FAAS.

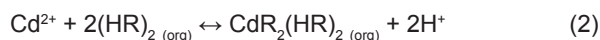
Finally, the method was applied to analyze Cd(II) in a sample from the estuary of the Guadalete River (Cadiz, Spain). This sample had been previously analyzed by ICP-MS and a cadmium concentration of 0.01 µg L⁻¹ had been obtained. In order to be analyzed by the proposed method, three aliquots of this sample were spiked with increasing Cd(II) concentration (0.5 µg L⁻¹, 1.0 µg L⁻¹ and 1.5 µg L⁻¹) and the extraction experiments were carried out at a volume ratio organic:aqueous phase

1:4. This ratio was selected in order to preconcentrate the analyte and also reduce wastes coming from the organic reagent. The aqueous phases obtained after back-extraction were analyzed for Cd(II) by graphite furnace atomic absorption spectrometry (GFAAS).

3. Results and discussion

3.1. Preliminary studies

The results obtained showed low cadmium extraction efficiencies when both organophosphorus extractants were assayed. On the one hand, the extraction of cadmium(II) with Cyanex 272 can be explained by taking into account the global mechanism of complex formation between free cadmium ion from aqueous samples and phosphoric, phosphinic or phosphonic acid (HR) [27]:



In this reaction, a displacement in the equilibrium towards the left side of the reaction was assumed, with the subsequent decrease in the extraction. As a consequence, the selection of an appropriate buffer solution was necessary to maintain the pH in the extraction system. Having in mind that the extraction method will be applied to the determination of cadmium in natural waters, HEPES was selected as the most suitable buffer solution. All experiments were thus carried out with buffered aqueous samples to maintain the pH of the whole process.

On the other hand, taking into account that Cyanex 923 acts as a solvating reagent, the extraction of cadmium(II) will depend on the presence of suitable ion-pair species in the solution.

3.2. Selection of the extracting agent and co-ion

From previous results, the chemical mechanism for cadmium extraction with organophosphorus derivatives was assumed to be a complex formation by co-extraction, being the overall free cadmium extraction process governed by [16]:



where HR denotes the organic acid and L the co-ion required for cadmium to be extracted as a neutral complex in the organic phase. The complex formed between the metal ion, the co-ion and the organic extractant will be transported across the interphase, due to the concentration gradient created between both phases. This chemical mechanism has been considered

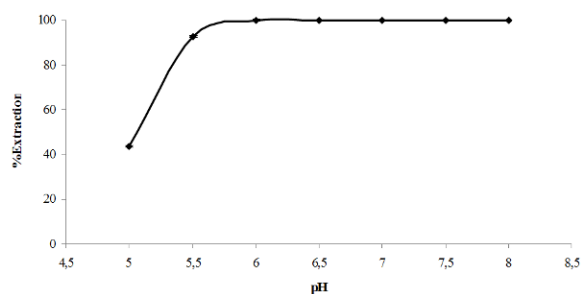


Figure 1. Variation of extraction efficiency (%) with pH of aqueous solution. *Aqueous solution:* 1 mg L⁻¹ Cd²⁺, 0.1 M HEPES, 0.1 M NaNO₃. *Organic solution:* 0.1M Cyanex 272 in kerosene.

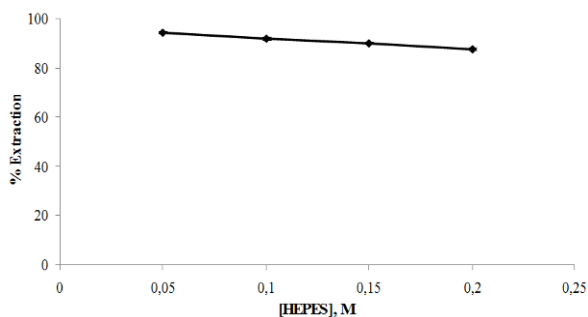


Figure 2. Effect of the buffer concentration in aqueous solution on the extraction. *Aqueous solution:* 1 mg L⁻¹ Cd²⁺, 0.1 M NaNO₃. *Organic solution:* 0.1 M Cyanex 272 in kerosene.

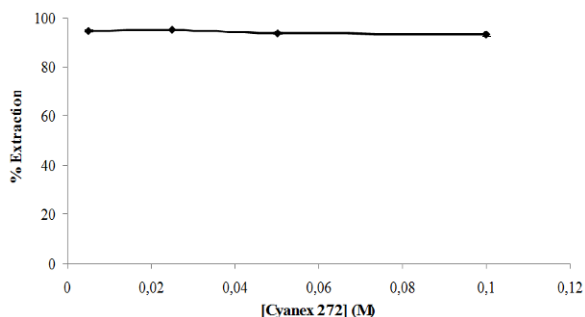


Figure 3. Variation of extraction efficiency (%) with Cyanex concentration in organic solution. *Aqueous solution:* 1 mg L⁻¹ Cd²⁺, 0.1 M HEPES, 0.1 M NaNO₃. *Organic solution:* Cyanex 272 in kerosene.

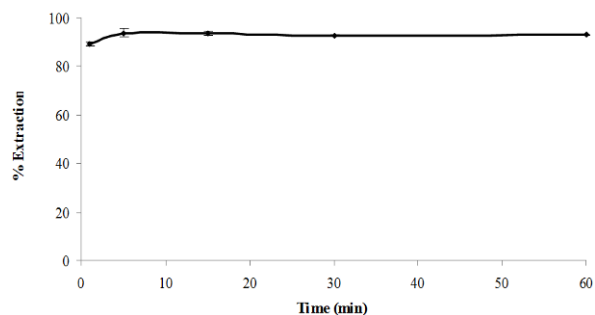


Figure 4. Variation of extraction efficiency (%) with agitation time. *Aqueous solution:* 1 mg L⁻¹ Cd²⁺, 0.1 M HEPES, 0.1 M NaNO₃. *Organic solution:* 0.1 M Cyanex 272 in kerosene.

in other studies for the extraction of Fe(III) with Cyanex 272 proving that, when adding NO₃⁻ ions to the aqueous media, a complex between the metal ion, the extracting agent and the nitrate ions is obtained [16].

Different aliquots of aqueous samples buffered at pH 6.7 with 0.25M HEPES solution were prepared with the addition of chlorides or nitrates at 0.1M concentration as co-ion, as reported in literature [16]. LLE experiments were performed for Cyanex 272 and Cyanex 923 extractants, both dissolved in kerosene, at 0.1M concentration. The results obtained for cadmium extraction efficiencies showed that, when using nitrates as co-ion higher values were obtained for both extractants (100% Cyanex 272 and 77% Cyanex 923) if compared with those of chlorides (80% Cyanex 272 and 26% Cyanex 923). On the other hand, an improvement in the extraction of cadmium was obtained when Cyanex 272 was employed as the extractant for both co-ions assayed.

According to the results, nitrate and Cyanex 272 were selected as the co-ion and extractant agent, respectively. Further experiments were performed employing these chemical compounds.

3.3. Optimization of the extraction and back-extraction method

To perform the univariate optimization, firstly, pH of the aqueous phase was varied in the range 5-8 to verify the suitability of the system for natural waters. An increase in the extraction efficiency of cadmium with pH was observed, obtaining the highest cadmium extraction efficiency for pH 6 and above, as it is shown in Fig. 1a. A pH value of 7.5, close to that of natural waters, was selected for further experiments.

Next, 2-hydroxyethyl piperazine-N'-(2-ethanesulphonic acid) (HEPES) concentration in the aqueous solution was studied in the range 0.05-0.2 M (Fig. 2). A slight decrease of 6.75% ± 0.29% in the extraction efficiency was obtained as the buffer solution concentration was increased in the aqueous phase. As a 0.05 M concentration proved to be too low to correctly buffer the solution, a 0.1 M concentration was found to be the most appropriate for the system.

The results obtained when Cyanex 272 concentration was studied in the range 0.005-0.1 M are shown in Fig. 3. As it can be seen no significant improvement in the extraction efficiency was obtained. As a consequence, a 0.1 M concentration of Cyanex 272 (93.9% ± 0.82%) was selected in order to guarantee the extraction of cadmium in real samples.

Finally, extraction time was studied between 1 and 60 min, obtaining the highest extraction efficiency for 5 min and above (Fig. 4). Even though beyond that time extraction does not improve significantly, a 15 min time

Table 1. Experimental values of cadmium extracted (%) under the presence of inorganic ligands.

[Cl ⁻], mol L ⁻¹	Cd _e (%)	[HCO ₃ ⁻] × 10 ³ , mol L ⁻¹	Cd _e (%)	[SO ₄ ²⁻] × 10 ³ , mol L ⁻¹	Cd _e (%)	[Br ⁻] × 10 ³ , mol L ⁻¹	Cd _e (%)
0.08	87.89 ± 1.69	0.1	94.02 ± 0.65	0.52	90.82 ± 2.18	1	92.50 ± 1.37
0.26	88.05 ± 0.50	1	93.15 ± 0.75	1.04	91.85 ± 1.27	5	91.07 ± 0.00
0.43	81.54 ± 1.38	5	94.02 ± 0.35	4.17	93.32 ± 0.73	10	89.79 ± 0.40
0.60	80.52 ± 1.47	10	93.41 ± 0.36				

Table 2. Analysis of cadmium in spiked water sample.

Sample	Added (μg L ⁻¹)	Found (μg L ⁻¹)	Recovery (%)
Guadalete River	0.50	0.52 ± 0.02	102
	1.00	1.03 ± 0.06	102
	1.50	1.51 ± 0.16	100

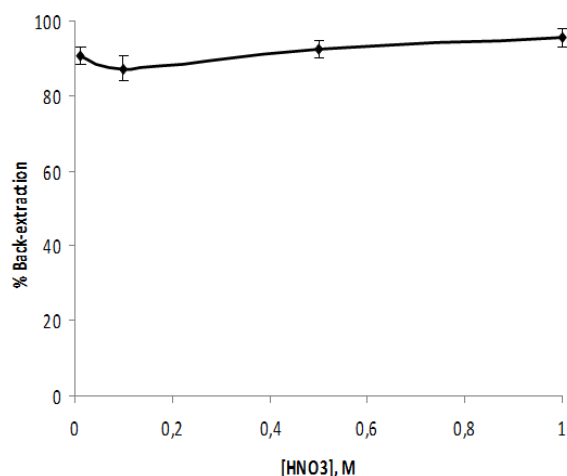


Figure 5. Effect of HNO₃ concentration in back-extraction efficiency.

(93.7% ± 0.91% extraction efficiency) was selected as the most suitable to guarantee that equilibrium is reached when analyzing real samples.

Once the extraction parameters were established, the back-extraction process was carried out employing HNO₃, which concentration was varied in the range 0.1-1 M. The organic solutions containing cadmium were obtained from previous LLE experiments at optimum conditions. Next, they were employed to study the effect of HNO₃ concentration on the extraction efficiency. The results obtained, as shown in Fig. 5, revealed a slight increase in the extraction up to the highest concentration assayed (95.47% ± 2.45%). As a consequence, a 1 M HNO₃ concentration was selected as the most appropriate for the system.

3.4. Effect of the presence of ligands in the aqueous solution

The results obtained when inorganic ligands were added to the sample in the different concentrations assayed are shown in Table 1. As it can be seen, only chlorides had a significant effect on the extraction efficiency, with a decrease of about 14% for the highest concentration studied. This negative effect can be related with the increase of concentration of complexed anionic species CdCl₃⁻ and CdCl₄²⁻ which are not extracted by Cyanex 272 at selected conditions. Similar results were reported by Levit *et al.* (28) decreasing up to 30% the cadmium free forms when chloride concentration was increased from 0.05M to 0.45M.

When humic acids (HA) were added to the aqueous solution, a negligible decreasing tendency of 4.46% ± 1.27% in the extraction of cadmium was observed. According to literature [29], it has been experimentally demonstrated that, when the total concentration of cadmium is increased in a media with purified peat humic acids (PPHA), the increase of free cadmium ions outstands that of cadmium bound to HA. These findings support the experimental results obtained.

3.5. Application

In order to demonstrate the applicability of the method, LLE experiments were performed on spiked water samples from the estuary of the Guadalete River (Cadiz, Spain) and cadmium concentration was obtained. After extraction/back-extraction was completed, the aqueous phase was measured by GFAAS. The results obtained are shown in Table 2 as the mean of three replicate LLE experiments of each spiked sample, and calculated taking into account the recovery of the extraction (93.9%) and that of back-extraction (95.47%) processes. As can be observed, the results obtained are in good agreement with those values used as reference, which is indicative of the reliability of the method to quantify cadmium in natural waters.

4. Conclusion

A LLE method for the separation and determination of cadmium ions in aqueous samples with Cyanex 272 dissolved in kerosene was developed. The most suitable chemical and physical conditions of the system were: pH 7.5, 0.1 M buffer concentration, 0.1M Cyanex 272 in kerosene and 15 min of agitation time. Back-extraction was also studied and 1 M HNO₃ selected as the most suitable back extractant concentration for the study.

It was observed that only in the case of chlorides there was a significant effect on the extraction efficiency,

with a 14% decrease for the highest concentration studied. In the case of organic ligands, humic acids proved to form unstable complexes with cadmium, not affecting its extraction at concentrations typically found in natural waters. Finally, the system was successfully applied to spiked real samples.

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References

- [1] S.N. Luoma, P.S. Rainbow, In: S.N. Luoma, P.S. Rainbow (Eds.), *Metal contamination in aquatic environments: Science and lateral management* (Cambridge University Press, New York, 2008) 18
- [2] M.S. Safazardeh, M.S. Bafghi, D. Moradkhani, M.O. Ilkhchi, *Min. Eng.* 20, 211 (2011)
- [3] J.M. Kumar, V. Kumar, J. Jeong, Lee, *J. Hydrometallurgy* 111-112, 1 (2012)
- [4] M. Tomaszewska, A. Borowiak-Resterna, A. Olszanowski, *Hydrometallurgy* 85, 116 (2007)
- [5] A. Parus, K. Wieszczycka, A. Olszanowski, *Hydrometallurgy* 105, 284 (2011)
- [6] B. Gupta, A. Deep, P. Malik, *Hydrometallurgy* 61, 65 (2001)
- [7] A.M. Rodríguez, D. Gómez-Limón, F.J. Alguacil, *J. Chem. Technol. Biotechnol.* 80, 967 (2005)
- [8] B.R. Reddy, D.N. Priya, *J. Power Sources* 161, 1428 (2006)
- [9] N.S. Rathore, A. Leopold, A.K. Pabby, A. Fortuny, M.T. Coll, A.M. Sastre, *Hydrometallurgy* 96, 81 (2009)
- [10] G. Nikam, K. Mahanwar, S. Sabale, B. Mohite, *Sep. Sci. Technol.* 48, 493 (2013)
- [11] M.D. Granado-Castro, M.D. Galindo-Riaño, M. García-Vargas, *Spectrochimica Acta Part B* 59, 577 (2004)
- [12] B.R.Reddy, D.N.Priya, J.R.Kumar, *Hydrometallurgy* 74, 277 (2004)
- [13] B.R. Reddy, S.V. Rao, D.N. Priya, *Sep. Purif. Technol.* 59, 214 (2008)
- [14] S.I. El Dessouhy, Y.A. El-Nadi, I.M. Ahmed, E.A. Saad, J.A. Daoud, *Chem. Eng. Process.* 47, 177 (2008)
- [15] I. Szilassy, L. Sumeghy, K. Vadasdi, *Miner. Process. Extr. Metall. Rev.* 17, 227 (1997)
- [16] N. Miralles, A.M. Sastre, E. Figuerola, M. Martinez, *Hydrometallurgy* 31,1 (1992)
- [17] S.D. Dogmane, R.K. Singh, D.D. Bajpai, J.N. Mathur, *J. Radioanal. Nucl. Chem.* 253, 477 (2002)
- [18] B.R. Reddy, J.R. Kumar, V. Reddy, *Anal. Sci.* 20, 501 (2004)
- [19] A.M.I. Ali, I.M. Ahmad, J.A. Daoud, *Sep. Purif. Technol.* 47, 135 (2006)
- [20] N.S. Madane, B.S. Mohite, *J. Radioanal. Nucl. Chem.* 290, 649 (2011)
- [21] D.S. Flett, *J. Organ. Chem.* 690, 2426 (2005)
- [22] K. Staszak, K. Wieszczycka, P. Burmistrz, *Sep. Sci. Technol.* 46, 1495 (2011)
- [23] F.J. Alguacil, H. Tayibi, *Desalination* 180, 181 (2005)
- [24] T. Duan, X. Song, J. Xu, P. Guo, H. Chen, H. Li, *Spectrochimica Acta Part B* 61 (2006)
- [25] K. Ndung'u, R.P. Franks, K.W. Bruland, A.R. Flegal, *Anal. Chim. Acta* 481, 127 (2003)
- [26] J.J. Ma, X. Du, J.W. Zhang, J.C. Li, L.Z. Wang, *Talanta* 80, 980 (2009)
- [27] P.K. Parhi, N.N. Das, K. Sarangi, *J. Hazard. Mater.* 172, 773 (2009)
- [28] R.L. Levit, E.I. Faustova, *Russ. J. App. Chem.* 82, 2065 (2009)
- [29] E. Tipping, M.A. Hurley, *Geochim. Cosmochim. Acta* 56, 3627 (1992)