

## THE CHROMATOGRAPHIC SEPARATION OF D AND F METAL IONS USING DIALKYLDITHIOPHOSPHORIC ACIDS AS COMPLEXING AGENTS

Soran Maria-Loredana, Stegarescu Adina

National Institute of Research & Development for Isotopic and Molecular Technology,  
Cluj-Napoca, Romania

Soran Maria-Loredana: loredana.soran@itim-cj.ro

**Abstract:** The metal ions separation by chromatographic techniques, using dialkyldithiophosphoric acids (HDADTP) as extracting agents is presented in this paper. The mechanism of extraction chromatography is briefly described. The separation mechanism of metal ions by TLC using HDADTP is a complex process based on adsorption-desorption, cation exchange and extraction, the later ones being dominantly. The nature of organic mobile phase containing HDADTP plays a decisive role in extraction chromatography of metal ions, especially for lanthanides and actinides.

**Key words:** cations exchangers, chromatographic techniques, dialkyldithiophosphoric acid, extraction chromatography, metal ion.

### Introduction

In the last years, the trace metal ions determination has received particular attention due to a strong environmental impact. Many studies are devoted to the separation and identification of metal ions in particular samples. Uranium and thorium, natural occurring actinide elements, are found at trace level in the environment or associated with other ions in different complex matrices, monazite sands, geological materials and fission products. Many methods have been proposed for the separation of these elements including ion exchange, liquid-liquid extraction and chromatography and any combination of them have been popularly applied to the selective separation of radionuclides or metal impurities from radioactive materials [1]. Out of these methods, chromatographic separation is more suitable due to their simplicity in handling the radioactive materials and heavy metals. In particular, separation techniques based on extraction chromatography, which combines the selectivity of organic compounds in solvent extraction with the multistage feature of chromatographic process have been extensively applied in the analysis of radioactive materials [2-4, 5].

The closed column extraction chromatography and thin layer extraction chromatography, too, is used for metal ions separation using various complexing agents. In this paper are presented some cases when the metal ions are separated using dithiophosphoric acids (HDADTP) as complexing agents.

### Mechanism of separation

The extraction chromatography is based on partition mechanism, combined with another mechanism, depending on extractant type: cationic exchange, anionic exchange, solvation and synergic systems [4]. The derivatives used in extraction chromatography could be: chelating (derivatives of thiophosphoric acids,  $\beta$ -diketones etc) or nonchelating (derivatives of organophosphoric acids, carboxylic acids etc) cations exchangers, neutral compounds, anions exchangers or mixture of these. The cation exchangers with chelating effect are most used from these.

In the case of chelating cations exchangers, the extraction process develops in two stages: the formation of extractable species in organic phase and partition of these into those phases (Eq.(1) and Eq.(2)).



where *HA* – acid extractant.

The most used cations exchanger are HDADTP, especially for hard metals and rare earths separation.

### Dithiophosphoric acids used in extraction chromatography

**a) Dimethyldithiophosphoric acid** was used for separation and quantitative determination of Bi(III), Cu(II) and Pd(II) by high performance liquid chromatography (HPLC) [6, 7]. In this goal was used a Licrosorb Si (250×4 mm), 5μ, column impregnated with dimethyldithiophosphoric acid. The mobile phase was a chloroform + acetonitrile + 1,2-dichlorethane (25:70:5, v/v) mixture with a 0.8 mL / min flow rate. The detection was performed at 295 nm. The detection limit for these cations was 0.1–0.2 ng / injection [7].

**b) Diethyldithiophosphoric acid (HDEDTP)** impregnated on columns with C18 chemically modified silica gel was used for metals separation from water and biological samples [8-14]. The mobile phase used for uranium, silver, tellurium and gold separation from water and biological samples was methanol. The detection limit of uranium and tellurium was very low: 0.05, and 2.24 pg / mL respectively [9]. The water samples were acidified with HNO<sub>3</sub> at 0.14M for preconcentration and quantitative determination of mercury from sea water. The detection limit was 5 pg/mL [10]. In the case of hard metals preconcentration (Cu, As, Se, Cd, Pb) it was obtained a concentration factor between 5 - 61; the detection limit of Bi was 0.43 pg / mL and 33 pg/mL for Cu [11].

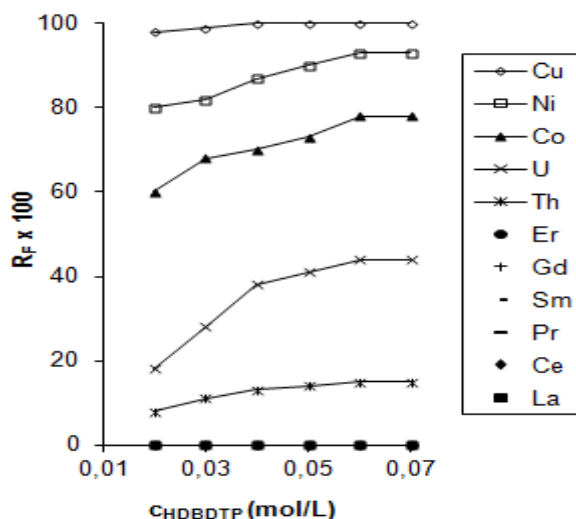
The lead complexed with HDEDTP was fixed on mini-column with C18 silica gel, and on active coal. The ethanol was the mobile phase. The best results were obtained on C18 chemically modified silica gel, the detection limit being 0.3 ng / mL for silica gel, and 3 ng / mL for active coal [12]. The column with active coal impregnated with HDEDTP was used with success for gold, silver and palladium determination from aluminum and manganese salts, too. The mobile phase used was a 2M ammonia solution in acetone. The recovery percent of these metals was higher than 95% [13, 14].

Ma and Adams [15] analyzing the influence of carbon atoms chain length from HDADTP on Cd, Cu and Pb extraction, have observed that the extraction by column chromatography decrease with increasing of the number of carbon atoms. Thus, the best extracting agent was HDEDTP, in the case of di(n-hexyl)dithiophosphoric acid the extraction being very weak. However, it was observed that in the presence of masking agents like as oxalate or citrate radical, the extraction not decrease such drastic with the chain length.

**c) Hodişan and coworkers [16, 17] have used di(iso-propyl)dithiophosphoric acid (HDiPrDTP) as complexing agent for UO<sub>2</sub>(II) and Th(IV) separation from Ag(I), Pb(II), Zn(II), Co(II), Ni(II), Fe(III), Al(III), Zr(IV) and were obtained good results. Silica gel 60 F254 plates were used as stationary phase and the mixture of o-xylene + methyl-ethyl-ketone (MEK)+N,N-dimethylformamide (DMF) (16:2:1, v/v) with 0.02–0.1M HDiPrDTP**

was the mobile phase. The spots visualizing was performed with Arsenzo I aqueous solution or at 254 nm in UV light. After separation it was observed that the retention factors of the studied metal ions increase with concentration of HDiPrDTP and it is constant after 0.07M HDiPrDTP. In this case it was suppose that the metal ions have formed a complex with HDiPrDTP ( $M(iPrDTP)_n$  ( $n = 1-4$ )). The best separation was obtained at 0.05M HDiPrDTP and the detection limit was  $1.21 \mu\text{g} / \mu\text{L}$  for uranium and  $1.26 \mu\text{g} / \mu\text{L}$  for thorium [16, 17].

**d) Dibutyldithiophosphoric acid (HDBDTP).** The thin layer chromatography (TLC) behavior on silica gel H of U(VI), Th(IV), lanthanides(III), Co(II), Ni(II), Cu(II) using di(n-butyl)- (HDBDTP) (Figure 1) and di(iso-butyl)dithiophosphoric acids (HDiBDTP) as complexing agents in organic mobile phase was investigated. Choosing appropriate conditions concerning mixture of organic solvents and concentration of complexing agent, the separation of U(VI) – Th(IV) and Co(II) – Ni(II) – Cu(II) systems was obtained.



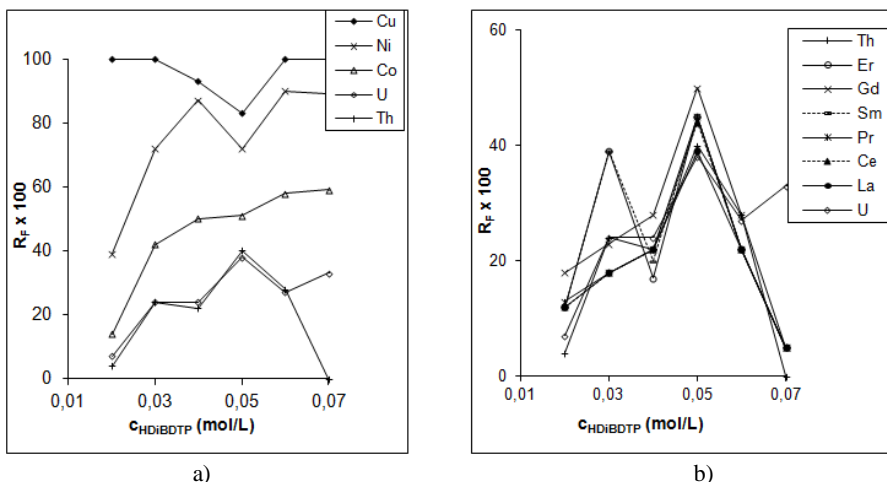
**Fig. 1.** The influence of HDBDTP concentration on chromatographic behavior of U(VI), Th(IV), La(III), Ce(III), Pr(III), Sm(III), Gd(III), Er(III), Co(II), Ni(II) and Cu(II). Stationary phase: silica gel H; Mobile phase: *o,m,p*-xylene – MEK – DMF (16 + 2 + 1, v/v)

The results obtained show that dithiophosphate anion play a decisive role in the migration of metal ions investigated. The branching chain improves significantly RF values for lanthanides(III) (Figure 2b). The presence of electron donor solvents in the mobile phase increases the retention factors especially for U(VI), Th(IV) and lanthanides(III). The effect is explained by increasing the solubility of the metal chelate with dithiophosphoric anion in organic mobile phase due to a solvation process. Using HDiBDTP in electron donor solvents, the separation of light lanthanides from heavy lanthanides and separation of Pr(III) – Sm(III), Sm(III) – Gd(III) and Gd(III) – Er(III) pairs can be achieved (Figure 2b) [18]. TLC separation of U(VI), Th(IV), Ln(III) (La(III), Ce(III), Pr(III), Sm(III), Gd(III), Er(III)), Co(II), Ni(II) and Cu(II) have been studied using tributylphosphate (TBP) and trioctylphosphine oxide (TOPO) besides (HDBDTP) in mobile phase. The results obtained

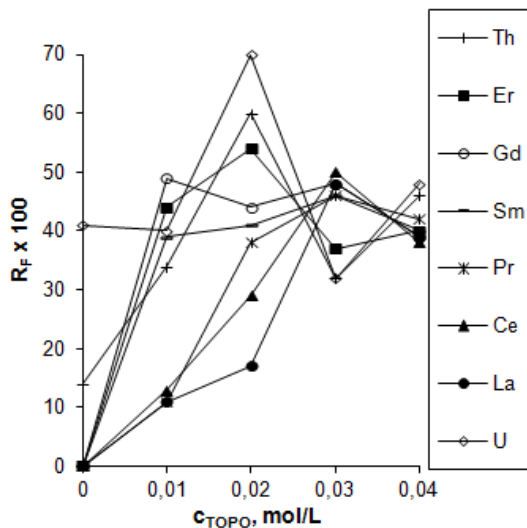
showed that a greater enhancement of the retention factor of U(VI), Th(IV) and Ln(III) is realized with mixture of HDBDTP and TOPO (Figure 3) and a synergic effect is suggested. An improvement of the resolution is achieved especially for Ln(III) separation from each other [19]. Di(sec-butyl)dithiophosphoric acid was used by Ma and Adams [20] for zinc separation in the iron presence, at pH = 3. 0.1M citrate solution was used for iron masking. The zinc extractability increase with the chain length of carbon atoms from extractant and with chain branching.

**e) Dipentylidithiophosphoric acid (HDPDTP).** HDPDTP was used for transitional and rare earth separation [21, 22]. In the case of Ni(II), Co(II) and Mn(II) separation was observed an increasing extractability with length of alkyl chain from extractant. It was obtained a quantitative extraction at pH = 3 for alkyl groups higher than butyl. These three ions were selectively extracted from a mixture with Cd(II), Cu(II), Pb(II), Fe(III) at the high concentration of HDPDTP. This method was used for trace extraction of Ni(II) from salt water samples (sea water and estuary water), obtaining good results [21].

**f) Di(2-ethylhexyl)dithiophosphoric acid (HDEHDTP)** is the dithiophosphoric derivative most used as extractant. In the most cases, this extractant is impregnated on various polymeric resins (chemically bonded or physically adsorbed), like as poly(4-vinylpyridine) and poly(N-dimethylacrylamide) [23, 24].



**Fig. 2.** The influence of HDiBDTP concentration on chromatographic behavior of a) Th(IV), U(VI), Co(II), Ni(II), Cu(II); b) Th(IV), U(VI), La(III), Ce(III), Pr(III), Sm(III), Gd(III), Er(III). Stationary phase: silica gel H; Mobile phase: *o,m,p*-xylene – MEK – DMF (16+2+1, v/v)



**Fig. 3.** The chromatographic behavior of Th(IV) and Ln(III). Stationary phase: silica gel H; mobile phase: *o,m,p*-xylene – EMK – DMF (16+2+1, v/v); extractants: TOPO + HDBDTP ( $CHDBDTP = 0.04 M$ )

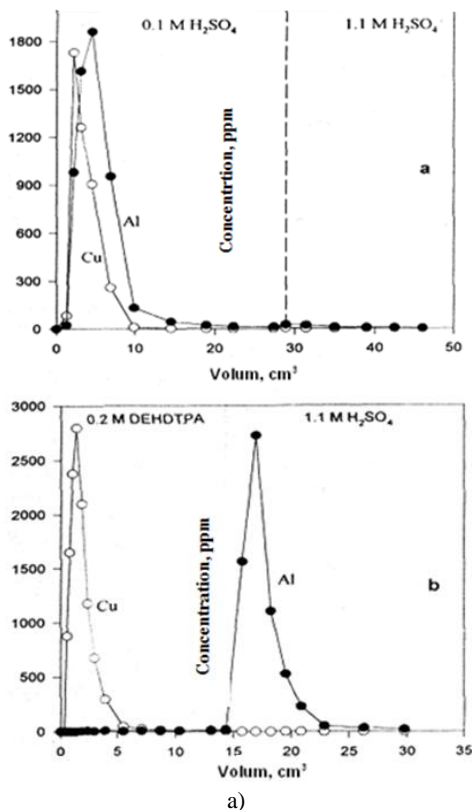
The solvents impregnated resins (SIR) were used for identification and separation of metallic ions from aqueous solutions by Flett as far back as in 1977. These combine the SIR advantages with the specific properties of extractants, obtaining high distribution ratios and a good selectivity with a simple equipment [25]. In Warshawsky [26] vision, the SIR consist in a liquid complexing agent homogeneous dispersed in a solid polymeric medium. The impregnation agent must present a strong affinity for matrix.

The following conditions must be fulfilling for efficiently SIR: i) the extractant must to be a liquid or must to remove him in the liquid phase by adding a diluents; ii) the extractant and diluent to be more less soluble in aqueous phase; iii) the polymeric support must to be porous; iv) the method used for impregnation to not destroy the extractant or polymer properties [26].

Impregnated resins with HDEHDTP [27, 28] were used as stationary phases for selective extraction of hard metals from relative concentrated solutions or for recuperation of these metals from residual waters, the separation process basing on ionic exchange. The impregnated resins with HDEHDTP have proved a good selectivity at Cd(II), Pb(II) and Zn(II) separation [27]. The same type of stationary phase was used for purification of waters polluted with Cd, Pb and Cu, establishing that 1kg ions exchange resin can treat 1 m<sup>3</sup> residual water polluted with 200 µg Cd / L water. This concentration is specific for metal ion in surface water. The concentration of these three metals in water was decreased a 100 times, from 1mg/l to less than 0.001mg / L [28].

Resins impregnated with HDEHDTP were used for extraction of Cu, Pb, Zn, Cd, Ni from aqueous solutions, too [26, 29-32], and it was succeeded to separate Pb(II) from Zn(II) and Pb(II) from Ni(II). It was observed an arrange of hard metals in HDEHDTP extractability order from acid aqueous solutions, like follows: Ag(I) > Hg(II) > Bi(III) > Cu(II) > Pb(II) > As(III) > Cd(II) > In(III) > Fe(III) > Ni(II) > Zn(II) [26]. After separation,

the metal ions were extracted from ligand matrix by washing with mineral acids, the ligand turning in mass of the polymeric support. Thus, the extraction of Cu(II) like  $\text{CuCl}_2(\text{HA})_8$  and  $\text{CuClX}(\text{HA})_8$  complexes ( $\text{HA} = \text{HDEHDTP}$ ,  $\text{X} = \text{inorganic anion}$ ) it was performed [30].



**Fig. 4.** The curves concentration – volume obtaining at the elution of Cu(II) and Al(III):  
a) 0.1 M and 1.1 M H<sub>2</sub>SO<sub>4</sub>, b) 0.2 M HDEHDTP and 1.1 M H<sub>2</sub>SO<sub>4</sub>

HDEHDTP impregnated on resins was used by Muraviev, too, for separation of zinc from cadmium [31]. This has compared the results with those obtained with di(2-ethylhexyl)phosphoric acid (HDEHP) and di(3-propylphenyl)dithiophosphoric acid (HDPPDTP) impregnated on resins. The best results were obtained with HDEHDTP – SIR. Oleinikova and coworkers [32] have used HDEHDTP like mobile phase for column separation of Al(III), Cu(II) and Zn(II). The results were compared with those obtained using H<sub>2</sub>SO<sub>4</sub>, and HDEHP as eluents. This has combined the ionic exchange separation techniques with solvent extraction and has demonstrated the efficiency of this method. It was observed from the graphic  $c = f(v)$  ( $c$  – metal ions concentration,  $v$  – volume of used acid) that the metal ions are not completely separation using water impregnated polyacrylic resin as stationary phase, and 0.1 – 1.1M H<sub>2</sub>SO<sub>4</sub> as mobile phase. Using 0.2M HDEHDTP

in heptane as mobile phase and than a 1.1M H<sub>2</sub>SO<sub>4</sub> solution it was observed the selective separation of Cu(II) (Figure 4).

Adding 0.2M HDEHP in the elution system it was find that the 0.2M HDEHDTP solution have selectively extracted of Cu(II), and 1.1M H<sub>2</sub>SO<sub>4</sub> have selectively extracted of Al(III) with high purity. Zn(II) was completely extracted in the organic eluent [32].

The results of this study show that HDEHDTP have a high affinity for Cu(II), achieving quantitative extraction of these metal ions.

Separation of U(VI) and Th(IV) from some rare earths by TLC has been studied using silica gel H and silica gel H impregnated with ammonium nitrate as the stationary phase. The solvent mixture methyl-ethyl-ketone + tetrahydrofuran (6:3, v/v) containing HDEHDTP was used as the mobile phase. When silica gel H impregnated with 2.5 M NH<sub>4</sub>NO<sub>3</sub> was used as stationary phase, the resolution was much improved and the separation of rare earths from each other was also achieved [33, 34].

The dithiophosphoric acids were used as masking agents of copper at bismuth extraction from various ores [35].

**g) The di(n-octyl)dithiophosphoric acid (HDODTP)** was used in the same system like HDBDTP, HDPDTP, HDEHDTP, and the results were not semnificated [36].

**h) The dithiophosphoric acids** with cyclic substituents are used as extractants, too. The metal ions form less stable complexes with these ligands than that formed with acyclic substituent and can be used as selective reactive [37].

### Conclusions

The increasing of extraction efficiency was obtained by combination of ionic exchange with liquid-liquid extraction in a single process. Thus, the extraction chromatography could be applied for nonferrous and hard metals separation from waste waters and for removing the ionic contaminants from diluted solutions.

The separation mechanism of metal ions by TLC using HDADTP is a complex process based on adsorption-desorption, cation exchange and extraction, the later ones been dominantly. The nature of organic mobile phase containing HDADTP plays a decisive role in extraction chromatography of metal ions, especially for lanthanides and actinides. In the presence of HDADTP appear an ionic exchange process between metal cation and hydrogen ion from HDADTP, in this process is formed a neuter chelating complex with dithiophosphat anion, M(DADTP)<sub>n</sub>. The compound solubility in organic solvent influence the distribution of metal cations in the mobile phase, and the increasing the retention factors of those cations.

HDEHDTP is the most used HDADTP, using silica gel and silica gel impregnated with 2.5 M NH<sub>4</sub>NO<sub>3</sub> as stationary phase.

The increasing of alkyl chain length guide to the decreasing of the retention factors of UO<sub>2</sub>(II) and Th(IV) and an increasing of lanthanides retention factors.

The chain branching promotes just the lanthanides migration, that in the systems with HDADTP with linear chain generally remain at start.

### References

- 1. Rodriguez, M., Gascón, J.L., Suarez, J.A.** Study of the interferences in the determination of Pu, Am and Cm in radioactive waste by extraction chromatography. In: *Talanta*, 1997, 45, pp.181-187.
- 2. Lee, C.H., Suh, M.Y., Choi, K.S., Kim, J.S., Park, Y.J., Kim, W.H.** Determination of Ru, Rh, Pd, Te, Mo and Zr in spent pressurized water reactor fuels by ion exchange and extraction chromatographic separations and inductively coupled plasma atomic emission spectrometric analysis. In: *Analytica Chimica Acta*, 2003, 475, pp.171-179.
- 3. Lee, C.H., Suh, M.Y., Choi, K.S., Kim, J.S., Song, B.C., Jee, K.Y., Kim, W.H.** Separation of fission products from spent pressurized water reactor fuels by anion exchange and extraction chromatography for inductively coupled plasma atomic emission spectrometric analysis. In: *Analytica Chimica Acta*, 2001, 428, pp.133-142.
- 4. Braun, T., Ghersini, G.** *Extraction Chromatography*. Budapest: Akadémiai Kiadó, 1975.
- 5. Liteanu, C., Gocan, S., Hodişan, T., Naşcu, H.** *The liquid chromatography*. Bucharest, Scientifique Ed, 1974.
- 6. Khuhawar, M.Y., Channar, A.H., Lanjwani, S.N.** Reverse Phase Liquid Chromatographic Determination of Bismuth(III), Copper(II) and Palladium(II) using Dimethyldithiophosphate as Complexing Reagent. In: *Journal of the Chemical Society of Pakistan*, 1997, 19, pp.135-137.
- 7. Khuhawar, M.Y., Channar, A.H., Lanjwani, S.N.** Use of Malathion for High Performance Liquid Chromatographic Determination of Bismuth(III), Copper(II) and Palladium(II) based on Complexation with Dithiophosphate. In: *Journal of the Chemical Society of Pakistan*, 1998, 20, pp.257-260.
- 8. Sella, S.M., Avila, A.K., Campos, R.C.** The Determination of Cd, Cu and Pb in Potable Water and Plant Material by Flame-AAS after on-Line Preconcentration of DDTP-NH<sub>4</sub> Metal Complexes on a C18 Column. In: *Anal. Lett.*, 1999, 32, pp.2091-2104.
- 9. Dressler, V.L., Pozebon, D., Curtius, A.J.** Determination of Ag, Te, U and Au in waters and in biological samples by FI-ICP-MS following on-line preconcentration. In: *Analytica Chimica Acta*, 2001, 438, pp.235-244.
- 10. Seibert, E.L., Dressler, V.L., Pozebon, D., Curtius, A.J.** Determination of Hg in seawater by inductively coupled plasma mass spectrometry after on-line preconcentration. In: *Spectrochimica Acta, Part B*, 2001, 56, pp.1963-1971.
- 11. Dressler, V.L., Pozebon, D., Curtius, A.J.** Determination of heavy metals by inductively coupled plasma mass spectrometry after on-line separation and preconcentration. In: *Spectrochimica Acta, Part B*, 1998, 53, pp.1527-1539.
- 12. Quináia, S.P., Silva, J.B.B., Rollemberg, M.C.E., Curtius, A.J.** Preconcentration of lead complexed with *O,O*-diethyl-dithiophosphate by column solid-phase extraction using different sorbents in a flow injection system coupled to a flame atomic absorption spectrometer. In: *Talanta*, 2001, 54, pp.687-696.
- 13. Soyлак, M., ElçI, L., Narin, I., Doğan, M.** Separation and Preconcentration of Gold, Silver and Palladium from Some Aluminum and Manganese Salts on Activated Carbon Column. In: *Asian Journal of Chemistry*, 2001, 13(2), pp.699-703.



14. **Soylak, M., Elçi, L., Doğan, M.** A Sorbent Extraction Procedure for the Preconcentration of Gold, Silver and Palladium on an Activated Carbon Column. In: *Analytical Letters.*, 2000, 33, pp.513-525.

15. **Ma, R., Adams, F.** Flow injection sorbent extraction with dialkyldithiophosphates as chelating agent for the determination of cadmium, copper and lead by flame atomic absorption spectrometry. In: *Spectrochimica Acta, Part B*, 1996, 51, pp.1917-1923.

16. **Hodişan, T., Curtui, M., Haiduc, I.** Separation and quantitative determination of dioxouranium(VI) and thorium(IV) ions in the presence of different metallic ions by TLC using iso-propyldithiophosphoric acid as complexing agent. In: *Journal of Radioanalytical and Nuclear Chemistry*, 1998, 238, pp.129-133.

17. **Hodişan, T., Curtui, M., Cobzac, S., Cimpoiu, C., Haiduc, I.** The limit of detection improvement in TLC determination of uranium and thorium in the presence of other metal ions. In: *Journal of Radioanalytical and Nuclear Chemistry*, 1998, 238, pp.179-182.

18. **Ma, R., Van Mol, W., Adams, F.** Flow injection sorbent extraction with dialkyldithiophosphates as chelating agent for the determination of zinc by flame atomic absorption spectrometry. In: *Analytica Chimica Acta*, 1995, 309, pp.395-403.

19. **Soran, M.L., Curtui, M.** Use of Di(n-butyl) and Di(iso-butyl)dithiophosphoric Acids as Complexing Agents in the TLC Separation of Some d and f Transition Metal Ions. In: *Journal of Planar Chromatography - Modern TLC*, 2007, 20, pp.153-158.

20. **Curtui, M., Soran, M.L.** TLC Separation of Metal Ions Using Di(n-butyl)dithiophosphoric Acid and Neutral Organophosphorus Ligands. In: *Journal of Planar Chromatography - Modern TLC*, 2006, 19, pp.310-314.

21. **Ma, R., Adams, F.** Flow injection sorbent extraction with dialkyldithiophosphates as chelating agent for nickel, cobalt and manganese determination by atomic absorption spectrometry. In: *Analytica Chimica Acta*, 1995, 317, pp.215-222.

22. **Soran, M.L., Măruţoiu, C., Curtui, M., Hodişan, T., Oprean, R.** Separation of nickel (II) and copper (II) from different cations by TLC using dipentyldithiophosphoric acid as complexing reagent. In: *Acta Universitatis Cibiniensis, Seria F, Chemia*, 2002, 5, pp.69-73.

23. **Bromberg, L.** Swelling of Polymeric Resins in Organic Solvents Induced by Dialkyldithio-Containing Extractants. In: *The Journal of Physical Chemistry*, 1996, 100, pp.1767-1770.

24. **Strikovskiy, A.G., Warshawsky, A., Hankova, L., Jerabek, K.** Morphology of solvent-impregnated resins based on reactive supports. In: *Acta Polymerica*, 1998, 49, pp.600-605.

25. **Strikovskiy, A.G., Jerabek, K., Cortina, J.L., Warshawsky, A.** Novel solvent impregnated resins containing di-(2-ethylhexyl)dithiophosphoric acid on the reactive support. In: *Solvent Extraction and Ion Exchange*, 1997, 15, pp.259-283.

26. **Juang, R.S.** Preparation, properties and sorption behavior of impregnated resins containing acidic organophosphorus extractants. In: *Proceedings of the National Science Council, Republic of China, Part A: Physical Science and Engineering*, 1999, 23, pp.353-364.

27. Warshawsky, A., Strikowsky, A.G., Fernandez, F.M., Jerábek, K. Synthesis of novel chelating resins containing dithiophosphoric functionality and comparison to analogous solvent impregnated resins. In: *Separation Science and Technology*, 2002, 37, pp.823-846.
28. Warshawsky, A., Strikowsky, A.G., Vilensky, M.Y., Jerabek, K. Interphase mobility and migration of hydrophobic organic metal extractant molecules in solvent-impregnated resins. In: *Separation Science and Technology*, 2002, 37, pp.2607-2622.
29. Vilensky, M.Y., Berkowitz, B., Warshawsky, A. In situ remediation of groundwater contaminated by heavy- and transition-metal ions by selective ion-exchange methods. In: *Environmental Science & Technology*, 2002, 36, pp.1851-1855.
30. Strikovskiy, A.G., Jerabek, K., Cortina, J.L., Sastre, A.M., Warshawsky, A. Solvent impregnated resin (SIR) containing dialkyl dithiophosphoric acid on Amberlite XAD-2: extraction of copper and comparison to the liquid-liquid extraction. In: *Reactive and Functional Polymers*, 1995, 28, pp.149-158.
31. Muraviev, D., Ghantous, L., Valiente, M. Stabilization of solvent-impregnated resin capacities by different techniques. In: *Reactive and Functional Polymers*, 1998, 38, pp.259-268.
32. Oleinikova, M., Muraviev, D., Valiente, M. Aqua-Impregnated Resins. 2. Separation of Polyvalent Metal Ions on Iminodiacetic and Polyacrylic Resins Using Bis(2-ethylhexyl) Phosphoric and Bis(2-ethylhexyl) Dithiophosphoric Acids as Organic Eluents. In: *Analytical Chemistry*, 1999, 71, pp.4866-4873.
33. Soran, L., Hodişan, T., Curtui, M., Casoni, D. TLC Separation of Rare Earths Using Di(2-ethylhexyl) dithiophosphoric Acid as Complexing Reagent. In: *Journal of Planar Chromatography - Modern TLC*, 2005, 18, pp.160-163.
34. Soran, M.L., Curtui, M., Măruţoiu, C. Separation of U(VI) and Th(IV) from Some Rare Earths by thin layer chromatography with Di(2-ethylhexyl)dithiophosphoric acid on silica gel. In: *Journal of Liquid Chromatography & Related Technologies, Special Issue on Thin Layer Chromatography*, 2005, 28, pp.2515-2524.
35. Takase, I., Campos, R.C. A study of the dithiophosphoric acid diacyl ester as a masking agent for the determination of bismuth in the presence of copper by hydride generation atomic absorption spectrometry. In: *Talanta*, 2000, 51, pp.441-445.
36. Soran, L., Măruţoiu, C., Hopirtean, E., Haiduc, I. Separation of some cations by TLC using di(n-octyl) dithiophosphoric acid as complexing reagent. In: *Acta Universitatis Cibiniensis, Seria F, Chemia*, 2003, 6, pp.3-7.
37. Ovchinnikov, V.V., Toropova, V.F., Garifzyanov, A.R., Cherkasov, R.A., Pudovik, A.N. Complexing, redox and extractive properties of cyclic and acyclic derivatives of phosphorus dithioacids. In: *Phosphorus Sulfur*, 1985, 22, pp.199-210.