



**“BABEȘ-BOLYAI” UNIVERSITY**  
**FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING**



**ORGANOTHIOPHOSPHORIC LIGANDS**  
**– AGENTS FOR METAL IONS SEPARATION**

**PhD Thesis Abstract**

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**KEYWORDS:**

Liquid-liquid extraction

Thin layer chromatography (TLC)

Dialkyldithiophosphoric acids

Metal ions

Uranium(VI)

Thorium(IV)

Lanthanides(III)

## INTRODUCTION

The problem of analyzing and separating metal species has been and remains a topical issue. In the last years, when the environment has an ever growing importance, identification and separation of metal ions captures the attention in a special way.

Extraction is known as one of the oldest and most important techniques of concentration, separation and purification of the chemical compounds that occurs in different technologies. The applications of extraction were perfected, diversified and expanded continuously from a laboratory level to an industrial scale. In the 1940s, extraction began to be used in the modern hydrometallurgy, and then it became important for obtaining some metals from natural sources; for refining uranium and thorium for being used in the nuclear reactor; for separating elements with similar properties as Zr – Hf, Nb – Ta or lanthanides; for the recovery and separation of fissionable elements (U, Th) from irradiated nuclear fuel.

Extraction has proved its efficiency in the separation metals through both liquid-liquid extraction and extraction chromatography. The latter combines the selectivity of the organic compounds used in liquid-liquid extraction with the step-process character of chromatography. Using a wide range of complexing agents in the extraction chromatography, separation selectivity can be influenced by both the structure and stability of the complexes formed.

For the separation of metal ions, the extraction chromatography is used both on column and on thin layer with a wide variety of complexing agents. Literature data show that organophosphorus derivatives have been widely used in the extraction of metal ions. Less studied are analogues with sulphur, the organothiophosphorus ligands.

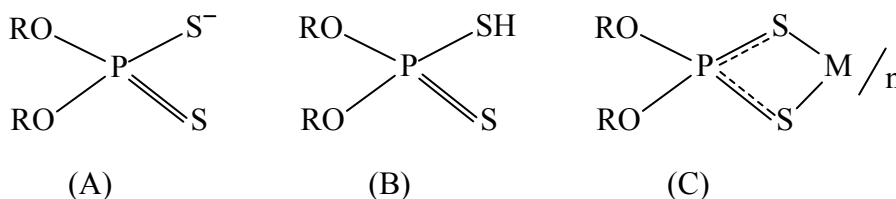
The purpose of this paper is to study the possibility of separation by liquid-liquid extraction and thin layer chromatography extraction of metal ions of major importance:  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$ ,  $\text{Ln}(\text{III})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$ . Uranium and thorium, important elements due to their nuclear properties, occur in nature or in nuclear fission products together with lanthanides or other transitional metals like nickel, cobalt and copper.

The paper comprises two parts. The first part aims to systematize some literature data on metal separation by solvent extraction and chromatography extraction in general and the utilization of extractive properties of organothiophosphorus derivatives in particular. The second part studies the behavior of organothiophosphorus derivatives in liquid-liquid extraction systems and in thin layer chromatographic systems involving the metal ions mentioned above.

## ORIGINAL CONTRIBUTIONS

### IV. THE USE OF ORGANODITHIOPHOSPHORIC ACID DERIVATIVES IN THE EXTRACTION OF URANIUM(VI), THORIUM(IV) AND LANTHANIDES(III)

The use of dialkyl dithiophosphoric acids  $(RO)_2P(S)SH$  as complexing agents for metals in general, and specifically for some elements of great interest, such as: Uranium(VI), Thorium(IV) and Lanthanides(III) raised interest for comparisons with their correspondents with oxygen, dialkylphosphoric acids,  $(RO)_2P(O)OH$ . Examples of dialkylphosphoric acids applications were synthesized in the volume Gmelin Handbook of Inorganic Chemistry [209] and in other articles and publications. But there are only a few informations about the extraction of Uranium(VI), Thorium(IV) and Lanthanides(III) with dialkyl dithiophosphoric acids [210,211]. This is surprising, because the reagents with sulphur were used very often for the extraction of some other metals [212-214]. Their extractive properties are emphasized also by their ability to extract even the alkaline metals from aqueous solutions [215]. Dithiophosphate anions (A) of dialkyl dithiophosphoric acids (B) act, almost always, as a bidentate ligand (C):



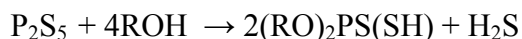
to form chelatic complexes soluble in organic solvents and insoluble in water, which makes them useful for the extraction of several metal ions.

The purpose of this paper is to investigate the extractive properties of some dialkydithiophosphoric acids on uranium, thorium and lanthanides, metals involved in the use of nuclear energy. The intention is to fill some existing data in the literature on this area, in order to be compared with results obtained by extraction chromatography.

## IV.1. EXPERIMENTAL DATA

### IV.1.1. Reagents preparation

Dialkyldithiophosphoric acids (DADTPA) listed in table 1, were synthesized in laboratory, by direct reaction of phosphorus pentasulfide [216-219] and the corresponding alcohols.



**Table 1.** Dialkyldithiophosphoric acids used in the extraction of metal ions.

Acid	Formula	Symbol
Diethyldithiophosphoric acid	$(C_2H_5O)_2PSSH$	DEDTPA
Dipropyldithiophosphoric acid	$(C_3H_7O)_2PSSH$	DPrDTPA
Diisopropyldithiophosphoric acid	$(iC_3H_7O)_2PSSH$	DiPrDTPA
Dibutyldithiophosphoric acid	$(C_4H_9O)_2PSSH$	DBDTPA
Diisobutyldithiophosphoric acid	$(iC_4H_9O)_2PSSH$	DiBDTPA
Di(2-ethylhexyl)dithiophosphoric acid	$(C_8H_{17}O)_2PSSH$	DEHDTPA

## IV.2. DIALKYLDITHIOPHOSPHORIC ACIDS IN WATER – ORGANIC SOLVENT SYSTEMS

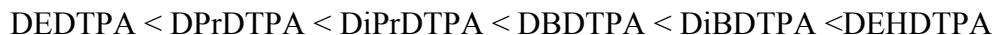
Dialkyldithiophosphoric acids, as stated above, proved to be good extractants for metal ions. In their reaction with metals in the partition systems, they are different from dialkylphosphoric acids, which is explained in part by their different behavior in organic solvents.

The existing data in literature [223-226] show that dialkyldithiophosphoric acids present lower polymerization tendencies compared to dialkylphosphoric acids, so that in diluted solutions they are in monomer form. Their way of existence in organic solvents, associated or unassociated, determined by interactions that may or may not occur between the extractant molecules (hydrogen bonds) are often reflected on the mechanism of metal ion extraction [227]. Studies on extraction of metals with dialkyldithiophosphoric acids suggest a mechanism of extraction which differs from the one given in literature for extraction of uranium with dialkylphosphoric acids (which has been extensively studied, the mechanism being fully understood).



To explain some particularities observed in the extraction of uranium from aqueous nitrate solutions with diethyl-, dipropyl-, diisopropyl-, dibutyl- and di(2-ethylhexyl)dithiophosphoric acids in water-butanol system and water-benzene system, the behavior of these acids was studied in the mentioned distribution systems. The variation of the distribution ratio of the acids was determined as a function of the acid concentration in the aqueous or organic phase or as a function of the concentration of hydrogen ions in the aqueous phase; the partition constants and the splitting constants were calculated from the obtained data.

The data obtained indicate only small changes in acidity constants of studied dialkyldithiophosphoric acids, which is in good agreement with those mentioned in literature. Differences can be observed in the values of partition constants of acids, which similar to pKa increase in the order:



The results obtained for dipropyl-, diisopropyl-, dibutyl- and di(isobutyl)-dithiophosphoric acids suggests that ramification of alkyl chain of the acid leads to a drop of splitting constant and a slight increase in partition constant.

Comparing the two extraction systems: water - benzene and water - butanol, by the values of partition constants obtained, we conclude that dialkyldithiophosphoric acids are extracted in butanol better than in benzene. This can be explained by hydrogen bond formation between acid and solvent.

### **IV.3. THE SEPARATION MECHANISM OF METALS WITH DIALKYLDITHIOPHOSPHORIC ACIDS THROUGH LIQUID-LIQUID EXTRACTION**

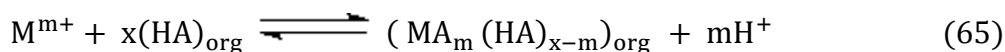
The experimental results on U(VI), Th(IV) and Ln(III) extraction from aqueous solutions  $\text{HNO}_3 + \text{NaNO}_3$  with dialkyldithiophosphoric acids, show a dependence of the extraction on the aqueous phase acidity and regarding the extraction capacity of these acids the nature of organic solvent used. When a polar solvent containing oxygen molecule is used, better partition constants are obtained.

As a result, in order to elucidate the extraction mechanism it was studied in detail, comparatively, the extraction of uranium from aqueous solutions, with the dialkyldithiophosphoric acids listed in Table 1 in butanol and benzene.

### IV.3.1. Mathematical approach

#### IV.3.1.1. Extraction systems with acid extractant

The extraction equilibrium of a metal  $M^{m+}$  with an organophilic reagent in monomer form (HA) can be described by the equation:



where index "org" is the organic phase.

The extraction equilibrium constant is given by the expression:

$$K = \frac{[MA_m(HA)_{x-m}]_{org} [H^+]^m}{[M^{m+}][HA]_{org}^x} \quad (66)$$

Assuming the predominant metal species in the system are  $MA_m(HA)_{x-m}$  in the organic phase and  $M^{m+}$  in the aqueous phase, the ratio  $[MA_m(HA)_{x-m}]_{org}/[M^{m+}]$  is the distribution ratio (D) of the metal. Introducing the distribution ratio D in equation (66) (after logarithmation), it follows that:

$$\log D = \log K + mpH + x \log [HA]_{org} \quad (68)$$

Equation (68) expresses the dependence of the distribution ratio versus different parameters of the extraction system: the pH of the aqueous phase and concentration of acid in the organic phase, under equilibrium conditions. Equation (68) can offer information concerning the nature of the species formed in the extraction system. A plot of  $\log D$  versus the pH (at a constant concentration of acid in the organic phase), give curves, which in certain areas of pH represent straight lines with the slope m. According to equation (65), m is the number of acid molecules involved in ion exchange reaction.

For the pH which provides 50% metal extraction, the distribution ratio D is equal to 1 and thus  $\log D = 0$ . Under these conditions, equation (68) becomes:

$$pH_{50\%} = -\frac{1}{m} \log K - \frac{x}{m} \log [HA]_{org} \quad (69)$$

From relation (69) the ratio  $x/m$  can be determined as the slope of the straight line obtained by plotting  $pH_{50\%}$  against the concentration of the dithiophosphoric acid in the organic phase.

Variation of distribution ratio of metal depending on pH, at constant acid concentration, for different metal concentrations, can give information about the presence of polymeric species in the system. An increase of the distribution ratio with an increase of the metal concentration

may be due to polymerization of the complex in the organic phase or to a salting-out effect, while a decrease can be attributed to polymerization in aqueous phase.

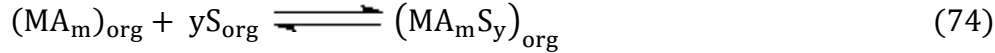
Equation (65) neglects interactions that can occur in the aqueous phases. Considering metal complexation phenomena that sometimes occur with acid extractant, in aqueous phase (due to the partition of the extractant between the two phases) in equation (68) a new term is introduced:

$$\log D = \log K + m\text{pH} + x \log [\text{HA}]_{\text{org}} - \log B \quad (73)$$

As shown in equation (73), the complexation phenomena occurring in the aqueous phase decreases the distribution ratio of metal and therefore, B term contribution tends to decrease the value obtained for m.

#### ***IV.3.1.2. Extraction system with acid and neutral extractant***

In the extraction systems containing donor solvents or a neutral ligand S, mixed complexes  $\text{MA}_m\text{S}_y$  may be formed (especially when  $\text{MA}_m$  compound is coordinatively unsaturated), according to the following equation:



Considering extraction equilibrium of the metal  $\text{M}^{m+}$  with a mixture of two organophilic extractants, one acid and one neutral, the following equation can be written:



The extraction equilibrium constant is given by the expression:

$$K_s = \frac{[\text{MA}_m\text{S}_y][\text{H}^+]^m}{[\text{M}^{m+}][\text{HA}]^m[\text{S}]^y} \quad (76)$$

$$K_s = \frac{D [\text{H}^+]^m}{[\text{HA}]^m[\text{S}]^y} \quad (77)$$

Which leads to the distribution ratio expression:

$$D = K_s [\text{HA}]^m [\text{S}]^y [\text{H}^+]^{-m} \quad (78)$$

Considering the concentrations  $[\text{HA}]_{\text{org}}$  and  $[\text{S}]_{\text{org}}$  equal to the initial concentrations  $c_{\text{HA}}$ , respectively  $c_{\text{S}}$ , after the logarithmation of expression (77) we obtain:

$$\log D = \log K_s + m \log c_{\text{HA}} + m \text{pH} + y \log c_{\text{S}} \quad (79)$$

Using the relation (79) the number of solvation y can be determined.

The combined effect of the acid complexing agent with the solvation properties of the neutral extractant can increase the extraction by to a synergic effect.

### **IV.3.2. Results and discussions**

Assuming that the extraction of studied metal ions with acid organodithiophosphorus extractant can be described by the mathematical model presented, we studied the influence of following parameters: the pH of the aqueous phase after extraction, dialkyldithiophosphoric acid concentration (DADTPA) and metal ion concentration.

#### ***IV.3.2.1. Uranium extraction***

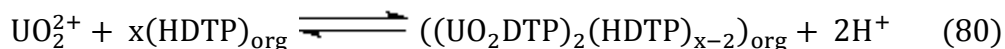
##### ***U(VI) - DADTPA - Butanol***

The influence of pH at three different concentrations of acid extractant in the organic phase was studied. The types of curves obtained are represented in Figures 15 and 16 for DEDTPA, DADTPA.

The slope values of: 1.7, 1.85, 1.85, 1.85 and 2 for the diethyl-, dipropyl-, diisopropyl-, dibutyl-, and di(2-ethylhexyl)dithiophosphoric acids respectively suggest second order power dependence of the distribution ratio of uranium versus pH (in equations (68) and (69)  $m = 2$ ).

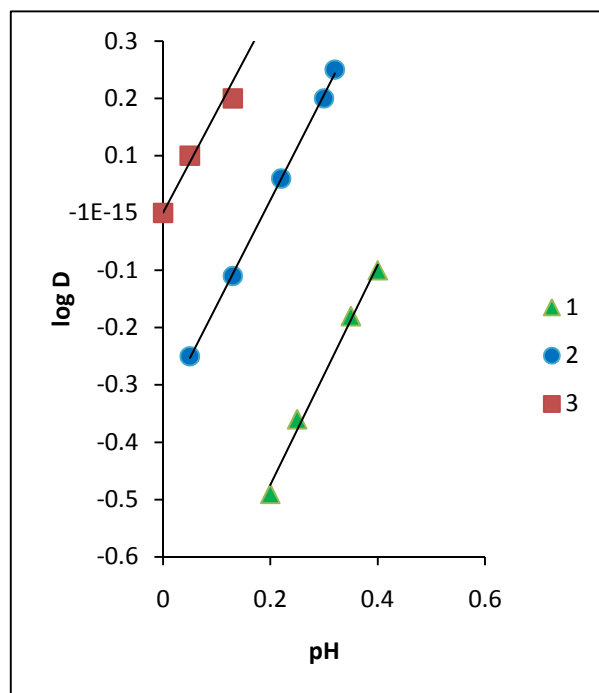
The deviation of the slope values from the expected value of 2 can be attributed to the uranium complexation in aqueous solution, due to the distribution of the dialkyldithiophosphoric acids between two phases. For systems with acid di(2-ethylhexyl)dithiophosphoric, deviations from the value 2 for the slope do not appear, suggesting that the phenomenon of complexation in the aqueous phase is negligible.

These results show that two dialkyldithiophosphoric acid molecules are involved in the ion-exchange reaction. Consistent with these data, it is assumed that uranyl ion predominates in aqueous solution, and equation (65) can be written as:



where DATP<sup>-</sup> represents (RO)<sub>2</sub>PSS<sup>-</sup> anion.

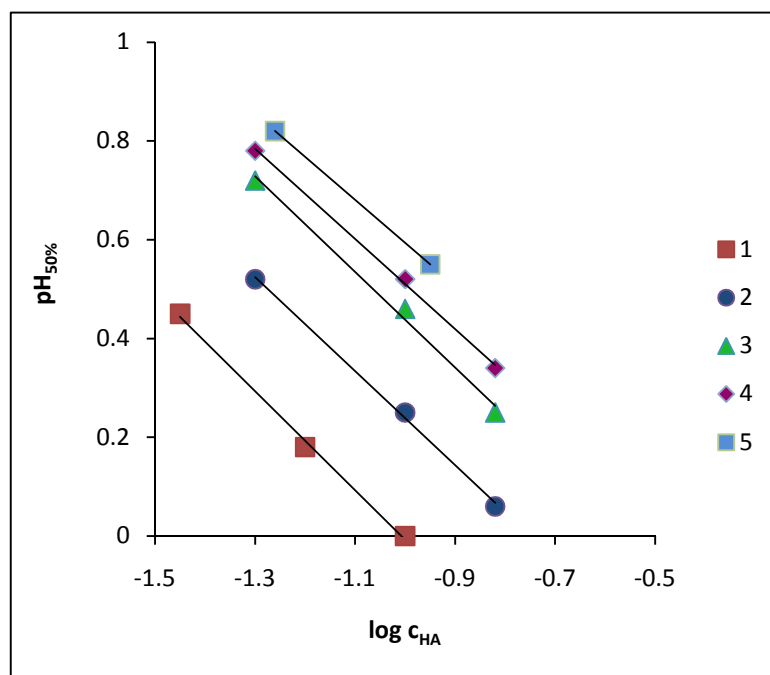
In order to obtain the total number of dialkyldithiophosphoric acid molecules involved in the formation of the species in the organic phase, from the variation  $\log D - \text{pH}$ ,  $\text{pH}_{50\%}$  values were determined for different concentrations of dialkyldithiophosphoric acid. They have been used to build the graphic in Figure 17.



**Fig. 15.** Extraction of uranium with DEDTPA in butanol. Influence of pH of the aqueous phase.

$c_{\text{DEDTPA}} = 0.05 \text{ M (1); } 0.1 \text{ M (2); } 0.15 \text{ M (3)}$

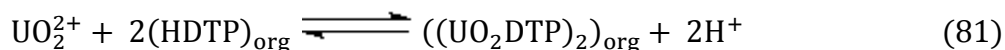
$c_{\text{U}} = 0.001 \text{ M; (HNO}_3 + \text{NaNO}_3 \text{ 1 M)}$



**Fig. 17.** pH<sub>50%</sub> variation as a function of the concentration of DADTPA in butanol

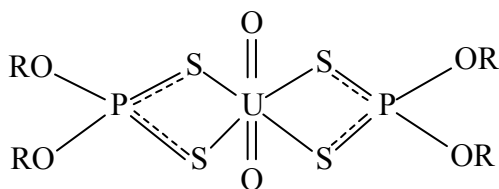
1 – DEDTPA; 2- DPrDTPA; 3 - DiPrDTPA; 4 – DBDTPA; 5 – DEHDTPA

The slope of the curves representing the variation  $\text{pH}_{50\%}$  depending on acid concentration in the organic phase (Figure 17) has values ranging between 0.9 - 1.00 for the studied acids. Whereas the slope value represents the ratio  $x/m$  (equation 69) it results that  $x = 2$ . Therefore, in the uranium extraction process participate only the acid molecules involved in ion exchange. Equation (80) becomes:

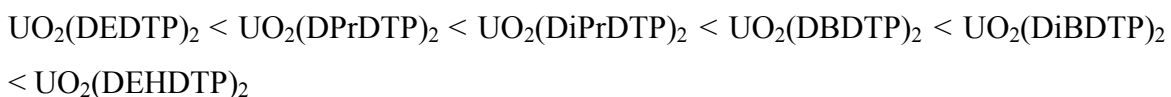


The variation of distribution ratio logarithm as a function of pH was studied for different metal concentrations. Dialkyldithiophosphoric acid concentrations were kept constant. Since for each of the studied acids it was obtained only one line, (like those presented in Figure 19 for diethyl- and di(2-ethylhexyl) dialkyldithiophosphoric acids), in the uranium concentration range between 0.0005 - 0.01M no polymeric species are formed, in either the aqueous phase or the organic phase. In conclusion, equation (81) reflects correctly the extraction of uranium(VI) from aqueous solution (1M  $\text{HNO}_3 + \text{NaNO}_3$ ) with dialkyldithiophosphoric acids in butanol, indicating a cation exchange mechanism.

Participation of two acid molecules to the ion exchange process excludes the possibility of nitrate ion participation in the formation of the extracted species. It is assumed that in the extraction process a chelated complex is formed between uranyl ion and dialkyldithiophosphoric acid like those described in the literature for other metals [232].



Distribution ratios of uranium increases in the series:



It is observed that the order of extraction of uranyl complexes coincides with the order of increasing distribution ratios of complexing agents, being determined of course by the increasing organophilic character of bigger alkyl groups. From the limited number of dialkyldithiophosphoric used in the extraction of uranium, it is noticed that the ramification of alkyl chain produces a slight increase in the distribution ratio of the metal.

### ***U(VI) - DADTPA - benzen***

The influence of pH on the extraction of uranium(VI) with dialkyldithiophosphoric acids in benzene was studied. The results obtained for diethyl-, dipropyl-, diisopropyl-, dibutyl-, respectively diisobutyl- and di(2-ethylhexyl)- dialkyldithiophosphoric acids show that the distribution ratio increases with increasing of pH of the aqueous phase. If we assume that the uranium is extracted through an ion exchange reaction, similar to the butanol system, the extraction equilibrium can be expressed with equation (81).

According to equation (84), the curves obtained by plotting  $\log D/pH$  should provide for the linear part, the value 2 of the slope. But deviations from the value of the slopes are observed for diethyl-, dipropyl-, diisopropyl-, dibutyl- and di(isobutyl)- dialkyldithiophosphoric acids. A slope deviation from the value 2 of the curves, which means uranyl ion charge, could be explained in two ways:

a) The formation of species in the organic phase, involving other anions than those of dithiophosphate.

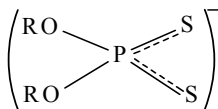
The results obtained show that there is a dependence between the distribution ratio of uranium and nitrate ion concentration, but it can not justify the participation of  $NO_3^-$  ion in the extraction process.

b) The uranium complexation phenomenon in aqueous phase can produce a decrease of the distribution ration and as a result, a decrease of curves's slope.

Therefore it can be assumed that in the uranium extraction process with short alkyl chain of dialkyldithiophosphoric acids  $C_2 - C_4$ , complex formation of  $UO_2(DTP)_2$  occurs, according to equation (81). Comparing the two extraction systems,  $UO_2^{2+} - DATPA - benzene$  and  $UO_2^{2+} - DATPA - butanol$ , it can be observed that in the polar solvent system containing n-butanol, higher distribution ratios are obtained. Because the ligand geometry and coordination number of uranium are favorable, we can assume the formation of complex species such as  $UO_2(DATP)_2B_y$  (where B is the molecule of n-butanol), with a higher solubility in organic solvents compared with the simple complex,  $UO_2(DATP)_2$ . This would justify the differences that arise between distribution ratios of uranium in the two systems.

The results obtained by the method of data extraction slopes were supported by spectral data. In the IR spectra of organic extracts saturated with uranium, absorption band due to

vibrations of SH group (about  $2500\text{ cm}^{-1}$ ) disappears. Changes in the frequency range  $\nu_{\text{a PS}_2}$  and  $\nu_{\text{S PS}_2}$  ( $450\text{-}700\text{ cm}^{-1}$ ), suggest that the anion  $(\text{RO})_2\text{P}(\text{S})\text{S}^-$

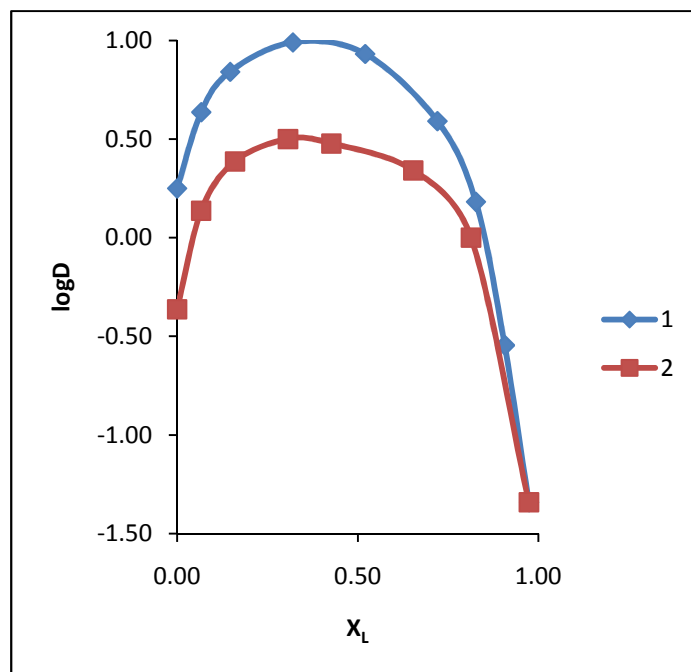


is involved in the formation of the metal ion complex.

### ***U(VI) – DADTPA – neutral ligand***

We studied the extraction of U(VI) with mixture of DiBDTPA and neutral ligand: TPPO and DPhSO in terms of pH and concentration of acid ligand mentioned in the systems referring to U(VI) - DiBDTPA.

It appears that there is a very low extraction of uranium with neutral ligands (TPPO and DPhSO) 0.1 M in benzene, from aqueous nitrate solution (Figure 22). DiBDTPA 0.1 M in benzene alone, extracts uranium with a low distribution ratio. Using a mixture of DiBDTPA and neutral ligand (S), a distribution ratio higher than the sum of the individual distribution ratios are obtained. Such an increase in the distribution ratio is known as synergic effect. Curves shown in Figure 22 are typical for the synergistic systems.



**Fig. 22.** U(VI) extraction with DADTPA and S  
DiBDTPA + TPPO (1); DiBDTPA + DPhSO (2)  
 $c_U=0.001\text{ M}$ ;  $\text{pH}=1$



### **Influence of pH of aqueous phase**

We studied the influence of the concentration of the aqueous phase acidity on the distribution ratio of uranium at constant concentration of DADTPA (0.1 M) and neutral ligand TPPO and DPhSO systems. The variation of  $\log D/pH$  shows that in the presence of neutral ligand (TPPO) uranium is extracted through an ion exchange mechanism involving two molecules of DADTPA.

In systems with DADTPA and TPPO, the distribution ratio values are significantly higher. As a result, the effect of synergistic increase of extraction, due to TPPO, is higher than the one determined by DPhSO.

### **The influence of neutral ligand concentration**

The influence of neutral ligand concentration  $S$  (TPPO, DPhSO) in the organic phase was studied (while maintaining constant the DADTPA concentration in benzene). The results show a linear dependence of  $\log D$  against  $\log c_S$ . The value two of the slope suggest the involvement of one ligand molecule in the formation of neutral species extracted in the organic phase. A mixed complex  $UO_2(DiBDTP) \cdot S$ ,  $S=TPPO$ , DPhSO is formed in the extraction process. In the TPPO extraction systems higher values of distribution ratio are obtained.

### **IR Spectra**

To confirm and to fill up distribution data, complexes involved in the extraction were isolated and studied in solid state. IR absorption spectra of mixed complexes in the solid state, were recorded in the  $400-3400\text{ cm}^{-1}$  range. Interpretation of IR spectra of the complexes was done by comparison with the IR spectra of free ligands.

The obtained data suggest that the four sulphur atoms bind to uranium(VI), forming chelated cycles of four atoms and an oxygen atom from neutral ligands  $S$ , are placed in equatorial plane occupying the corners of a pentagon. Uranyl group is placed perpendicular to the linear equatorial plane. Uranyl ion in these complexes is pentacoordinated, uranium atom being placed in the center of a pentagonal bipyramide. To confirm this pattern, attempts were made to determine the structure of these compounds by single crystal x-ray diffraction.

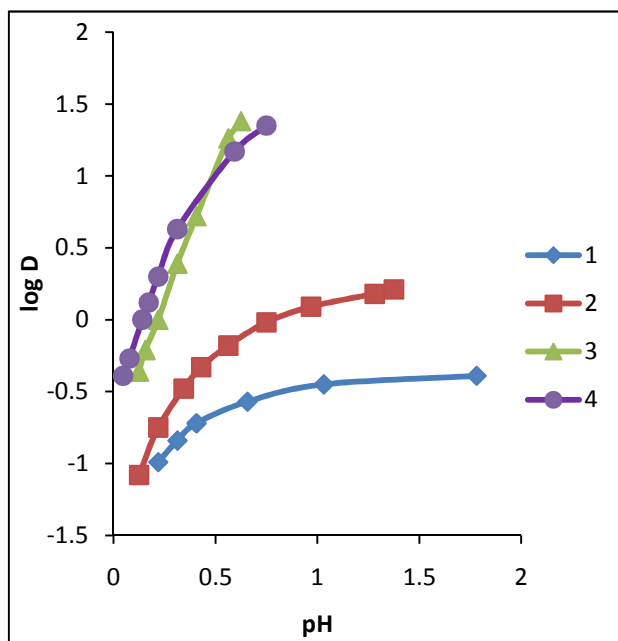
#### ***IV.3.2.2. Thorium extraction***

##### ***Th(IV) – DADTPA – benzene***

Phenomenon of complexation in the aqueous phase at the thorium extraction with dibutyl-diisobutyl- and di(2-ethylhexyl)-dialkyldithiophosphoric acids is neglected. The data presented in

Figure 25 show that thorium extraction is greatly influenced by alkyl chain length in the dialkyldithiophosphoric acid. An increase in the alkyl chain produces an increase in the extraction of thorium in benzene, non-polar solvent. The highest values of distribution ratio are achieved with DEHDTPA and DBDTPA. Decrease in the distribution ratio of this metal (equation 91) for acids with shorter alkyl chain can be explained by the forming in the aqueous phase of soluble complex species with dithiophosphate anions, favored by high water solubility of these acids, this lowering ion concentration of Th(IV) available for extraction.

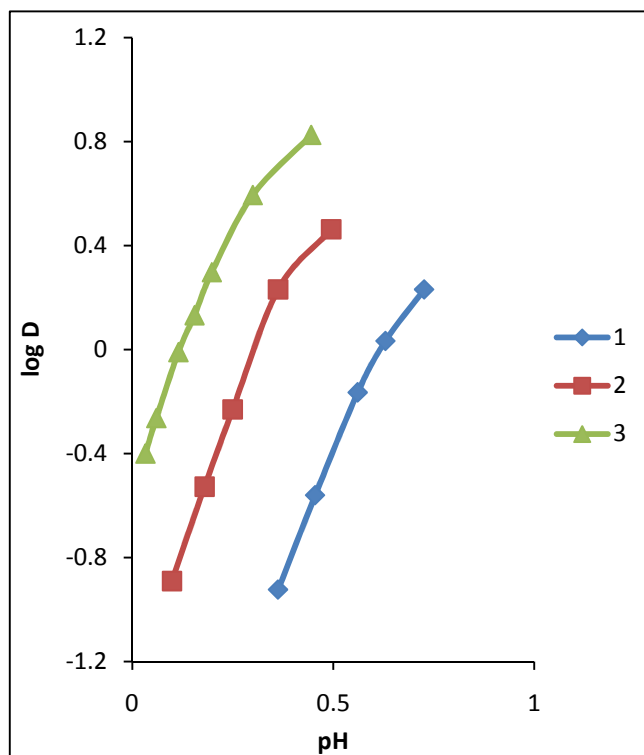
For both acids, the extraction mechanism was investigated in detail. Curves of the type shown in Figure 26 were obtained for acid di(2-ethylhexyl)dithiophosphoric acid, indicating an ion exchange mechanism involving four dithio acid molecules (slope 4) to neutralize the positive charge of the cations. This excludes nitrate ion participation in the formation of extracted species.



**Fig. 25.** Extraction of thorium(IV) with dialkyldithiophosphoric acids in benzene.

1 – DEDTPA; 2 – DiPrDTPA; 3 – DBDTPA; 4 – DEHDTPA;

$c_{\text{Th}} = 0.004 \text{ M}$ ;  $c_{\text{DADTPA}} = 0.1 \text{ M}$ ; ( $\text{HNO}_3 + \text{NaNO}_3 \text{ 1 M}$ )



**Fig. 26.** Extraction of thorium(IV) with DEHDTPA in benzene

$$c_{\text{DEHDTPA}} = 0.03 \text{ M (1); } 0.06 \text{ M (2); } 0.1 \text{ M (3)}$$

$$c_{\text{Th}} = 0.0004 \text{ M; (HNO}_3 + \text{NaNO}_3 \text{ 1 M)}$$

Representation of  $\text{pH}_{50\%}$  (values in Figure 26) as a function of the concentration of dithio acid suggests that at the formation of the extracted species in benzene participate only the acid molecules involved in the ion exchange. Variation of distribution ratio for the range of concentration  $5 \cdot 10^{-4} - 1 \cdot 10^{-2}$  shows that the extraction is not affected by thorium concentration. So, no polymeric species are formed in the studied systems.

Extraction of thorium with dialkyldithiophosphoric acids can be described by equation (93). The high values obtained for the distribution ratio of di(n-butyl)- and di(2-ethylhexyl) dithiophosphoric acids can be explained by the higher solubility of the complex  $\text{Th}(\text{DADTP})_4$  formed according to the equation:



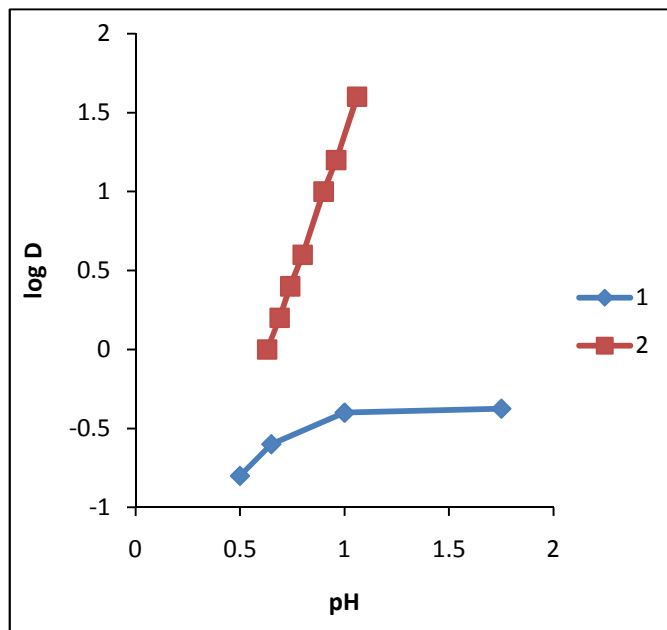
### ***Th(IV) – DADTPA – butanol***

Distribution ratio dependence on pH of the aqueous phase and of the acid concentration suggest that  $\text{Th}(\text{DATP})_4$  complex is formed. Distribution ratio values are higher in the systems containing dialkyldithiophosphoric acids in butanol. This behavior can be explained by the formation of complex species  $\text{Th}(\text{DEDTP})_4 \cdot n\text{BuOH}$ , due to the favorable geometry of the extractant and the large coordination number of thorium(IV).

### ***Th(IV) – DADTPA –neutral extractant***

The most common thorium coordination number is eight, achieved in  $\text{Th}(\text{DEDTP})_4$  complex, in which dithiophosphate anion acts as bidentate ligand [233]. However, thorium can form complexes with higher coordination number. It is the case of the  $\text{Th}(\text{DADTP})_4$  complexes, in which dithiophosphate ligand has a short alkyl chain and allows a second ligand coordination.

This is also suggested by the data obtained from the extraction of Th with short alkyl chain dithiophosphoric acid (diethyldithiophosphoric acid). Extraction of Th(IV) is favored in this case by an oxygen containing polar solvent (butanol) which can act as a donor. From this observation, we studied the influence of tri-n-octylphosphine oxide (TOPO), a neutral strong donor, on the extraction of Thorium(IV) with DEDTPA in benzene. Th(IV) was extracted from aqueous solutions at constant ionic strength 1 M ( $\text{HNO}_3 + \text{NaNO}_3$ ) with mixture of DEDTPA and TOPO. The distribution ratio values obtained in DEDTPA extraction systems, in the absence (curve 1) and in the presence of TOPO (curve 2) are represented in Figure 30. Significant increase of extraction in systems with extractant mixture is observed and value 4 of curve 2 indicates the participation of four dithiophosphate anions in forming of the extracted species.

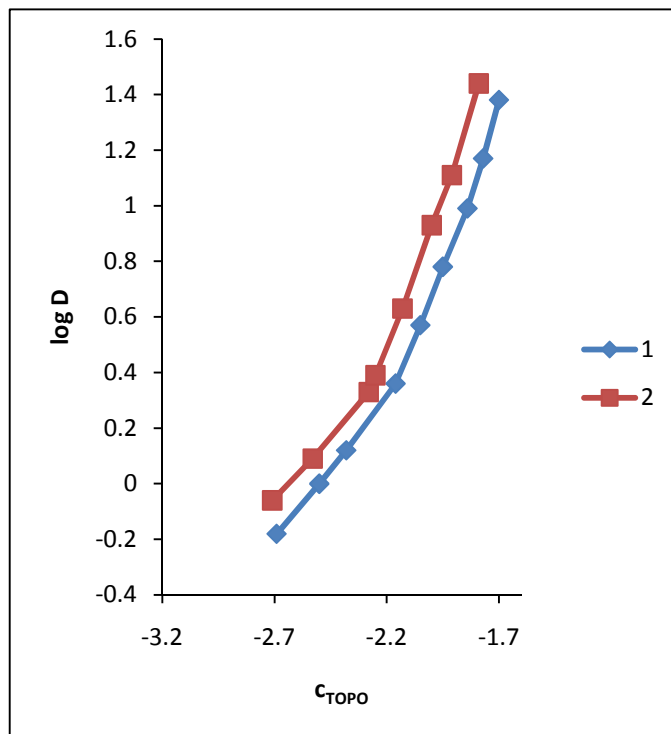


**Fig. 30.** Extraction of thorium(IV) with diethyldithiophosphoric acid and TOPO in benzene.

1:  $c_{\text{TOPO}} = 0$ ; 2:  $c_{\text{TOPO}} = 0.01 \text{ M}$ ; ( $\text{HNO}_3 + \text{NaNO}_3$ )

$c_{\text{Th}} = 0.0005 \text{ M}$  ;  $c_{\text{DEDTPA}} = 0.1 \text{ M}$

Results shown in figure 31 indicate an increase of extraction with increasing concentration of TOPO in benzene. Value of 1 of the slope (for TOPO concentration lower than 0.01 M), indicates one neutral extractant molecule involved in the mixed complex  $\text{Th}(\text{DADTP})_4\text{TOPO}$ . For TOPO concentration higher than 0.01 M the formation of a mixed complex  $\text{Th}(\text{DADTP})_4 \cdot 2\text{TOPO}$  is suggested.



**Fig. 31.** Extraction of Th(IV) with diethyldithiophosphoric acid (1) and di(2-ethylhexyl)dithiophosphoric acid (2) and TOPO in benzene.

$$c_{\text{DADTPA}} = 0.1 \text{ M}; c_{\text{Th}} = 0.5 \text{ M}; \text{pH} = 0.7 \text{ (1)}; \text{pH} = 0 \text{ (2)}$$

#### ***IV.3.2.3. Lanthanides extraction***

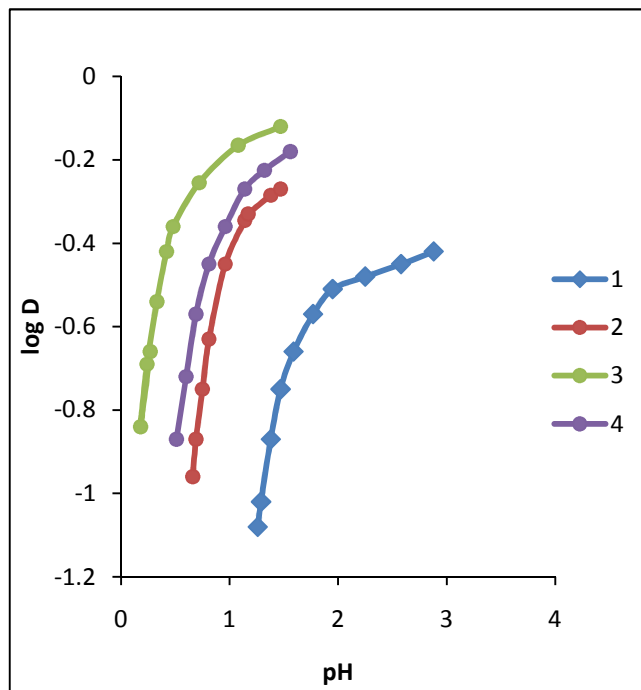
Literature data show that lanthanides form stable complexes with dialkyldithiophosphoric acids [234]. Preliminary experiments and published data on the extraction of Ln with dialkyldithiophosphoric acids in non-polar solvents generally indicate small distribution ratio [235]. However in polar solvents containing oxygen as donor atom, the distribution ratio values are higher.

In this paper we compared extraction of lanthanides with dithiophosphoric acids using non-polar solvent, benzene, and n-butanol as electron donor polar solvent.

#### ***Ln(III) – DADTPA – Benzene***

The pH dependence of  $\log D$  suggests an ion-exchange mechanism and the slope value of 3 for di-2-ethylhexyldithiophosphoric indicates that three molecules of extractant participate in the formation of extracted species (equation 65). Deviations from the slope value of 3 for the

other three acids diethyl-, dibutyl- and diisobutyl- dithiophosphoric acids may be caused by Ln(III) complexation in the aqueous phase with the formation of anionic complex species  $[\text{La}(\text{DADTP})_4]^-$ . Such complex species have been reported in literature [234,236]  $[\text{Ln}(\text{S}_2\text{PR}_2)]_n^-$  where  $\text{R} = \text{CH}_3-, \text{C}_6\text{H}_{13}-, -\text{OC}_2\text{H}_5$ ). Distribution ratio values increase only slightly with atomic number Z.



**Fig. 32.** Extraction of La(III) with dialkyldithiophosphoric acids in benzene.

1: ethyl; 2: n-butyl; 3: 2-ethylhexyl; 4: isobutyl

$c_{\text{La}} = 0.001 \text{ M}$ ;  $c_{\text{DADTPA}} = 0.1 \text{ M}$

The  $\text{pH}_{50\%}$  dependence on acid concentration shows that the extraction process involves only dithiophosphoric extractant molecules involved in ion exchange. In Ln(III) concentration range of  $5 \cdot 10^{-4} - 10^{-2} \text{ M}$  no polymer species are formed in the extraction system.

Extraction of Ln(III) with dialkyldithiophosphoric acids can be described by the equation:



$\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Sm}$

### ***Ln(III) – DADTPA – butanol***

Data obtained in the extraction systems with dialkyldithiophosphoric acids ( $\text{R} = \text{ethyl}, \text{butyl}, \text{isobutyl}$  and  $2\text{-ethylhexyl}$ ) suggest a mechanism similar to benzene extraction systems. Distribution ratio values are higher than in benzene for all investigated dithiophosphoric acids.

### **Solvent effect**

The results obtained in the lanthanides(III) extraction systems with dithiophosphoric ligands) show that extraction is dependent on the nature of the solvent used as diluent for organophosphorus extractant. Thus, in oxygen-containing polar solvents higher distribution ratio are obtained than in non-polar solvents, suggesting that the donor properties of the solvent are important. This can be understood taking into account that the process occurs in the presence of bidentate ligands. By complexing with dithiophosphate anion, not all coordination sites of the Ln(III) cations are occupied by the three donor groups. Water molecules or other donors can hold these sites reducing the solubility of lanthanides chelates in non-polar solvent. In the presence of oxygen containing polar solvent (alcohols, ketones, etc.) donor solvent molecules may occupy the residual coordination sites thus improving extraction.



## **V. THE USE OF ACID ORGANODITHIOPHOSPHORIC DERIVATIVES IN THE SEPARATION OF UO<sub>2</sub>(II), Th(IV), Ln(III), Co(II), Ni(II), Cu(II) IONS BY THIN LAYER CHROMATOGRAPHY**

### **V.2. THE STUDY OF CHROMATOGRAPHIC BEHAVIOUR ON TLC OF UO<sub>2</sub>(II), Th(IV), Ln(III), Co(II), Ni(II) and Cu(II) METAL IONS IN THE PRESENCE OF ORGANOTHIOPHOSPHORIC ACID LIGANDS**

We studied thin layer chromatographic behaviour on silica gel of ions UO<sub>2</sub>(II), Th(IV), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Yb(III) and the d transition elements (Co(II), Ni(II) and Cu(II)) in the presence of some dialkyldithiophosphoric acid, with short alkyl chain (C<sub>2</sub>-C<sub>4</sub>) in particular. In order to determine the alkyl chain influence, di(2-ethylhexyl)dithiophosphoric acid was used as extractant with long alkyl chain.

The aim of the study was:

- To determine the optimal conditions for separation
- To elucidate the mechanism of separation.

To achieve the intended purpose the following have been analyzed:

- The influence of the mobile phase
- The influence of the complexing agent
- The influence of the stationary phase

#### **V.2.1. The influence of the mobile phase**

We studied the chromatographic behavior on silica gel plates of metal ions: UO<sub>2</sub>(II), Th(IV), Ln(III), Co(II), Ni(II) and Cu(II) using alkyl chain organodithiophosphoric acids: ethyl-, propyl-, isopropyl-, butyl-, isobutyl- and 2-ethylhexyl as complexing agents added in a mobile organic phase.

Mobile phases used are listed in Table 7 together with the R<sub>F</sub> calculated for each case. Analyzing the obtained results we can observe a dependence of R<sub>F</sub> values of the nature of the mobile phase used.

The results obtained using different organic solvents presented in Table 7 as mobile phase allow us to draw the following conclusions:

- In systems with mobile phase consisting of an organic solvent or mixture of organic solvents metal ions migration in the absence of organothiophosphoric derivative does not occur.

The necessity of dithiophosphoric ligand presence indicates that complexation processes of metal ions with dithiophosphat ligand similar to liquid-liquid extraction are involved in the separation.

- Chromatographic behavior of studied ions is significantly influenced by the solvent nature - the mobile phase. Butanol with very similar polarity of chloroform increases the  $R_F$  values for actinides, lanthanides and Co(II). This can be explained by donor properties of butanol, oxygen molecule polar solvent.

- Significant increase in  $R_F$  values for Th and U in the presence of MEC or DMF, electron donors, supports the idea that the donor properties of the solvent play an important role.

The separation tendency of metal ions in four groups can be observed in the systems with n-butanol.

1. d transitional elements
2. Actinides
3. Light Lanthanides
4. Heavy lanthanides

To enhance the separation selectivity of metal ions we used solvent binary mixtures as mobile phase.

**Table 7.**  $R_F \cdot 100$  for studied cations. Mobile phase: organic solvent mixtures containing HDADTP; Stationary: silicagel H.

Mobile phase		$R_F \cdot 100$														
	P'	La (III)	Ce (III)	Pr (III)	Nd (III)	Sm (III)	Gd (III)	Dy (III)	Ho (III)	Er (III)	Yb (III)	Th (IV)	U (VI)	Co (II)	Ni (II)	Cu (II)
<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>
A	o,m,p-xylene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B	benzene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	n-butanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
D	chloroform	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
E	MEK	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F	DMF	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	<b>DEDTPA 0.04M</b>															
G	benzene	0	0	0	0	0	0	0	0	0	0	0	0	15	23	38
H	o,m,p-xylene	0	0	0	0	0	0	0	0	0	0	0	0	33	32	22
I	chloroform	0	0	0	0	0	0	0	0	0	0	0	5	38	77	80
J	n-butanol	33	31	31	31	33	38	43	44	44	33	27	27	77	77	83
K	DMF	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44
L	MEK	47	44	44	44	41	35	33	40	42	43	42	40	76	83	73
M	o,m,p-xylene+butanol (17 : 2, v/v)	27	25	27	27	25	25	25	25	27	25	25	24	50	66	72
N	o,m,p-xylene+DMF (17 : 2, v/v)	10	10	11	8	8	6	7	6	6	7	11	8	7	5	3

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
O	o,m,p-xylene+DMF+MEK (16 : 1 : 2, v/v/v)	2.94	5	6	7	12	13	13	16	15	16	17	16	20	17	6	6
	<b>DPrDTPA 0.04 M</b>																
P	o,m,p-xylene+DMF+MEK (16 : 1 : 2, v/v/v)	2.94	1	2	3	3	2	1	22	22	22	22	23	25	47	81	85
	<b>DBDTPA 0.04 M</b>																
R	o,m,p-xylene+DMF+MEK (16 : 1 : 2, v/v/v)	2.94	22	22	22		20	20			17		22	24	50	87	93
	<b>DEHDTPA 0.04M</b>																
S	benzene	2.70	0	0	0	0	0	0	0	0	0	0	0	7	52	98	98
T	o,m,p-xylene	2.50	0	0	0	0	0	0	0	0	0	0	0	5	32	100	100
U	chloroform	4.10	0	0	0	0	0	0	0	0	0	0	0	4	62	100	100
V	n-butanol	3.90	28	31	30	30	30	28	30	28	27	27	0	22	100	100	100
W	o,m,p-xylene+DMF+MEK (16 : 1 : 2, v/v/v)	2.94	16	25	25		20	8			15		14	36	50	53	96
	<b>DNDTPA</b>																
X	o,m,p-xylene+DMF+MEK (16 : 1 : 2, v/v/v)	2.94	22	24	24	24	24	25	27	27	24	22	23	22	80	97	98

### V.2.2. The influence of the dialkyldithiophosphoric ligand

The chromatographic behavior on silica gel H of UO<sub>2</sub>(II), Th(IV), Ln(III), Co(II), Ni(II) and Cu(II) was studied in the presence of organothiophosphoric acids presented in Table 1. Ligands were added in the mobile phase: *o*, *m*, *p*-xylene - dimethylformamide - methyl ethyl ketone (16:2:1 v / v / v).

It was investigated:

- The influence of DADTPA ligand concentration
- The influence of alkyl chain nature

#### V.2.2.1. The influence of the dialkyldithiophosphoric acid concentration

R<sub>F</sub> value was determined for different concentrations of DADTPA acids and for different DADTPA (DEDTPA, DPrDTPA, DBDTPA and DiBDTPA) in order to establish optimal conditions of separation.

For DPrDTPA systems, the variation of retention factor on the complexant concentration is shown in figure 39 and 40 for actinides, lanthanides and transitional d metals. Separation conditions between the two elements DPrDTPA appear at concentration of 0.06 M (Figure 41). Lanthanide elements in the system with DPrDTPA remain at the starting point.

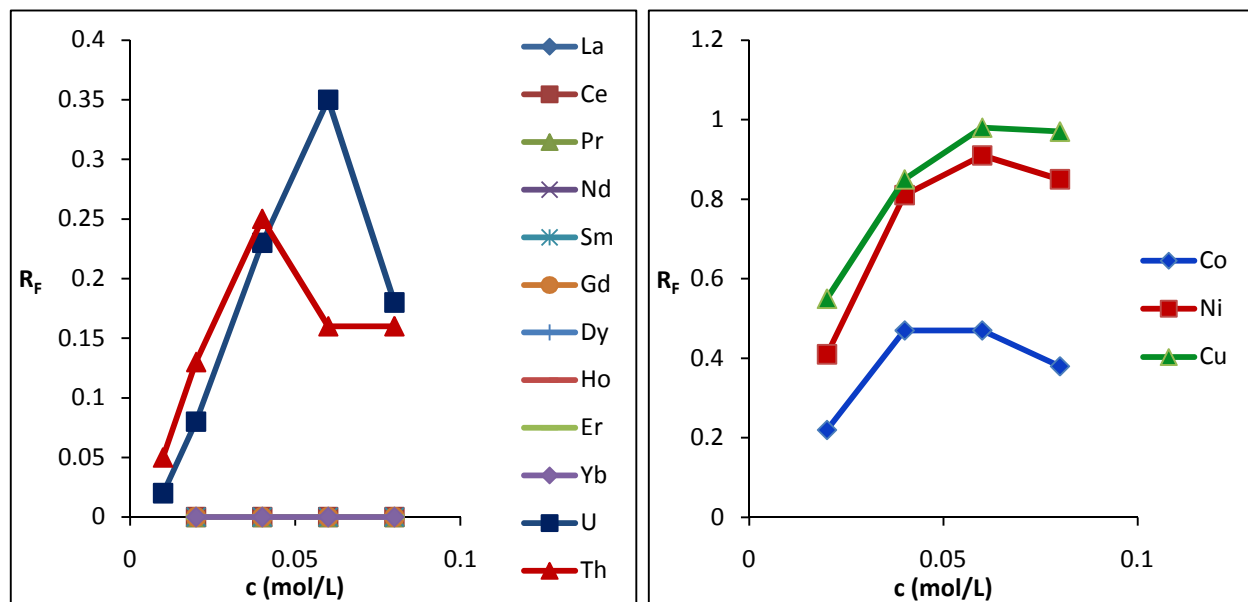
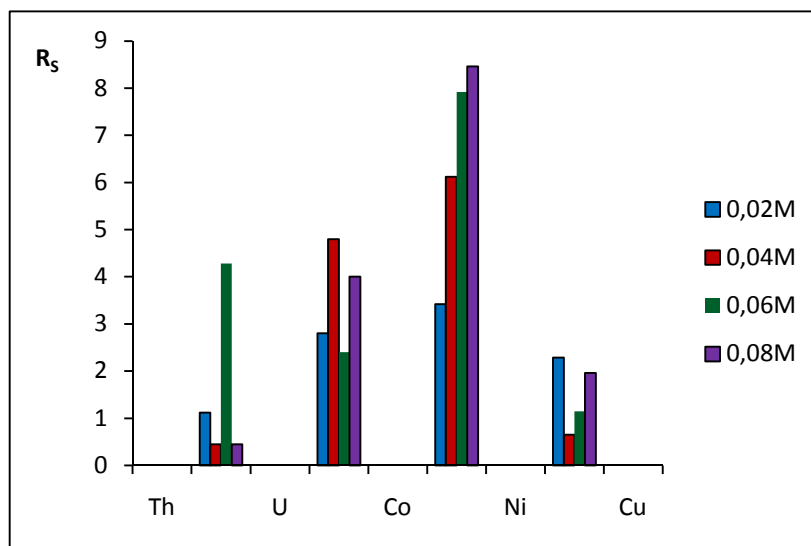


Fig. 39-40. Chromatographic behavior of metal ions studied using DPrDTPA

Stationary phase: silica gel

Mobile phase: *o,m,p*-xylene – MEK – DMF (16 : 2 : 1, v/v/v)



**Fig. 41.** Resolution separation of metal ions studied for different concentrations of DPrDTPA

Stationary phase: silica gel

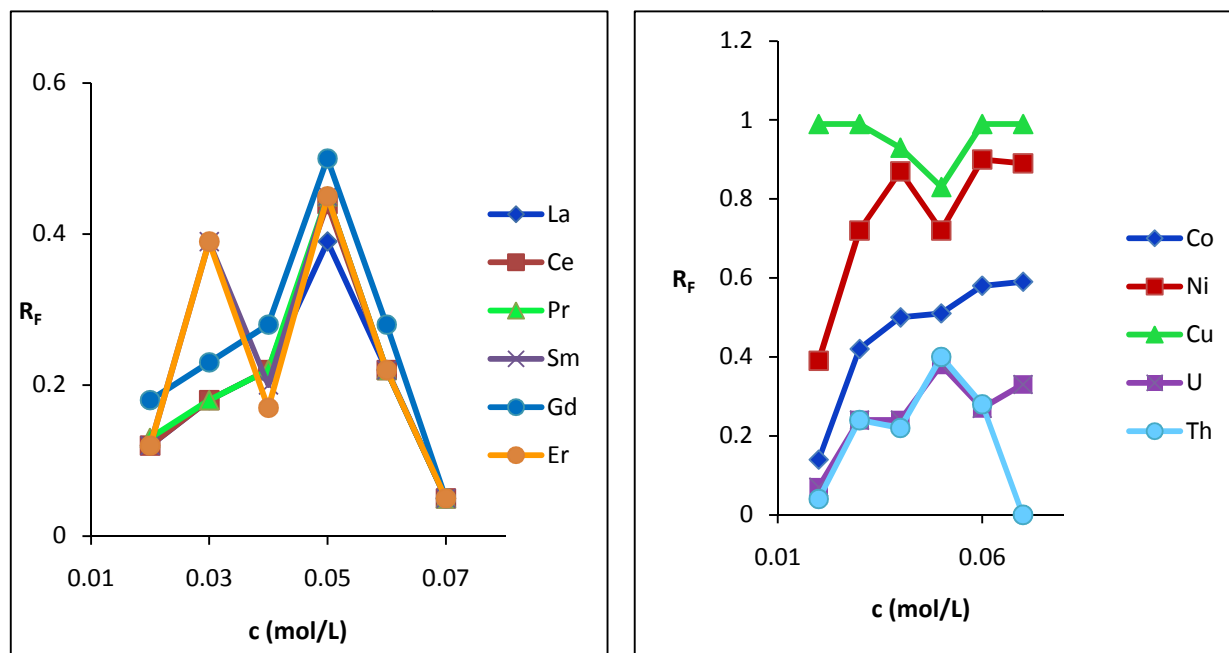
Mobile phase: *o,m,p*-xylene – MEK – DMF (16 : 2 : 1, v/v/v)

In DBDTPA system (Figure 42 and 43) all metal ions investigated except lanthanides migrate.  $R_F$  values increase with increasing extractant concentration.

In the system with low concentrations of DiBDTPA no significant differences from DBDTPA appear (Figure 44 and 45), but there is an increase of  $R_F$  for Th(IV), which reduces the separation possibilities for this element from  $UO_2(II)$  [243].

The data presented in Figure 45 shows that there are conditions for the separation of ions ( $UO_2(II)$ , Th(IV), Co(II), Ni(II) and Cu(II)) from each other at ligand concentrations of 0.07 M and of Co(II), Ni(II) and Cu(II) at concentration of 0.02 M DiBDTPA.

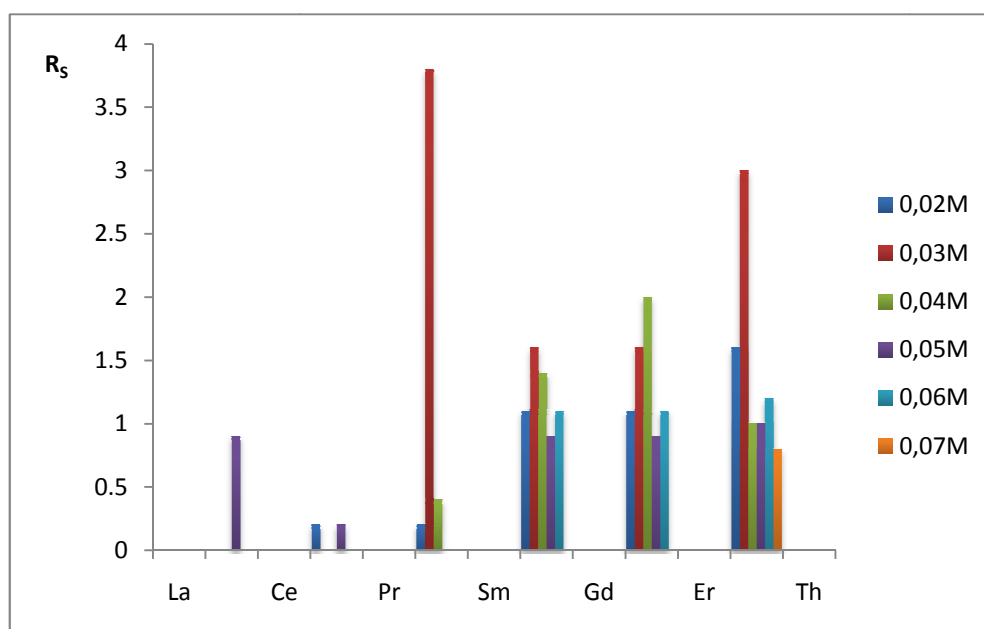
Figure 44 shows slight tendency of separation of light lanthanides (La, Ce, Pr, Sm) from heavy lanthanides (Gd, Er) and pairs of lanthanides Sm-Gd and Gd-Er at a complexant concentration of 0.04 M (Figure 46).



**Fig. 44-45.** Chromatographic behavior of metal ions studied using DiBDTPA

Stationary phase: silica gel

Mobile phase: *o,m,p*-xylene – MEK – DMF (16 : 2 : 1, v/v/v)



**Fig. 46.** Resolution separation of metal ions studied for different concentrations of DiBDTPA

Stationary phase: silica gel

Mobile phase: *o,m,p*-xylene – MEK – DMF (16 : 2 : 1, v/v/v)

#### ***V.2.2.2. The influence of the alkyl chain nature of dialkyldithiophosphoric acids***

The influence of alkyl chain nature of organothiophosphoric complexant on the chromatographic behavior of studied metal ions involves two aspects: the length and chain structure, linear or branched.

The retention factor values for different organothiophosphoric acids presented in Table 8, shows that:

- $R_F$  value increases with increasing alkyl unbranched chain length, for all studied ions. This is observed in the extraction systems too (Chapter II).
- Alkyl chain ramification affects differently the chromatographic behavior of studied ions:
  - $UO_2(II)$  - for DADTPA with large numbers of carbon atoms (octyl, 2 - ethylhexyl) an increase in the  $R_F$  value is observed.
    - for DADTPA with  $C_4$  alkyl chain it a decrease of  $R_F$  value is observed.
  - Th(IV) - alkyl chain ramification has an increasing effect on the  $R_F$  value.
  - Ln(IV) - alkyl chain ramification ( $C_4$ ) determines a significant growth of  $R_F$ . In DBDTPA presence, Ln(III) remain at starting point.
    - short alkyl chain ramification decreases the  $R_F$  value especially for the heavy lanthanides.
  - Co(II) - alkyl chain ramification decreases the  $R_F$  value.
  - Ni(II) - long alkyl chain ramification (2-ethylhexyl) decreases the  $R_F$  value.
  - Cu(II)- alkyl chain ramification does not influence chromatographic behavior of Cu(II).

These results indicate a similar behaviour to liquid - liquid extraction systems with. This supports a partition mechanism like in organic solvents extraction systems.



**Table 8.**  $R_F \cdot 100$  for the studied cations.Mobile phase: *o,m,p*-xilen – MEK – DMF (16 : 2 : 1, v/v/v)

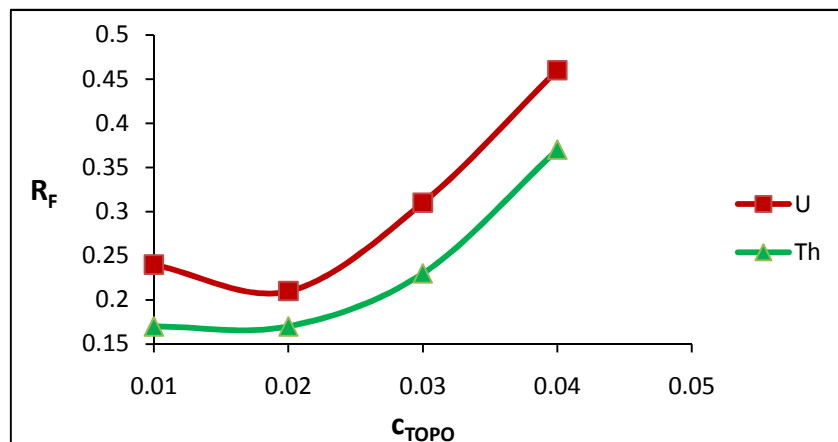
Mobile phase	$R_F \cdot 100$														
	La (III)	Ce (III)	Pr (III)	Nd (III)	Sm (III)	Gd (III)	Dy (III)	Ho (III)	Er (III)	Yb (III)	Th (IV)	U (VI)	Co (II)	Ni (II)	Cu (II)
DEDTPA	5	6	7	12	13	13	16	15	16	17	16	20	17	6	6
DP-rDTPA	1	2	3	3	2	1	22	22	22	22	25	23	47	81	85
DiPrDTPA	0	0	0	0	0	0	0	0	0	0	4	31	44	83	87
DBDTPA	-	-	-	-	-	-	-	-	-	-	14	38	70	85	100
DiBDTPA	22	22	22	-	22	22	-	-	17	-	22	24	50	87	93
DODTPA	27	27	27	-	27	27	-	-	27	-	7	36	57	75	98
DEHDTPA	16	25	25	-	20	28	-	-	15	-	14	36	50	53	96
DNDTPA	22	24	24	24	25	25	27	27	24	22	23	22	80	97	98

### V.2.3. The influence of the neutral ligand

Results of the study conducted on the influence of mobile phase on the chromatographic behavior of investigated ions in systems containing organophosphorus acids as complexing agents showed that the nature of the organic solvent plays a crucial role in their migration; namely, the presence in the mobile phase of polar solvents with donor properties influence decisively the possibility of separating metal ions. Consequently, a neutral complexant as trioctylphosphin oxide (TOPO) known for its donor properties and widely used in liquid-liquid extraction systems was tested.

#### DEHDTPA-TOPO system

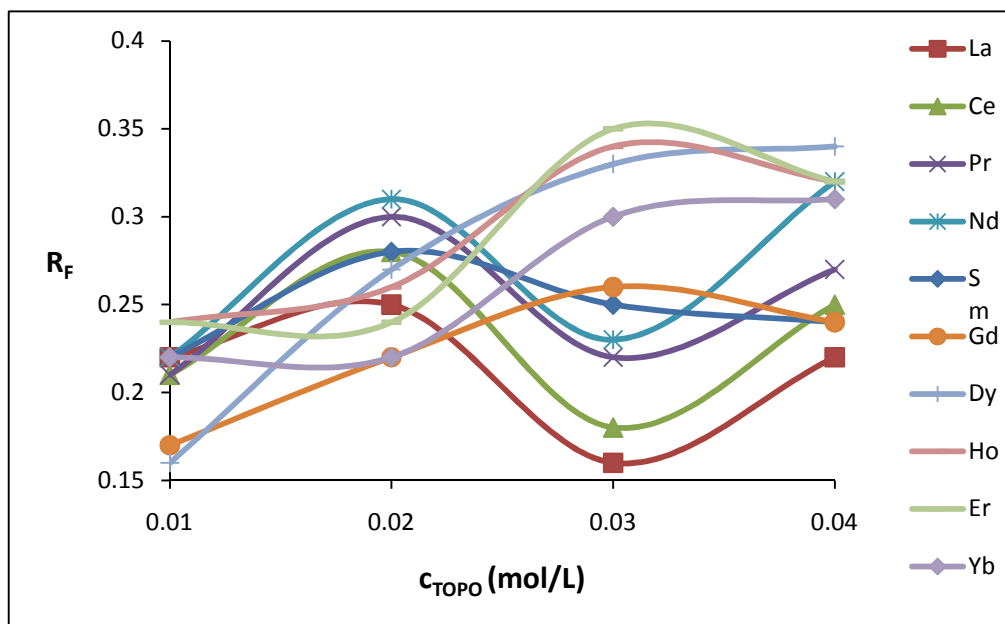
The chromatographic behavior of  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$  and  $\text{Ln}(\text{III})$  ions in chromatographic systems with two extractants: DEHDTPA and TOPO, present in the mobile phase was studied. The data obtained are shown in Figure 47 for U and Th, and in Figure 48 for Ln.



**Fig. 47.**  $R_F$  variation function of TOPO concentration (DEHDTPA 0.04 M)

Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)

Stationary phase: silica gel H +  $\text{NH}_4\text{NO}_3$  2.5 M



**Fig. 48.** R<sub>F</sub> variation function of TOPO concentration (DEHDTPA 0.04 M)

Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)

Stationary phase: silica gel H + NH<sub>4</sub>NO<sub>3</sub> 2.5 M

It can be seen that:

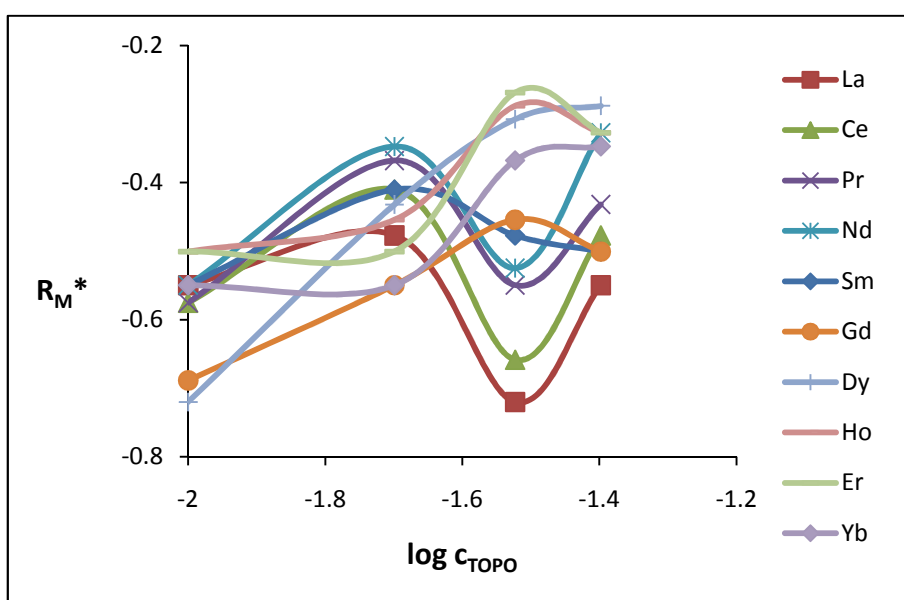
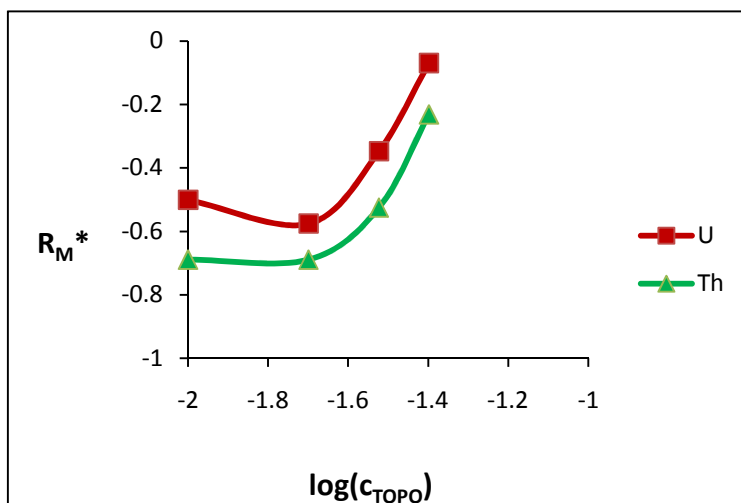
- the increase of R<sub>F</sub> for UO<sub>2</sub>(II) in the range of neutral ligand concentration investigated;
- the increase of R<sub>F</sub> for Th(IV) up to 0.03 M TOPO;
- different R<sub>F</sub> values for light and heavy lanthanides.

Different behavior of light and heavy Ln(III) is known and can be explained by the phenomenon called lanthanides contraction (ionic radius decrease with increasing atomic number Z).

Light Ln(III) form mixed complexes with different combining ratios Ln(III) : DADTPA : TOPO depending on the concentration of neutral ligand (Ln(III):HDADTP:TOPO= 1:3:2). Heavy Ln(III) have the tendency to form complexes with lower coordination number (due to the phenomena of ionic radius contraction - contraction of volume).

This tendency was observed in liquid-liquid extraction too (chapter VI), but it was evidenced by X-ray diffraction on isolated solid compounds [234].

In the chromatographic systems, this behavior is confirmed by the variation of R<sub>M</sub>\* values versus log c<sub>TOPO</sub>, depicted in Figures 49 and 50 for UO<sub>2</sub>(II), Th(IV) and Ln(III).

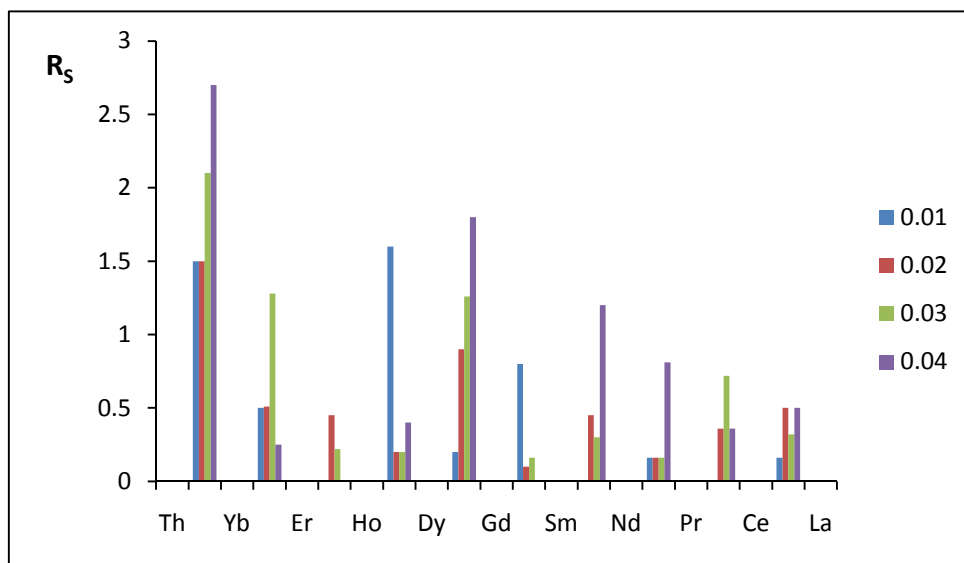


**Fig. 49-50.**  $R_M^*$  variation function of TOPO concentration (DEHDTPA 0.04 M)

Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)

Stationary phase: silica gel H +  $\text{NH}_4\text{NO}_3$  2.5 M

Complexation phenomenon that occur in the mixed extractant systems creates separation conditions between lanthanides at 0.03 M TOPO concentration (Fig.51). It is noteworthy that under these conditions (0.04 M TOPO and 0.03 M TOPO) the retention factor increases with increasing of the atomic number Z.



**Fig. 51.** Separation resolution of studied metal ions using a mixture of TOPO and DEHDTPA

Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)

Stationary phase: silica gel H +  $\text{NH}_4\text{NO}_3$  2.5 M

The increase of  $R_F$  observed in systems with DEHDTPA + TOPO mixture can be explained by a synergistic effect seen in liquid-liquid extraction. To illustrate the effect, the  $R_M$ - a logarithmic function of  $R_F$  value- is calculated.  $R_M$  is defined [9] using the relationship:

$$R_M = \lg \frac{1 - R_F}{R_F} \quad (95)$$

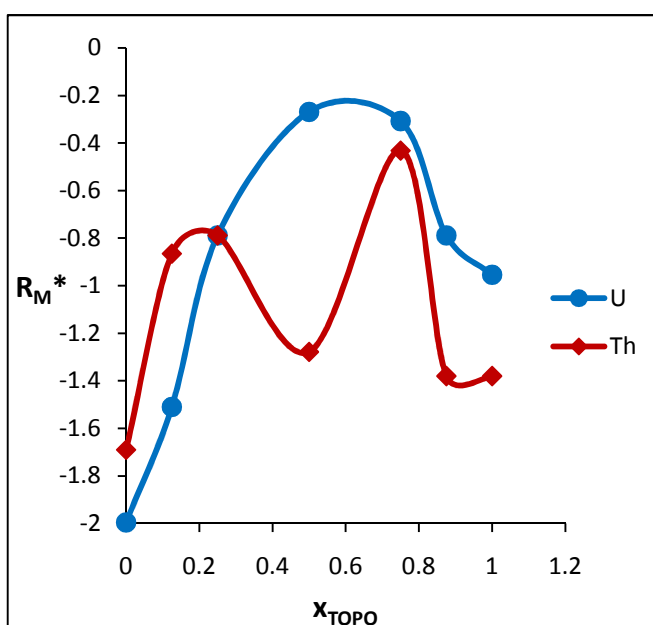
$$R_M^* = \lg \frac{R_F}{1 - R_F} \quad (96)$$

The term is defined above and the value of  $R_M^*$  according to mole fraction of TOPO ( $x_{\text{TOPO}}$ ) is plotted.  $R_M^*$  is chosen because the changes that occur in the values of  $R_F$  (increase or decrease of it) change  $R_M^*$  values in the same direction, while  $R_M$  and  $R_F$  vary in opposite direction.

The curve in Figure 52 for U has a specific maximum value of  $x_{\text{TOPO}}$ .  $R_F$  values corresponding peak are much higher than those obtained on unimpregnated plates. This shows that the two complexants, together, have a significant effect of increasing  $R_F$ . This increase is characteristic of synergistic systems. The presence of two maximum on the curve for Th in Figure 52 can be explained by the formation of two complexes in the system.

Curves for Ln(III) also show two peaks, suggesting the formation of mixed complex compounds with different coordination numbers. This behaviour of Ln(III) occurs also in liquid-liquid extraction systems.

Synergistic increase can be explained by the formation of a mixed complex with higher stability than simple complexes (like those with the dithiophosphoric ligand or with neutral ligand) and higher solubility in the solvent used as mobile phase. This behavior reinforces the assumption that separation in the studied systems is based on a complex mechanism. Besides adsorption, also occurs an ion exchange process with the formation of neutral complex species that are distributed between two solvents (mobile phase and stationary phase).



**Fig. 52.**  $R_M^*$  variation function of mole fraction of TOPO  
 Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)  
 Stationary phase: silica gel H +  $\text{NH}_4\text{NO}_3$  2.5 M

## V.2.4. The influence of the stationary phase

### V.2.4.1. The influence of the stationary phase acidity

Results of the study of the influence of mobile phase on chromatographic behavior of U(VI), Th(IV) and Ln(III), namely: the influence of solvent, of acid complexant (DADTPA) and of neutral complexant, suggest a complex mechanism involving complexing equilibrium for the studied metal ions. Comparing the results obtained in the chromatographic systems with liquid-liquid extraction systems reinforce this idea.

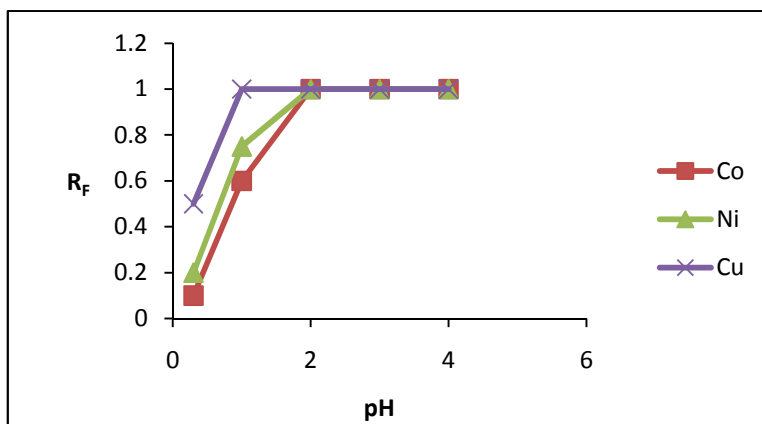
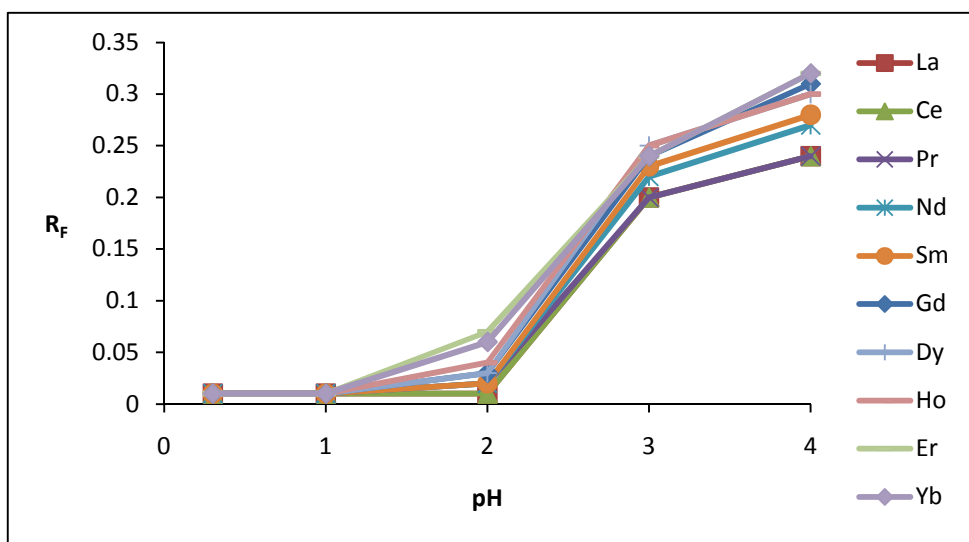
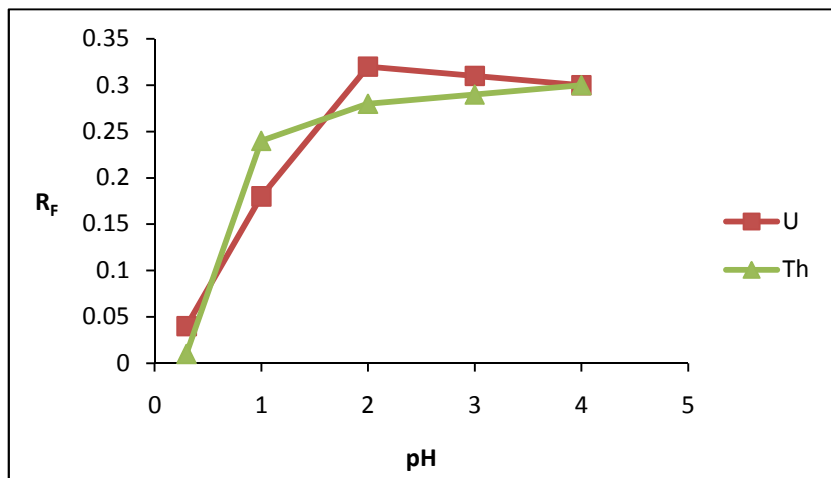
To bring some arguments in addition, the influence of acidity of the stationary phase on the chromatographic behavior of investigated ions was studied. To this end, a series of experiments were conducted on plates coated with silica gel H and impregnated with  $\text{HNO}_3 + \text{NaNO}_3$  solutions of different pH values.

The results obtained show that stationary phase acidity affects chromatographic behavior of  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$  and  $\text{Ln}(\text{III})$ . For illustration we chose di(2-ethylhexyl)dithiophosphoric acid present in the mobile phase consisting of a mixture of organic solvents, o,m,p-xylene-MEK-DMF.

In Figures 54, 55 and 56, are set  $R_F$  values function of pH of impregnating solutions for stationary phases for  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$  (Figure 54),  $\text{Ln}(\text{III})$  (Figure 55) and Co, Ni, Cu (Figure 56).

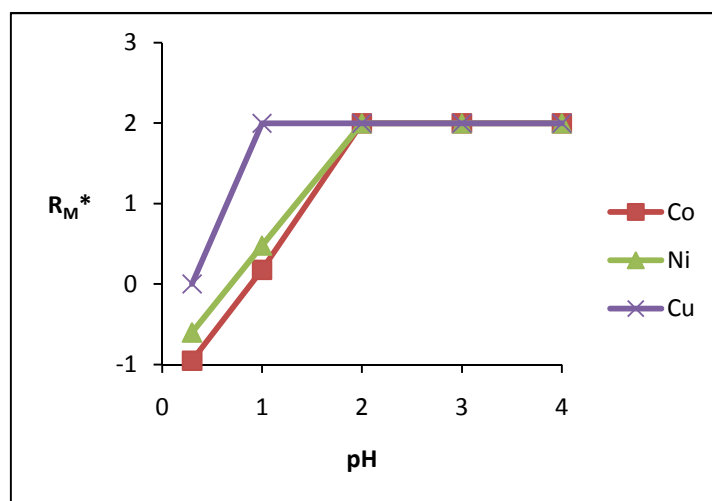
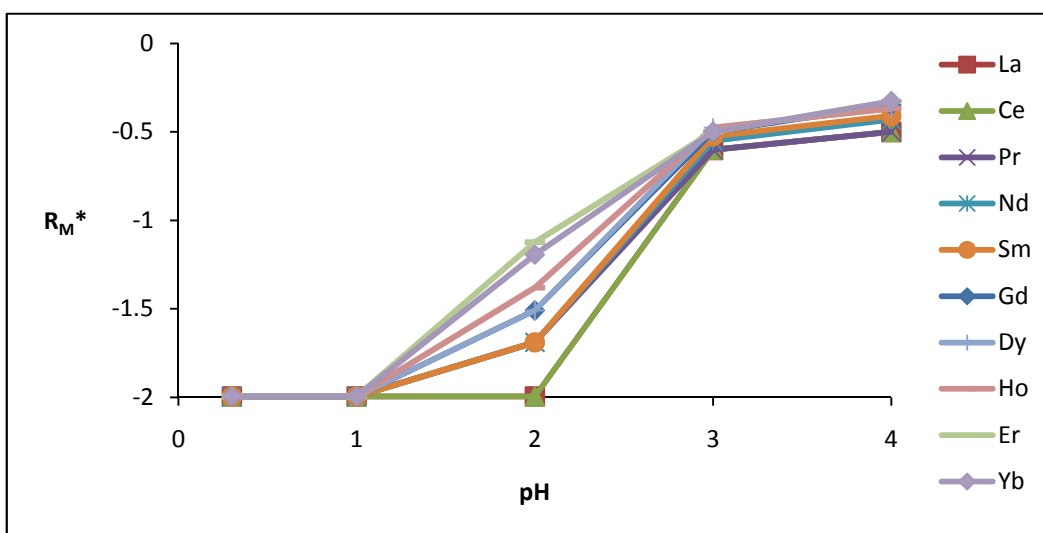
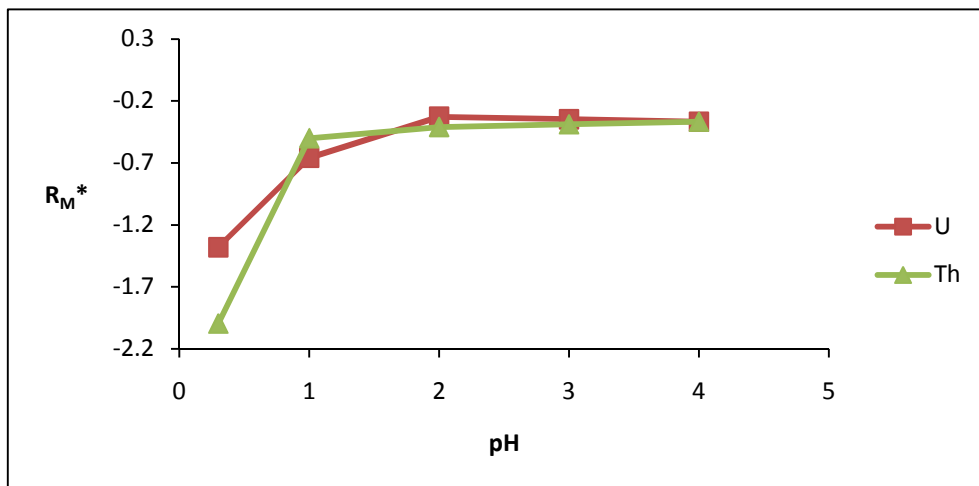
For all studied ions there is a  $R_F$  dependency of stationary phase acidity. We worked at constant ionic strength  $\text{HNO}_3 + \text{NaNO}_3 = 1\text{M}$ .  $R_F$  dependence of pH values for  $\text{UO}_2(\text{II})$ ,  $\text{Ln}(\text{III})$  and Co(II), Ni(II), Cu(II) ions supports the idea that the separation process takes an ion exchange mechanism involving metal ions and acid dithiophosphoric extractant.

$R_M^*$  values for DEHDTPA for actinides, lanthanides and transitional metal ions Co(II), Ni(II) and Cu(II) vary in the same direction as the  $R_F$  values (Figure 54-59).



**Fig. 54-56.** The influence of stationary phase acidity (DEHDTPA)  
 Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)  
 Stationary phase: silica gel H; HNO<sub>3</sub>+NaNO<sub>3</sub>=1M.





**Fig. 57-59.**  $R_M^*$  variation function of stationary phase acidity (DEHDTPA)

Mobile phase: o, m, p-xylene + MEK + DMF (16:2:1, v / v / v)

Stationary phase: silica gel H;  $\text{HNO}_3 + \text{NaNO}_3 = 1\text{M}$ .

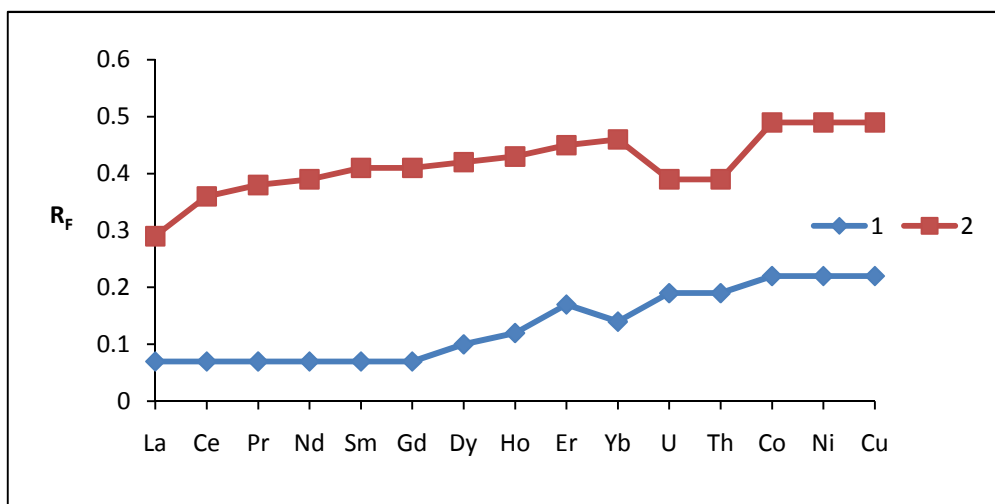
#### V.2.4.2. The influence of the stationary phase nature

Studies on the extractant influence on the chromatographic behavior on stationary phases: silica gel and silica gel impregnated with 1M NaNO<sub>3</sub> (to ensure constant ionic strength in stationary phase) showed the effect of increasing R<sub>F</sub> for studied ions. Salefication effect is produced by metal salts in the extraction systems that result in increased extraction efficiency. Therefore, in order to obtain optimal separation systems, the behavior of metal ions on silica gel impregnated with 2.5 M ammonium nitrate was investigated.

There were also tested two other phases: silica gel - Zirconium(IV) silicate mixture and silica gel - Titanium(IV) silicate mixture.

#### DEDTPA Systems

The chromatographic behavior of metal ions UO<sub>2</sub>(VI), Th(IV) and Ln(III) on silica gel H impregnated with NH<sub>4</sub>NO<sub>3</sub> 2.5 M in DEDTPA systems was studied. Since the R<sub>F</sub> values are low (curve 1) it was to appealed to a second elution.



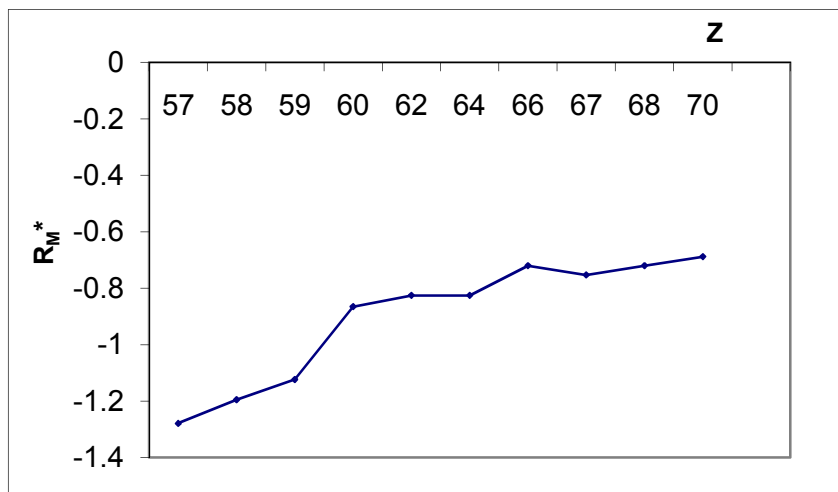
**Fig. 60.** 1 – simple elution; 2 – double elution

Mobile phase: MEK – THF (6.8 : 3.2, v/v) – DEDTPA 0.04 M

Stationary phase: silica gel H impregnated with NH<sub>4</sub>NO<sub>3</sub> 2.5 M

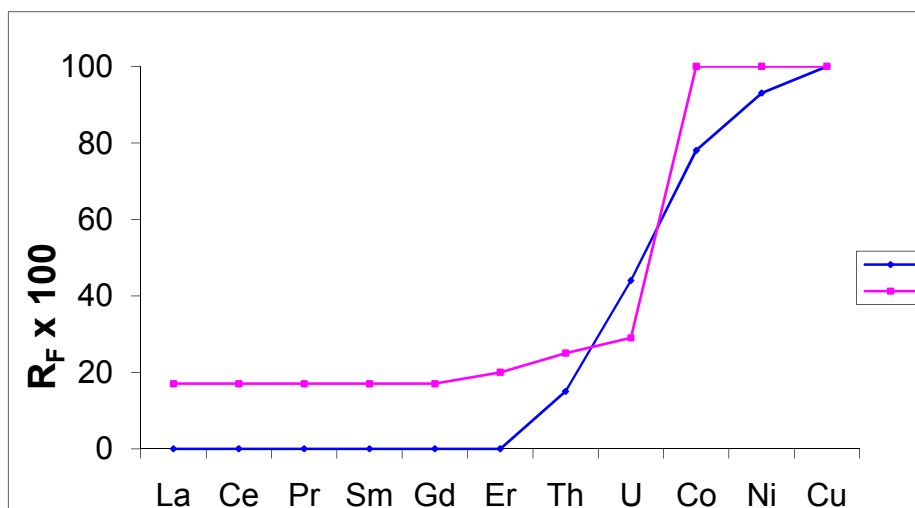
It was observed that after an initial elution the following trends appear: separation of light Ln(III) and heavy Ln(III), separation of heavy Ln(III) one from another, separation of U(VI) and Th(IV) from lanthanides, except Er. After the second elution is observed: lanthanides tendency of separation one from another, separation of U(VI) and Th(IV) from heavy lanthanides, separation of U(VI) and Th(IV) from Co(II), Ni(II), Cu(II). Generally, the migration order is the order of

increasing atomic number  $Z$  of the lanthanides. In Figure 62 a tetrad effect is observed in the variation of  $R_M^*$  function of  $Z$ .



**Fig. 62.**  $R_M^*$  function of  $Z$  for studied lanthanides.

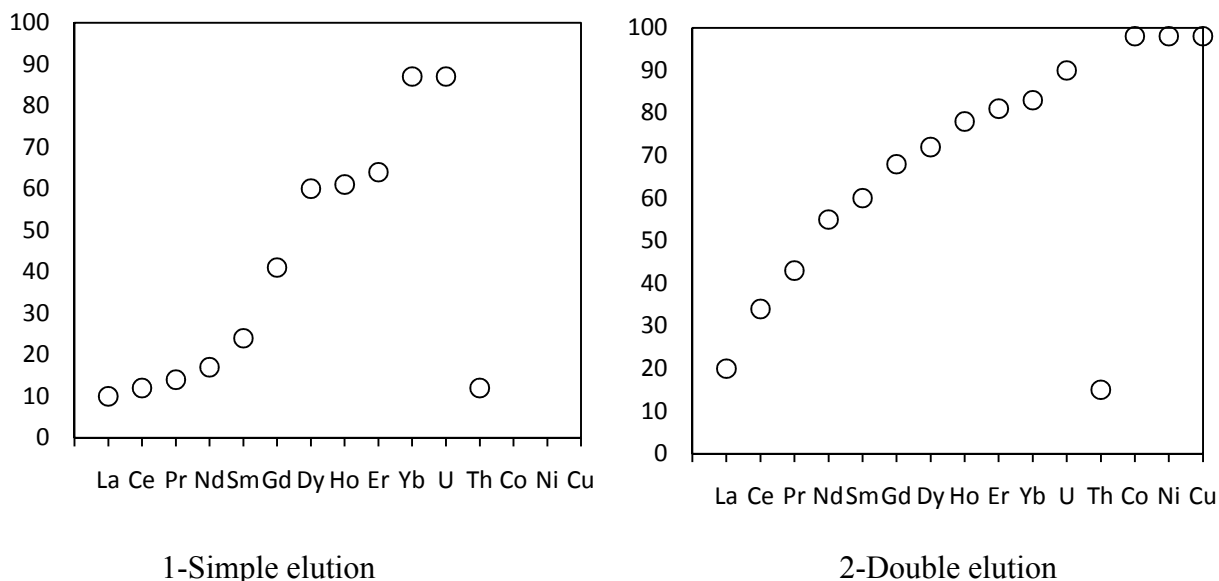
Stationary phases silica gel impregnated with 2.5 M  $\text{NH}_4\text{NO}_3$  were used in systems and with DiBDTPA and DBDTPA. In DBDTPA systems (Figure 62)  $R_F$  values increase for Th(IV), Ln(III), Co(II) and Ni(II), but their separation is not essentially influenced.



**Fig. 63.** Stationary phase influence

1 – silica gel H; 2 – silica gel impregnated with  $\text{NH}_4\text{NO}_3$  2.5 M  
o,m,p-xylene-MEK-DMF (16:2:1, v/v/v); DBDTPA 0.06M

In DBDTPA systems (Figure 64 and 65) there is a tendency of all lanthanides to separate from each other therefore we tried to separate these elements by double elution, when it was observed the separation of all lanthanides one from another, and also: U-Th separation, Separation of Th, U from Co, Ni, Cu; Co, Ni and Cu migrate together.



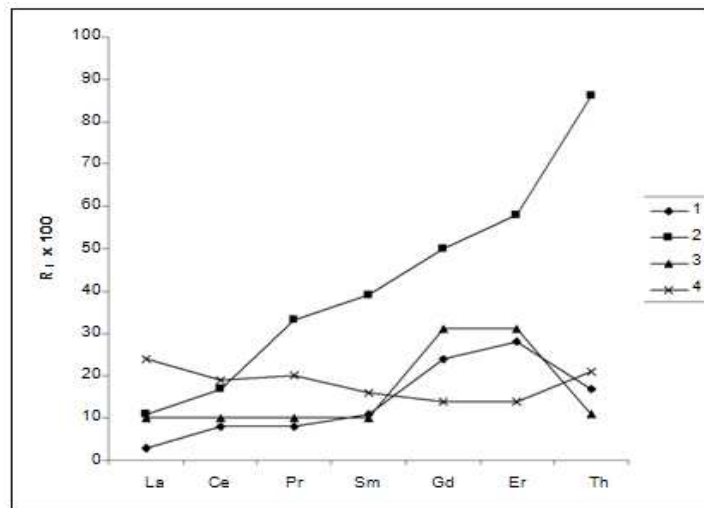
**Fig. 64-65.** Separation of studied metal ions with DiBDTPA

Stationary phase: silica gel H impregnated with  $\text{NH}_4\text{NO}_3$  2.5 M

Mobile phase: MEK – THF (6.8 : 3.2, v/v)

### DEHDTPA Systems

Different stationary phases were used for systems with DEHDTPA 0.04 M and mixture of MEK - THF (6,8:3,2, v/v). Data presented in Figure 66 (curve 1) suggest the possibility of separation on silica gel of Th(IV) from La(III), Gd(III), Er(III) and the separation tendency [244].



**Fig. 66.** Retention factors of metal ions for various stationary phases

Stationary phase: 1 – silica gel H; 2 – silica gel H impregnated with 2.5M  $\text{NH}_4\text{NO}_3$ ;

3 – silica gel H - Zr(IV) silicate mixture; 4 – silica gel H - Ti(IV) silicate mixture.

Mobile phase: MEK – THF (6.8 : 3.2, v/v) – 0.4 M DEHDTPA

### V.2.5. The nature of the separation mechanism of studied metal ions, by extraction chromatography with dialkyldithiophosphoric acids

The results obtained from studying the influence of mobile phase on thin layer chromatographic behavior of  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$ ,  $\text{Ln}(\text{III})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Cu}(\text{II})$  metal ions in the presence of dialkyldithiophosphoric acids (DADTPA), leads to some conclusions about the mechanism underlying the separation of these metal ions.

At the basis of the separation process is a cation exchange process between the metal ion and the hydrogen ion from the dithiophosphoric complexant, resulting neutral chelate complex with the dithiophosphoric anion:



The number of acid molecules,  $n$ , from equation (97), involved in ion exchange (and hence the composition of complex species formed by investigated metals) can be determined from the representations  $R_M^*/\text{pH}$  (Figures 67-71, the slope of the curve-linear portion).

High solubility of this complex in organic solvents favors the metal distribution in the mobile phase and therefore an increase of the retention factors for the involved ions in the presence of the complexing agent.

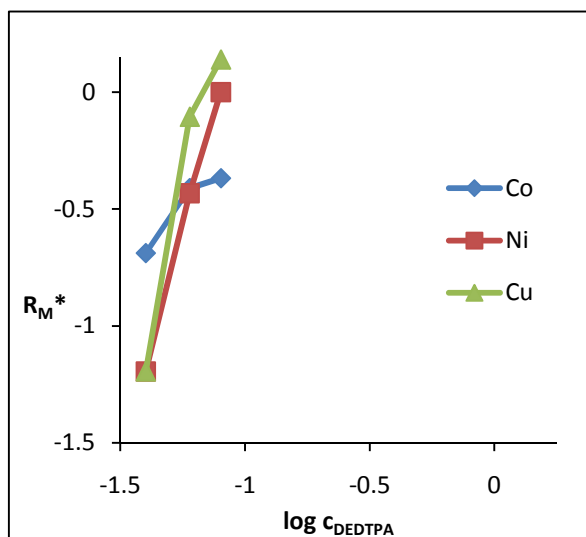
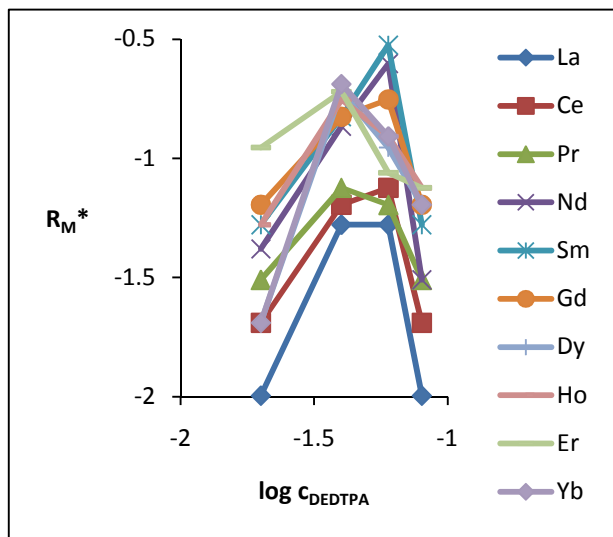
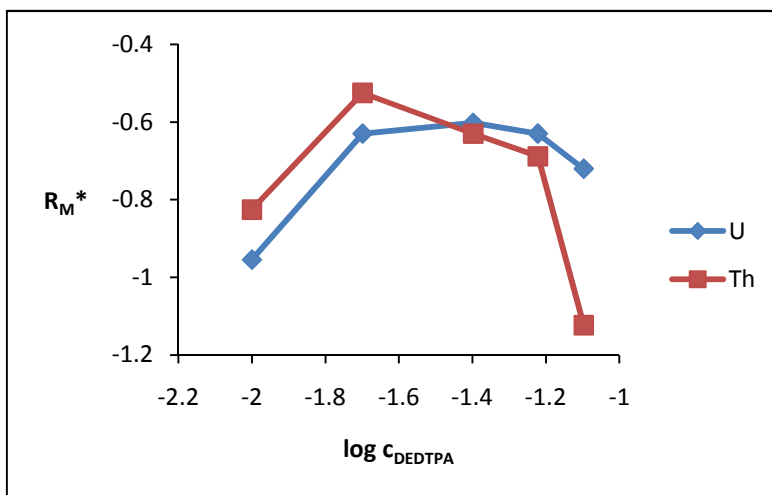
A similar behaviour occurs in liquid-liquid extraction of these metal ions with dialkyldithiophosphoric complexing agents (Cap.IV.).

It may be considered that in the thin layer chromatographic behavior of the mentioned metal ions, liquid-liquid distribution (extraction) plays an important role. Alongside the process of adsorption-desorption characteristic to the chromatographic method, extraction by cation exchange leaves a special mark. So, at the basis of chromatographic separation of  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$ ,  $\text{Ln}(\text{III})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Cu}(\text{II})$  ions on a thin layer of silica gel, in the presence of acid organothiothiophosphoric complexants is a complex mechanism.

Precisely this complex separating mechanism that comprises the distributive effects and adsorption phenomena explains the deviation of the value of  $n$  from the metal ion charge value.

The formation of a complex between the metal ion and the dithiophosphoric anion in the thin layer chromatographic separation system of the mentioned ions is confirmed by the variation  $R_F/C_{\text{DADTPA}}$ . From  $R_M^*/\log \text{DADTPA}$  representation (Figures 67-69 for DEDTPA) was determined the number of dithiophosphorus anions ( $n$ ) that participate in the formation of the extracted species. The value of  $n$  in equation (97) is: 2 ( $\text{UO}_2(\text{II})$ ), 4 ( $\text{Th}(\text{IV})$ ), 3 ( $\text{Ln}(\text{III})$ ) and 2

(Co(II), Ni(II), Cu(II)). Deviations from these values are easily understood in extraction chromatography, where complex processes are involved.



**Fig. 67-69.**  $R_M^*$  values function of DEDTPA concentration

Stationary phase: silicagel

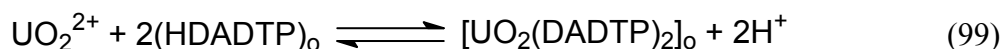
Mobile phase: *o,m,p*-xilen – MEK – DMF (16 : 2 : 1, v/v/v)

For transition d metal ions, Co(II), Ni(II) and Cu(II) equilibrium distribution can be described by the equation:



The literature mentions the formation of these compounds in liquid-liquid extraction systems [148]. The respective complexes were isolated and studied in solid state also through spectral methods.

In the case of uranium(VI), which in solution is found as uranyl ion UO<sub>2</sub>(II), equilibrium distribution in chromatographic systems can be described by the equation:



According to the above equation, two molecules of complexing agent DADTPA are involved in the formation of the neutral complex, soluble in organic solvents. That migration does not occur in non-polar solvent may suggest that this neutral complex is solvated with water molecules (hydrated), because U(VI) can attain a coordination number greater than 6 [245]. The low solubility of these solvated complexes with water molecules, in chloroform, explains the low values of R<sub>F</sub>. In mobile phase consisting of electron donors polar solvents, such as: butanol, MEK, DMF, THF, water molecules can be replaced by organic solvent molecules. Complexes solvated by solvent molecules UO<sub>2</sub>(DADTP)<sub>2</sub>S, with solubility greatly enhanced in the organic mobile phase explains the increase of the retention factor for the ion UO<sub>2</sub>(II), behavior similar to that of liquid-liquid extraction systems [149,150].

For Th(IV) equilibrium distribution can be described by the equation:



in which four acid organophosphoric complexant molecules are involved in the formation of the neutral species. As in the case of uranium(VI), higher values of R<sub>F</sub> obtained for Th(IV) in systems with electron donors solvents can be explained by solvation effects because Th(IV) may exceed the coordination number eight in the chelate formed with dithiophosphorus anions.

For lanthanides(III) the equilibrium distribution in the presence of organophosphoric complexant can be described by the equation:



in which three acid organophosphoric complexant molecules are involved in the ion exchange forming neutral complexes soluble in organic solvents.

Using mobile phases consisting of solvents with donor properties as DMF, MEK and butanol, Ln(III) migrates achieving high levels of  $R_F$  because, as in the case of uranium and thorium, conditions for replacing the hydrating water with solvent molecules are created, resulting in species with high solubility in organic solvents,  $\text{Ln}(\text{DADTP})_3\text{S}_2$ . Using silica gel impregnated with ion exchange, conditions were created for the separation of lanthanides ions, at the basis of the separation being a complex mechanism of adsorption-desorption, ion exchange and extraction.

In systems with mixtures of complexants, dialkyldithiophosphoric acid and a neutral ligand (TOPO), we assume the formation of mixed complexes from the ion exchange process with DADTPA and a solvation process with the neutral extractant molecules of the coordinative unsaturated chelate, according to the equation :



in which the  $\text{M}^{n+}$  represents the ions  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$  and  $\text{Ln}(\text{III})$  and S is the neutral ligand.

Formation of the mixed complex  $\text{M}(\text{DADTP})_n\text{S}_y$  in the organic phase determines a significant increases of the retention factor values for  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$  and  $\text{Ln}(\text{III})$  especially in TOPO systems through a synergistic effect encountered also in liquid –liquid extraction.

The curves shown in Figures 52 and 53, which represent the parameter  $R_M^*$  variation, depending on the TOPO molar fraction, presents a shape characteristic to synergistic curves. These curves prove that the extraction of  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$ ,  $\text{Ln}(\text{III})$  ions in organic phase is stronger when we use mixtures of TOPO and DADTPA extractants which causes a significant increase in retention factors values. But in the case of the thin layer chromatography extraction, to obtain a synergistic effect is not always equivalent to obtaining a superior separation resolution.

#### V.2.6. Quantification of U(VI), Th(IV)

Calibration curves for  $\text{UO}_2(\text{II})$  and  $\text{Th}(\text{IV})$  were plotted, cations which present industrial importance and are present in large quantities in the ores in our country and together are byproducts of nuclear fission, their separation being needed.

For measuring the spot area have been used two methods: densitometry, using a DESAGA CD 60 densitometer connected to a computer and plate scan method using a scanner



connected to a computer, measuring the areas with the help of a PC using the software UTHSCSA Image Tool.

Quantitative determination of U(VI) ions present in mine water from exploitation Băița (Bihor county) was done spectrophotometrically, using also previously processed samples and thin layer chromatography.

**Tabel 9.** Results of analyzing water with U(VI) content [249].

<b>Determined cation</b>	<b>Limit values in used water (mg / L)</b>	<b>Nature of the analyzed sample</b>	<b>Method / found concentration (mg / L)</b>		
			<b>Spectrophot.</b>	<b>TLC</b>	<b>e<sub>r</sub> (%)</b>
<b>U(VI)</b>	0,021	Mine water Băița	1,50	1,48	-1,33

Results from thin layer chromatography using dithiophosphoric acids as extractants are consistent with those obtained by spectrophotometric method.

## VI. CONCLUSIONS

The purpose of this paper is to study the possibility of separation by extraction of some metal ions of major importance:  $\text{UO}_2(\text{II})$ ,  $\text{Th}(\text{IV})$ ,  $\text{Ln}(\text{III})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$  using organothiophosphoric ligands as complexing agents. We used both liquid-liquid extraction and thin layer chromatography extraction. Uranium and thorium, important elements due to their nuclear properties, occur in nature or in byproducts of nuclear fission with lanthanides or transition metals such as nickel, cobalt and copper.

1. We studied the behavior of these extractants in water - polar solvent and water - non-polar solvent systems in order to explain some features observed in the extraction of investigated ions with dialkyldithiophosphoric acid. The partition constants and acidity constants of the used acids were calculated.

The obtained results show that with increasing alkyl chain appear small variations in the values of the constants for the short chain acids, but a significant increase in partition constants.

2. We studied the extraction of  $\text{U}(\text{VI})$ ,  $\text{Th}(\text{IV})$  and  $\text{Ln}(\text{III})$  in liquid-liquid extraction systems with DADTPA alone and in combination with neutral extractant (TOPO) in polar solvent (butanol) and non-polar solvent (benzene) .

The extraction mechanism for the investigated metal ions and the nature of extracted species in organic solvents was established by the slope method (from the variation of the distribution ratio as a function of extraction system parameters: the pH of the aqueous phase, the concentration of organothiophosphoric extractant in organic phase and the metal concentration in aqueous phase). In the DADTPA systems with short alkyl chain ( $\text{C}_2\text{-C}_4$ ) complexation phenomena that can occur in aqueous solution were considered.

The obtained results argue for an ion exchange mechanism with the formation of an  $\text{MA}_m$  type complex between the metal ion and the dialkyldithiophosphate anion  $(\text{RO})_2\text{PSS}^-$  (A) in systems with organodithiophosphoric acid ligand in non-polar solvent and a joint complex such as  $\text{MAMSy}$  in systems with organodithiophosphoric acid ligand in polar solvent or mixed with neutral extractant in non-polar solvent.

The alkyl chain length does not affect the composition of extracted species, but it influence the metals distribution ratio. Increasing alkyl chain determines an increase in extraction due to the organophil increasing nature of extracted species.

High values of distribution ratio are obtained in systems with organodithiophosphoric acid and neutral ligand (TPPO and TOPO), fact explained by the synergistic effect. High stability and high solubility of mixed complexes (synergic adducts) in the organic phase significantly increase the extraction.

Synergic adducts composition was confirmed by IR study of solid isolated compounds from the organic phase of mixed extractant systems that consist of organodithiophosphoric acid with short alkyl chain and TPPO.

Results obtained from the conducted study on the extraction of uranium(VI), thorium(IV) and lanthanides(III) in the presence of organodithiophosphoric acids allowed us to establish optimal conditions for separating these elements from aqueous nitrate solution.

3. We studied the possibility of using organodithiophosphoric ligands in thin layer chromatography separation on silica gel H of U(VI), Th(IV) and Ln(III) ions and some transitional d elements (Co(II), Ni(II), Cu( II)).

To establish the underlying mechanism for the separation of the mentioned metal ions, the chromatographic behavior of these ions in various chromatographic systems was studied. The influence of the dialkyldithiophosphoric acid concentration and structure, the influence of mobile phase system and the stationary phase on the chromatographic behavior of these ions were studied.

The obtained results for diethyldithiophosphoric acid (DEDTPA) show that the presence of the organothiophosphoric complexant in the mobile phase is crucial and the nature of the organic solvent used as mobile phase significantly influences the migration of metal ions in the presence of organothiophosphoric acid ligand. It appears that the donor properties of solvent are the dominant factor in the migration of metal ions, and not the solvent polarity.

These results suggested a similar behaviour of studied chromatographic systems with that of liquid-liquid extraction systems and therefore a similar separation mechanism involving complexation equilibria. Different stability of complexes of  $\text{UO}_2(\text{II})$ , Th(IV), Ln(III), Co(II), Ni(II), Cu(II) determines differences in the migration of metal ions and creates conditions for their separation.

The study of dithiophosphoric complexant influence shows that an increase in unbranched alkyl chain leads to an increase in retention factor for all studied ions.

Chain ramification determines an increase of the  $R_F$  values for almost all studied ions, except for  $UO_2(II)$  and heavy  $Ln(III)$ , for short and branched alkyl chain acids, and also for  $Co(II)$  and  $Ni(II)$ , especially for long and branched alkyl chain, which may be explained considering the steric factor .

The presence in the mobile phase of neutral ligand (TOPO) together with dialkyldithiophosphoric acids determines an increase in retention factor for the studied ions.

We studied the chromatographic behavior of investigated ions on different stationary phases: silica gel impregnated with  $NH_4NO_3$ , silica gel - Zr silicate and silica gel - Ti silicate. Separation is significantly influenced by the presence of  $NH_4NO_3$  when separation conditions for  $Ln(III)$  are created.

The influence of the stationary phase pH on chromatographic behavior of investigated metal ions in systems with stationary phase silica gel impregnated with 1M  $NaNO_3$  as the constant ionic strength was studied. The increase of  $R_F$  values as a result of the pH increase has reinforced the belief that the chromatographic separation process involves equilibrium with complexing ligands present in the mobile phase and distribution of these complexes between the two phases plays an important role.

From size variation of the  $R_M^*$  (correlation factor between chromatographic extraction data and liquid-liquid extraction) function of pH, dialkyldithiophosphoric acid ligand and neutral extractant S concentration, was established the composition of the species involved in the distribution.

The results obtained from the study undertaken on chromatographic behavior of uranium(VI), thorium(IV) and lanthanides(III) in the presence of dialkyldithiophosphoric acids allowed us to establish optimal conditions for separating these elements.

Some results from these studies were used for quantitative determination of ions (U, Th) from industrial wastewater; results were consistent with those obtained by spectrophotometric methods ( $UO_2$ ).

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