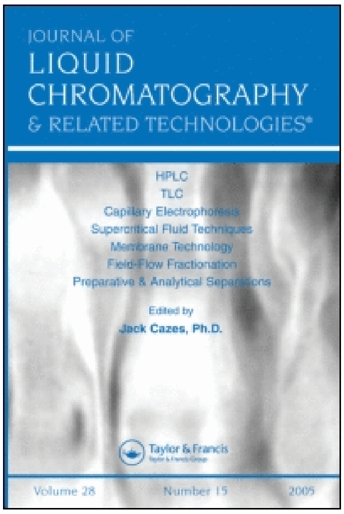

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Separation of U(VI) and Th(IV) from Some Rare Earths by Thin Layer Chromatography with Di-(2-Ethylhexyl)-Dithiophosphoric Acid on Silica Gel

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Abstract: 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 ethyl-methyl-ketone–tetrahydrofuran (6 : 3, v/v) containing di-(2-ethylhexyl)-dithiophosphoric acid was used as the mobile phase. When silica gel H impregnated with 2.5 M NH_4NO_3 was used as stationary phase, the resolution was much improved and the separation of rare earths from each other was also achieved. The tetrad-effect was observed in variation of R_m^* versus the atomic number of rare earths.

Keywords: Uranium(VI), Thorium(IV), Rare earths, TLC, Di-(2-ethylhexyl)-dithiophosphoric acid, Silica gel

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INTRODUCTION

Uranium and thorium are naturally occurring actinide elements found at trace level in the environment or associated with other metal ions in different complex matrices, nuclear fission products, monazite sands, and geological materials. Quantitative chemical analysis and separation of these elements requires development of elaborate and high sensitivity analytical techniques by use of which quantity of radioactive sample and associated waste can be minimized. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is widely selected as the technique of choice to perform the analysis of metals owing to its high sensitivity and simultaneous measurement capability.[1,2] But this technique is not always suitable for trace elements because of spectral and chemical interferences and, therefore, a preseparation procedure is required in advance of spectroscopic analysis.

Many methods have been proposed for separation of these elements, including liquid-liquid extraction and ion exchange. However, chromatographic separation is more suitable because it requires less manipulation than solvent extraction due the simplicity in handing the radioactive samples. In particular, extraction chromatography, which combines the advantages of both these procedures, i.e.; selectivity of organic compounds in solvent extraction with easier use and the multistage feature of the chromatographic process, have been extensively employed.[3–5] The range of organic extracts is large, including carboxylic acids, β-diketones, long chain tertiary or quaternary amines, and organophosphorus derivatives. The complexants are usually retained on the stationary phase.[1,2,6–10] Complexing agents have also been included in the mobile phase.

The choice of chromatographic technique depends on the problem to be solved. For the separation of U(VI) and Th(IV) and rare earths from complex samples, thin-layer chromatography (TLC) is a preferable chromatographic method, one of advantages being the possibility to optimize the resolution by choosing the proper elution conditions. A wide variety of stationary phases, mobile phases, and detection methods have been investigated. Later, TLC techniques have been employed using different complexants fixed on silica gel[11–13] or included in different organic solvents as mobile phases.[14–16]

Selective separations of these elements by TLC have been achieved using acidic organophosphorus compounds.[15–19] The most investigated was di(2-ethylhexyl)phosphoric acid in various organic solvents (ethers, ketones, tetrahydrofuran) as mobile phases. Silica gel, CN-cellulose, and other supports were used as the stationary phase.[17–20] Dialkyldithiophosphoric acids, well known as good complexing agents for metal ions, have also been used in chromatographic separation of metal ions, but to a lesser extent.

Di(2-ethylhexyl)monothiophosphoric, di-(2-ethylhexyl)-dithiophosphoric and di(2,4,4-trimethylpentil)dithiophosphinic acids were investigated as selective extractants impregnated on different polymer supports.[21–23] Di-

(2-ethylhexyl)-dithiophosphoric in hexane was used as a selective mobile phase for separation of different metal ions on iminodiacetic acid and polyacrilic resins.[24] The ammonium salt of diethyldithiophosphoric acid was used as complexing agent in HCl and HNO_3 medium for preconcentration of heavy metals from waters and biological materials, using different sorbents.[25]

In our earlier papers we have studied the extraction of U(VI), Th(IV), and rare earths by different dialkyldithiophosphoric acids.[26–29] Later, we extended our investigation to the separation of U(VI) and other elements by TLC using short chain dialkyldithiophosphoric acids in the mobile phase.[30–35]

The aim of this work is to study the separation of U(VI) and Th(IV) from rare earths by TLC on plain silica gel H and silica gel H impregnated with NH_4NO_3 using di-(2-ethylhexyl)-dithiophosphoric acid (HDEHDTP) complexing agent.

EXPERIMENTAL

Materials

Silica gel H (supplied by "Raluca Ripan" Institute for Research in Chemistry, Cluj-Napoca, Romania), ethyl-methyl-ketone (EMK), ammonium nitrate (Chimopar, Bucharest, Romania), tetrahydrofuran (THF) (Merck, Darmstadt, Germany), di-(2-ethylhexyl)-dithiophosphoric acids (synthesized according to a published procedure[36]) Arsenazo III, and metal nitrates (Sigma-Aldrich Chemie, Steinheim, Germany) were used. All other reagents used were of analytical grade.

Apparatus

An unsaturated normal chromatographic chamber (ABL&E Jasco, Cluj-Napoca, Romania), micropipettes (BlauBrand®, Sigma-Aldrich Chemie, Steinheim, Germany), and a densitometer Desaga CD 60 (Wiesloch, Germany) were used.

Procedure

The chromatographic plates with silica gel H were prepared in the laboratory. The organic binder composed of amidon and agar-agar (1 : 1, g/g) was added in demineralized water and the silica gel powder was poured in.[37] Clean glass plates (20 × 20 × 0.3 cm) were coated with the slurry thus obtained, using a special applicator,[37] to give a layer of 0.3 mm thickness. After preparation the plates were allowed to dry in moisture free and acid- or base- vapor free air.

The silica gel H plates impregnated with NH_4NO_3 were prepared by development with a 2.5 M NH_4NO_3 aqueous solution. The plates were left to dry in a drying oven for 1 h 70°C.

The 5×10^{-3} M standard solutions of cations prepared in demineralized water of the studied cations were spotted onto the chromatographic plates using 5 μL Brand micropipettes. Plain silica gel H and silica gel H impregnated with 2.5 M NH_4NO_3 were tested as stationary phases. A mixture of EMK-THF containing di-(2-ethylhexyl)-dithiophosphoric acid (1 M) as complexing agent (6 : 3 : 1, v/v/v) was used as the mobile phase.

The plates were developed in unsaturated normal chromatographic chambers. The mobile phase was allowed to ascend 10 cm, and then the plates were dried for 15 min in a hood. The spots were visualized by spraying the plates with 0.05% Arsenazo III aqueous solution to give a blue-green color. All operations were performed at room temperature.

RESULTS AND DISCUSSION

Separation of uranium(VI) and thorium(IV) from rare earths was studied on plain silica gel H and silica gel H impregnated with 2.5 M NH_4NO_3. The mixture of polar solvents EMK-THF containing HDEHDTP as complexing agent was used as the mobile phase because earlier investigations showed that the presence of a polar solvent with donor properties in addition to HDEHDTP is crucial for the migration of rare earths and actinides.[35]

The R_F values obtained for different stationary phase-mobile phase systems are presented comparatively in Figure 1.

It can be seen that when the stationary phase is silica gel H, low values of R_F are obtained. However, a clear tendency of separation of U(VI) and Th(IV) from rare earths is observed. Besides, the R_F values of U(VI) and Th(IV) are quite different, suggesting that separation of these two actinides from each other can be achieved.

A clear separation of U(VI) and Th(IV) from rare earths occurs on silica gel H impregnated with NH_4NO_3. U(VI) can also be separated from Th(IV), and rare earths are separated from each other as well. Generally, the order of migration for rare earths is the order of increasing atomic number Z, on both plain silica gel H and silica gel H impregnated with NH_4NO_3. The tetrad-effect appears in the variation of R_m^* (equation 1)[38] with the atomic number of rare earths.

$$R_m^* = \lg \frac{R_F}{1 - R_F} \tag{1}$$

where R_F is the retention factor of rare earth.

The tetrad-effect is clearly seen after double elution. The plots of R_m^* versus atomic number are represented in Figure 2.

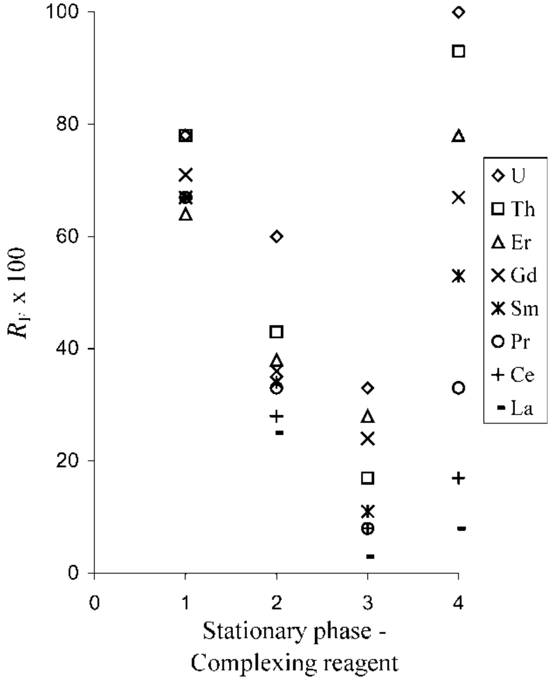

Figure 1. The R_F values of U(VI), Th(IV) and some rare earths for different stationary phase-complexing agent systems. 1—silica gel-HDiBDTP; 2—silica gel impregnated with 2.5 M NH_4NO_3-HDiBDTP; 3—silica gel-HDEHDTP; 4—silica gel impregnated with 2.5 M NH_4NO_3-HDEHDTP.

In the interest of clarity and understanding, the R_m^* values were preferable instead of R_m because changes in R_F alter R_m^* in the same direction, whereas R_m and R_F change in opposite directions. It can be observed that rare earths are divided in four groups: La-Nd, Pm-Gd, Gd-Ho, and Ho-Yb.

In order to asses the quality of separation, the TLC parameters: selectivity (β) and resolution (R_s) were calculated according to equations 2 and 3, respectively;[38,39]

$$\beta = \frac{R_{F2} - R_{F1} \times R_{F2}}{R_{F1} - R_{F1} \times R_{F2}} \tag{2}$$

where R_{F1}, R_{F2} are the retention factors of a neighboring pair of substances.

$$R_s = \frac{\Delta R_F \sqrt{z_f - z_0}}{2(\sqrt{R_{F1} H_1} + \sqrt{R_{F2} H_2})} \tag{3}$$

where $z_f - z_0$ is the distance between the origin and mobile phase front, H is the theoretical plate height, $H = (z_f - z_0)/N$, N is the number of plates,

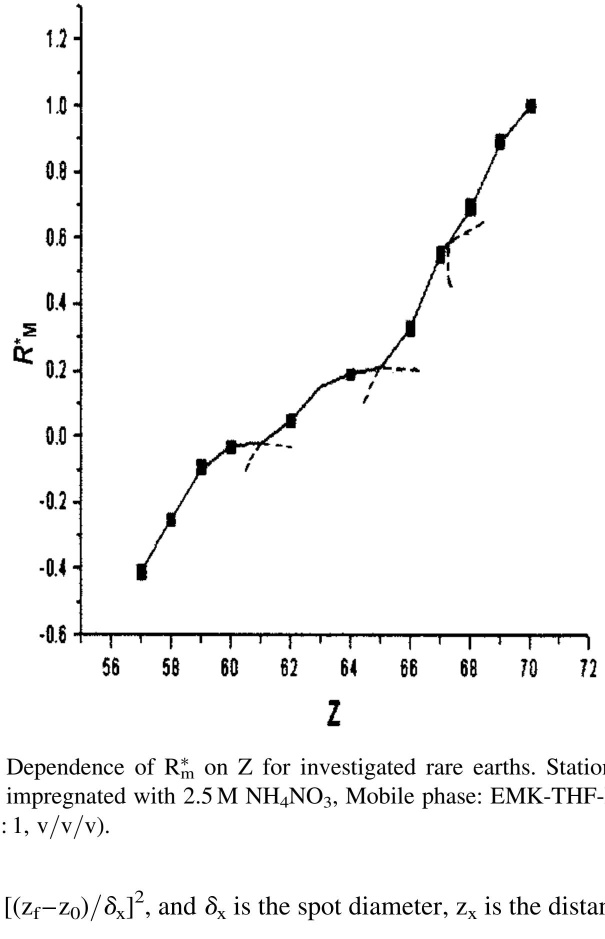

Figure 2. Dependence of R^*_m on Z for investigated rare earths. Stationary phase: silica gel H impregnated with 2.5 M NH_4NO_3, Mobile phase: EMK-THF-HDEHDTP (1 M) (6 : 3 : 1, v/v/v).

$N = 16R_F\,[(z_f - z_0)/\delta_x]^2$, and δ_x is the spot diameter, z_x is the distance of spot migration.

The data presented in Tables 1 and 2 show that very good resolution was obtained on silica gel H impregnated with NH_4NO_3. For the pairs La(III)-Ce(III) and Th(IV)-U(VI), R_s values are situated between 1.0 and 1.5, while for the all other pairs they are higher than 1.5. The R_s values obtained on plain silica gel H (Table 1) are smaller than 1 except for the pairs Sm(III)-Gd(III), Er(III)-Th(IV), and Th(IV)-U(VI) for which the R_s values are higher than those obtained on silica gel H impregnated with NH_4NO_3. The highest selectivity is obtained on silica gel impregnated with NH_4NO_3 (Table 1), except for the pairs La(III)-Ce(III), Sm(III)-Gd(III), and U(VI)-Th(IV).

CONCLUSIONS

The separation of U(VI) and Th(IV) from rare earths can be achieved by TLC on plain silica gel H and silica gel H impregnated with NH_4NO_3 using

Table 1. The chromatographic parameters for the separation of U(VI), Th(IV) and some rare earths by TLC on silica gel H

Complexing reagent	HDiBDTP		HDEHDTP	
	β	R_s	β	R_s
U(VI)	1.0	0	2.0	4.802
Th(IV)	2.0	2.292	1.9	2.476
Er(III)	1.4	1.050	1.2	0.720
Gd(III)	1.2	0.600	2.6	2.341
Sm(III)	1.0	0	1.4	0.540
Pr(III)	1.0	0	1.0	0
Ce(III)	1.0	0	2.8	0.900
La(III)				

HDiBDTP—di(*iso*-butyl)dithiophosphoric acid.
HDEHDTP—di-(2-ethylhexyl)-dithiophosphoric acid.

HDEHDTP as complexing agent in the mobile phase. The separation of U(VI) and Th(IV) from each other is also obtained. When silica gel H impregnated with NH_4NO_3 is used as the stationary phase, the resolution is much improved and the separation of rare earths from each other is also achieved. The tetrad-effect is observed in variation of R_m^* versus the atomic number of rare earths.

It can be concluded that HDEHDTP is a better extractant in TLC separation of U(VI) and Th(IV) from rare earths than short alkyl chain dithiophosphoric acid [the chromatographic data for di(*iso*-butyl)dithiophosphoric acid (HDiBDTP) are presented for comparison in Figure 1].

Table 2. The chromatographic parameters for the separation of U(VI), Th(IV) and some rare earths by TLC on silica gel H impregnated with 2.5 M NH_4NO_3

Complexing reagent	HDiBDTP		HDEHDTP	
	β	R_s	β	R_s
U(VI)	2.0	6.666	0	1.334
Th(IV)	1.2	3.187	3.7	2.518
Er(III)	1.1	0.682	1.8	1.703
Gd(III)	1.1	0.250	1.8	2.049
Sm(III)	1.1	0.125	2.3	2.956
Pr(III)	1.3	0.625	2.5	2.457
Ce(III)	1.2	0.375	2.3	1.294
La(III)				

HDiBDTP—di(*iso*-butyl)dithiophosphoric acid.
HDEHDTP—di-(2-ethylhexyl)-dithiophosphoric acid.

It may be considered that effective separation of U(VI) and Th(IV) from rare earths and separation of rare earths from each other is achieved by a combined sorption-desorption, ion exchange, and partition process. In this complex mechanism, the solubility of actinide and rare earth complexes with dithiophosphate anions plays a decisive role.

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