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In memoriam prof. dr. Ioan A. Silberg

TLC SEPARATION OF Th(IV) AND LANTHANIDES(III) ON VARIOUS STATIONARY PHASES USING HDEHDTP AS COMPLEXING AGENT

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ABSTRACT. The separation of thorium(IV) and lanthanides(III) (Ln(III)) using different stationary phases: silica gel, silica gel – zirconium(IV) silicate mixture, silica gel – titanium(IV) silicate mixture, and silica gel impregnated with NH_4NO_3 2.5M has been investigated. The solvent mixtures *o,m,p*-xylene – methyl-ethyl-ketone (MEK) - N,N-dimethylformamide (DMF) (16 + 2 + 1, v/v) and methyl-ethyl-ketone – tetrahydrofuran (THF) (6.8 + 3.2, v/v) containing di(2-ethylhexyl)dithiophosphoric acid (HDEHDTP) 0.04 M as complexing agent were used as mobile phases. The results obtained show that the separation of Th(IV) from Ln(III) and Ln(III) from each other is achieved using silica gel impregnated with NH_4NO_3 2.5 M and MEK – THF (6.8 + 3.2, v/v) – HDEHDTP 0.04 M as mobile phase.

INTRODUCTION

Dialkyldithiophosphoric acids, well known as good complexing agents have been efficiently used for solvent extraction of metal ions [1-7]. Di(2-ethylhexyl) monothiophosphoric, di(2-ethylhexyl)dithiophosphoric and di(2,4,4-trimethylpentyl)dithiophosphinic acids were investigated as selective extractants impregnated on polymer supports [8-10]. The ammonium salt of diethyldithiophosphoric acid was used for preconcentration of heavy metals from water and biological material, using different sorbents [11].

In our earlier paper, we have studied the extraction of U(VI) by different dialkyldithiophosphoric acids (HDADTP) [5-7,12] and the separation of uranium and *d* transition metal dithiophosphates by TLC technique [13]. Later, we extended our investigation on the separation of U(VI), Th(IV), Ln(III) and other elements using dithiophosphoric complexants in solvent extraction and chromatographic systems [14-18].

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In several papers we described the use of dialkyldithiophosphoric acids for separation of metal cations mentioned by thin-layer chromatography on silica gel H [14-18]. In order to improve the separation conditions we investigated the TLC behavior of these cations on various stationary phases [16, 19].

The goal of this work is to obtain information about the separation of thorium(IV) and lanthanides(III) (Ln(III)) on silica gel H, silica gel H impregnated with 2.5M NH_4NO_3, silica gel H – Zr(IV) silicate and silica gel H – Ti(IV) silicate mixtures, using di(2-ethylhexyl)dithiophosphoric acid (HDEHDTP) in organic mobile phase.

RESULTS AND DISCUSSIONS

TLC separation of Th(IV) and Ln(III): La(III), Ce(III), Pr(III), Sm(III), Gd(III) and Er(III) on silica gel H, silica gel H impregnated with 2.5M NH_4NO_3, silica gel H – Zr(IV) silicate and silica gel H – Ti(IV) silicate mixtures was studied using HDEHDTP as complexing agent in the mobile phase.

A mixture of organic solvents containing MEK, DMF or THF were used as mobile phase since previous studies have shown that the presence of a polar solvent with electron-donor properties in addition to dialkyldithiophosphoric ligand is crucial for actinides and lanthanides migration [22].

The results obtained using stationary phases mentioned above and *o,m,p*-xylene – MEK – DMF (16 + 2 + 1, v/v) mixture containing 0.4M HDEHDTP as mobile phase are presented in Table 1.

Table 1

R_F values of the studied cations obtained on various stationary phases.
Mobile phase: *o,m,p*-xylene – MEK – DMF (16 + 2 + 1, v/v)
mixture containing 0.4M HDEHDTP

No.	Stationary phase	R_F x 100						
		La(III)	Ce(III)	Pr(III)	Sm(III)	Gd(III)	Er(III)	Th(IV)
1.	Silica gel H	17	23	23	20	8	15	14
2.	Silica gel H - Zr(IV) silicate	18	14	17	18	18	14	9
3.	Silica gel H - Ti(IV) silicate	24	19	20	16	5	14	21

It can be noticed that Th(IV) and the lanthanides migrate on all stationary phases investigated. The R_F values show that on silica gel Th(IV) can be separated from La(III), Ce(III) Pr(III), and Gd(III) and a tendency of separation of Ln(III) from each other excepting for Ce(III) - Pr(III) pair. The separation of Th(IV) from Ln(III) studied is also observed when silica gel H-Zr(III) silicate mixture is used as stationary phase. In this case the pairs La(III)-Ce(III), Ce(III)-Pr(III) and Gd(III)-Er(III) are separated too. The results obtained on silica gel H - Ti(IV) silicate mixture show that Th(IV) can be separated from La(III), Sm(III), Gd(III) and Er(III). The pairs La(III)-Ce(III), Pr(III)-Sm(III), Sm(III)-Gd(III) and Gd(III)-Er(III) can also be separated.

Series of experiments were also carried out on different stationary phases using MEK – THF mixture (6.8:3.2, v/v) containing 0.4M HDEHDTP as mobile phase. Data presented in Figure 1 (curve 1) suggest the possibility of separation on silica gel H of Th(IV) from La(III), Gd(III), Er(III) and tendency of Ln(III) separation from each other excepting for Ce(III) – Pr(III) pair.

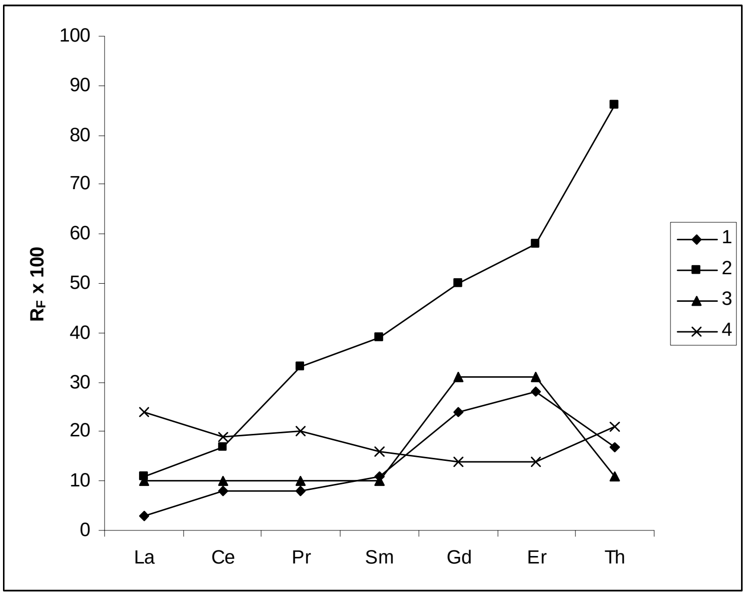

Fig. 1 - Retention factors of metal ions for various stationary phases
Stationary phase: 1 – silica gel H; 2 – silica gel H impregnated with 2.5M NH_4NO_3;3 –silica gel H - Zr(IV) silicate mixture;
4 – silica gel H - Ti(IV) silicate mixture.
Mobile phase: MEK – THF (6.8 : 3.2, v/v) – 0.4 M HDEHDTP

A similar chromatographic behavior is observed on silica gel H -Zr(IV) silicate mixture as stationary phase (Fig 1, curve 3). In this case, Gd(III) and Er(III) can be separated from La(III), Ce(III), Pr(III), Sm(III) and Th(IV). Clear separation of Th(IV) from Ln(III) occurs on silica gel H impregnated with NH_4NO_3 when using this mobil phase. Ln(III) are also separated from each other (Fig 1, curve 2). Generally, the order of migration of Ln(III) is the order of increasing atomic number Z, on both plain silica gel H and silica gel H impregnated with NH_4NO_3, effect observed in Ln(III) separation by liquid-liquid extraction.

In order to asses the quality of separation of metal ions investigated on silica gel impregnated with 2,5M NH_4NO_3 the values of resolution factor R_f were calculated according to Ecuation (1) [23, 24]:

$$R_S = \frac{\Delta R_F \sqrt{z_f - z_0}}{2(\sqrt{R_{F1} H_1} + \sqrt{R_{F2} H_2})} \tag{1}$$

where R_{F_1} and R_{F_2} are retention factors of a neighboring pair of ions; z_f-z_0 is the distance between the origin and mobile phase front; $H = \frac{z_f - z_0}{N}$ is the theoretical plate height; $N = 16 R_F \left(\frac{z_f - z_0}{\delta_x}\right)^2$ is the number of plates; δ_x is the spot diameter; and z_x is the distance of spot migration.

Data obtained are presented in Figure 2 (for simple and double development). R_S values higher than 1,5 show that very good resolution is obtained on silica gel H impregnated with NH_4NO_3 especially by duble development with MEK-THF mixture containing HDEHDTP as complexing agent. For the pairs Ce(III)-Pr(III) and Er(III)-Th(IV) separation is poorer after double elution but is still suitable for quantitation ($R_S > 1,5$).

Under these conditions separation of more lantanides (La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Hb(III), Er(III) and Yb(III) was attempted. The order of migration folowed that of increasing atomic number, but very close R_F values were obtained for consecutive lantanides. Double development was therefore performed to achieve better separation. The R_F values obtained for double development where used to calculate $R_M^* = \log \frac{R_F}{1 - R_F}$ [23] where R_F is the retention factor of lanthanide (R_M* is a quantity used to understand the correlation between the extraction chromatography and liquid-liquid extraction).

The plots of R_M* versus atomic number of lantanides a represented in Figure 3. The tetrad – effect very similar to that observed in liquid – liquid extraction is clearly seen after duble elution. It can be noticed that lanthanides a divided in four groups.

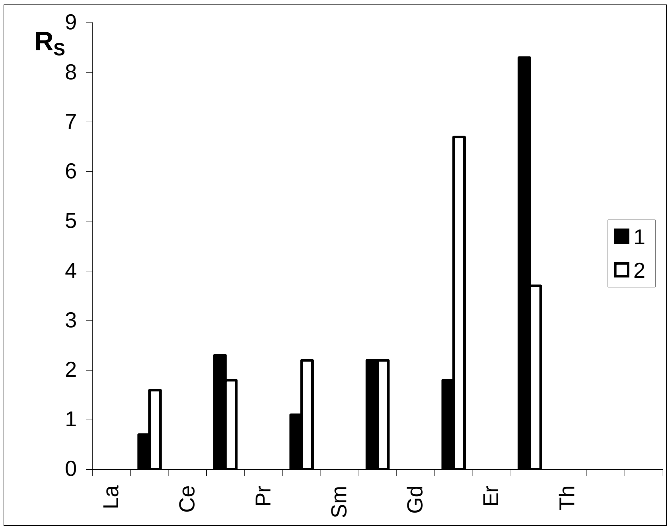

Fig. 2 - Resolution of separation of Th(IV) and Ln(III) on silica gel H impregnated with 2.5M NH_4NO_3;
Mobile phase: MEK – THF (6.8 : 3.2 , v/v)– 0.4 M HDEHDTP mixture;
1 – simple elution; 2 – double elution.

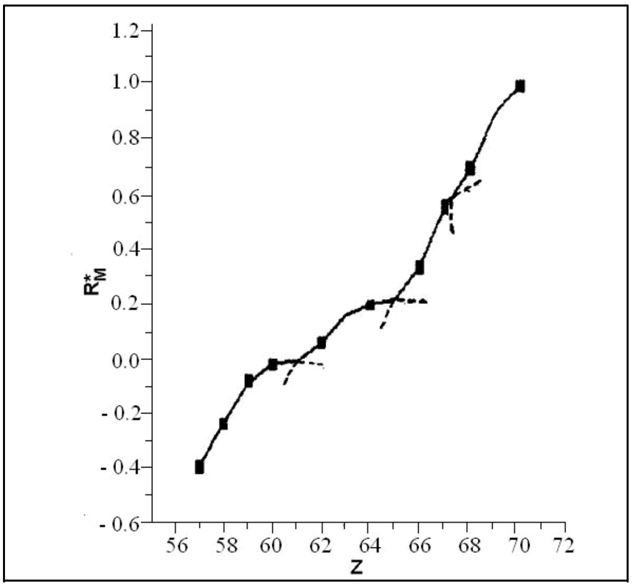

Fig. 3 - Dependence of R^*_M on Z for the investigated lanthanides. Stationary phase: silica gel H impregnated with 2.5 M NH_4NO_3;
Mobile phase: MEK-THF (6.8 : 3.2, v/v)- 0.4 M HDEHDTP

CONCLUSIONS

It has been found that separation of Th(IV) from Ln(III) and separation of certain lantanide (III) pairs can be achieved on silica gel H, silica gel H - Zr(IV) silicat and silica gel H - Ti(IV) silicat using o,m,p-xylene-MEK-DMF and MEK-THF mixtures containing HDEHDTP as mobile phase. When silica gel H impregnated with NH_4NO_3 is used as stationary phase there is a marked difference between TLC behavior of the metal ion investigated. By use of the binary mobil phas MEK-THF containing HDEHDTP the resolution is much improved and the separation of lanthanides from each other is also achieved. The tetrad – effect is observed in variation of R_m* versus atomic number of lantanides.

EXPERIMENTAL PART

Materials

TLC plates coated with silica gel H, silica gel H impregnated with 2.5M NH_4NO_3, silica gel H – Zr(IV) silicate and silica gel H – Ti(IV) silicate mixtures were prepared in laboratory as described elsewhere [20].

Metal nitrates and Arsenazo III were supplied by Aldrich Chemie (Germany). HDEHDTP was synthesized by published procedure [21] and its purity was higher than 95%. All other reagents were of analytical grade supplied by Chimopar, Bucharest (Romania). Standard solutions of metal ions (5 x 10^{-3} M) were prepared by dissolving of the metal salts in demineralized water.

Procedure

Silica gel H, silica gel H impregnated with 2.5M NH_4NO_3, silica gel H – Zr(IV) silicate and silica gel H – Ti(IV) silicate mixtures were tested as stationary phases. Mixtures of *o,m,p*-xylene – methyl-ethyl-ketone (MEK) – dimethylformamide (DMF) and MEK – tetrahidrofurane (THF) were used as mobile phase.

Standard solutions of metal ions were spotted on the chromatographic plates by means of Brand micropipettes. The plates were developed in unsaturated normal chromatographic chambers; the development distance was 10 cm. After development the plates were dried for 15 min in a hood and then, the spots were visualized by spraying with an aqueous solution of Arsenazo III (0.05%). The metal ions were detected as blue-green spots. All separations were performed at room temperature.

The evaluation of chromatograms was performed at 600 nm with a Desaga CD 60 densitometer. The results are means from 3 measurements.

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