TLC Separation of Th(IV) and Ln(III) on Various Stationary Phases Using HDEHDTP as Complexing Agent

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INTRODUCTION

In the last years, the trace metal ions determination has received particular attention due to a strong environmental impact. Many methods have been proposed for the separation of these elements including ion exchange, liquid-liquid extraction and chromatography and any combination of them have been popularly applied to the selective separation of radionuclides or metal impurities from radioactive materials [1].
The separation techniques based on extraction chromatography, which combines the selectivity of organic compounds in solvent extraction with the multistage feature of chromatographic process have been extensively applied in the analysis of radioactive materials [2-5].
The *aim of this work* was the investigation of the TLC 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 2.5 M, when HDEHDTP was the extracting agent in the mobile phase.

EXPERIMENTAL DATA

Stationary phase:
- silica gel;
- silica gel - zirconium(IV) silicate mixture;
- silica gel - titanium(IV) silicate mixture;
- silica gel impregnated with NH_4NO_3 2.5 M

Mobile phase:
- *o,m,p*-xylene - MEK - DMF (16 + 2 + 1, v/v)
- MEK - THF (6.8 + 3.2, v/v) containing HDEHDTP 0.04 M

where: MEK - methyl-ethyl-ketone
DMF - N, N-dimethylformamide
THF - tetrahydrofuran
HDEHDTP - di(2-ethylhexyl)dithiophosphoric acid

Visualising reagents:
·0.05% Arsenazo III in water for Th(IV) and Ln(III)

RESULTS AND DISCUSSIONS

The separation resolution (R_S) was calculated according to the equation

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

Where

$z_f - z_0$ is the distance between the origin and mobile phase front

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

H is the theoretical plate height, $H = \frac{z_f - z_0}{N}$

N is the number of plates, $N = 16 R_F \left(\frac{z_f - z_0}{\delta_x}\right)^2$

δ_x is the spot diameter

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

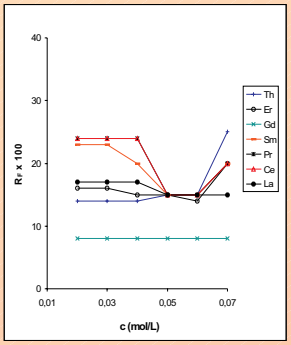

Figure 1. The chromatographic behavior of the studied ions using HDEHDTP as complexing agent.
Stationary phase: silica gel H;
Mobile phase: *o,m,p*-xylene-MEK-DMF (16 + 2 + 1, v/v)

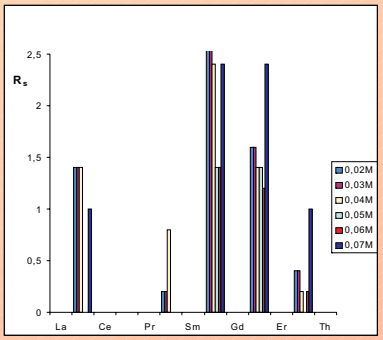

Figure 2. R_S values for Th(IV) and Ln(III) using HDEHDTP as complexing agent, on silica gel H.

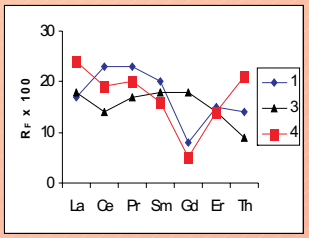

Figure 3. The retention factors for the separation of the studied cations on various stationary phases;
Mobile phase: *o,m,p*-xylene - MEK - DMF (16 + 2 + 1, v/v) containing 0.04 M HDEHDTP

Mobile phase: MEK - THF (6.8 + 3.2, v/v) containing HDEHDTP 0.04 M

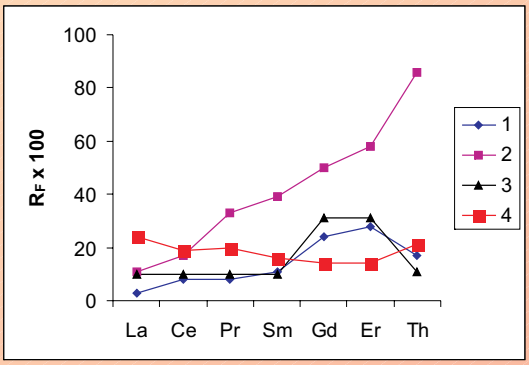

Figure 4. The retention factors of metal ions for various stationary phases
Stationary phase: 1. silica gel; 2. silica gel impregnated with NH_4NO_3 2.5 M;
3. silica gel zirconium(IV) silicate mixture; 4 silica gel titanium(IV) silicate mixture.

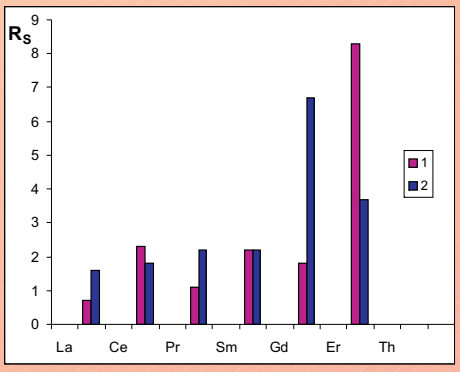

Figure 5. Resolution of Th(IV) and Ln(III) separation on silica gel impregnated with 2.5 M NH_4NO_3
1. Simple elution; 2. Double elution.

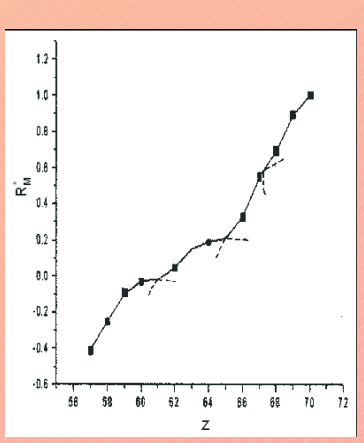

Figure 6. Dependence of factor with Z of studied lanthanides. Stationary phase: Silica gel impregnated with 2.5 M NH_4NO_3

CONCLUSIONS

- Using the mixture DMF - MEK - *o,m,p*-xylene (HDEHDTP) as mobile phase:
  - the separation of Sm(III) - Gd(III) and Gd(III) - Er(III) was obtained on silica gel.
  - the best separation of Ln(III) each from other and Ln(III) - Th(IV) was obtained with HDEHDTP 0.04 M.
  - a low tendency of Ln(III) separation was observed using silica gel - zirconium(IV) silicate mixture or silica gel - titanium(IV) silicate mixture as stationary phase.
- The tendency of Ln(III) separation was observed by the simple elution with MEK - THF (6.8 + 3.2, v/v) containing HDEHDTP 0.04 M, on silica gel impregnated with NH_4NO_3 2.5 M. An improving of the resolution was obtained by double elution. Thus, the following ten lanthanides: La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Yb(III) were separated from each other.

References

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Acknowledgment

This work was supported by the Romanian Ministry of Education and Research under the research programs, CEEX project nr. 2995 / 11.10.2005 and GRANT CNCSIS 18/170/2006