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# Investigation of adducts of lanthanide and uranium $\beta$ -diketonates with organophosphorus Lewis bases by supercritical fluid chromatography

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## Abstract

Formation of adducts of lanthanide (Ln) and uranium  $\beta$ -diketonates with neutral donors such as tributyl phosphate, tributyl phosphine oxide or trioctyl phosphine oxide, can greatly improve their SFC behavior. The adduct formation approach leads to the successful separation of lanthanide complexes of the same  $\beta$ -diketone ligand by SFC using neat CO<sub>2</sub> as the mobile phase. Solvation behavior, stability, and stoichiometry of the adducts of lanthanide and uranium  $\beta$ -diketonates in supercritical fluid were studied by SFC. The molar ratios of the lanthanide-FOD and uranyl-HFA with an organophosphorus reagent are 1:2 and 1:1, respectively. The stability sequence of lanthanide-FOD organophosphorus adducts follows the order Ln(FOD)<sub>3</sub>·2TOPO > Ln(FOD)<sub>3</sub>·2TBPO > Ln(FOD)<sub>3</sub>·2TBP. For the Ln-FOD-TBPO system, the relative stability of the adducts increases with the atomic number of lanthanide. © 1998 Elsevier Science B.V.

**Keywords:**  $\beta$ -Diketonates; Lanthanide; Uranium; Organophosphorus compounds

## 1. Introduction

The use of supercritical fluids (SF) as mobile phases in chromatography was first reported by Klesper et al. [1]. Since that time a considerable number of publications have demonstrated the usefulness of supercritical fluid chromatography (SFC) for analytical applications [2,3]. The desirable physical properties of SF as a mobile phase, including viscosity, solute diffusivity and solubility, were discussed by Lauer et al. [4]. The majority of previous studies have concentrated on the use of SFC for the separation and analysis of semivolatiles or-

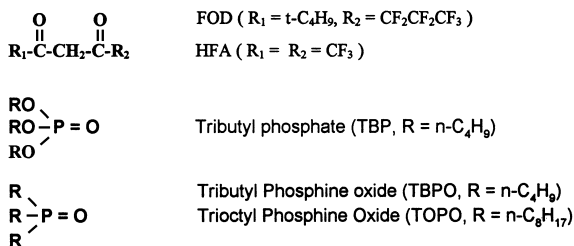
ganic compounds [2,3]. In particular, SFC is suitable for the analysis of compounds showing low thermal stability, which might decompose at temperatures required for gas chromatography (GC) and for those that cannot be separated by high-performance liquid chromatography (HPLC) due to lack of resolution from interfering compounds.

Although the majority of previous studies have been directed at organic compounds, the properties of SFC seem suitable for the analysis of organometallic compounds and metal chelates [5]. Laintz et al. demonstrated that SFC could be utilized to determine heavy metals extracted with dithiocarbamate ligands from environmental samples and in some cases for metal speciation studies [6,7]. One

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major problem in the SFC analysis of metal chelates is their instability when in contact with the separation columns [8]. This may be overcome, in some instances, by using methanol as a mobile phase modifier, which results in column deactivation [9,10]. The use of methanol as a mobile phase modifier, however, limits the choice of detection system and in particular precludes the use of the flame ionization detector (FID).

Developing clean techniques for the separation and analysis of lanthanides and actinides are of great interest to analytical chemists. Supercritical fluid extraction (SFE) and SFC techniques have been utilized previously for separation and analysis of lanthanides and actinides [11–14]. Our particular interest in the present work is the study of lanthanide (Ln) and uranium  $\beta$ -diketone complexes containing organophosphorus adducts, which have been reported to show enhanced stability in SF CO<sub>2</sub> relative to the complexes containing only the  $\beta$ -diketone ligands. The enhanced stability enables the use of SFC for the separation of the lanthanide complexes in the absence of any modifiers to the CO<sub>2</sub> mobile phase [14]. The  $\beta$ -diketone complexes chosen in this study are the lanthanide and uranium complexes with a highly fluorinated ligand, 2,2,-dimethyl-6,6,7,7,8,8,8,-heptafluoro-3,5,-octanedione (FOD) or 1,1,1,6,6,6,-hexafluoropentane-2,4,-dione (HFA). The choice of the fluorinated ligands was based on the fact that the solubilities of the fluorinated metal complexes in supercritical CO<sub>2</sub> are significantly higher than the non-fluorinated analogues [5,11–13]. The structures of FOD, HFA and the organophosphorus reagents used in this study are given as follows:



The formation of adduct complexes has been investigated in solvent extraction of metals, where a mixture of an acidic ligand such as a  $\beta$ -diketone and a coordinating ligand such as an organophosphorus

reagent, often results in enhanced extractions [15]. This is attributed to the ability of these ligands in combination to satisfy both the valency and coordination requirements of the central metal ions. Synergistic extraction is particularly important for the lanthanides and actinides where high coordination numbers are encountered.

## 2. Experimental section

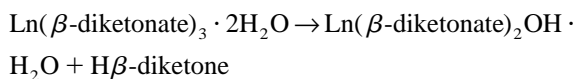
Chromatographic separations were performed using a Lee Scientific Series 600 SFC/GC (Dionex, Sunnyvale, CA, USA) coupled with a FID detector and the AI-450 Chromatography Work Station controlled by an IBM486 computer. An open tubular capillary column (100  $\mu$ m I.D., 200  $\mu$ m O.D., and 5 m in length) coated with a 0.25  $\mu$ m film of methyl silicone (Dionex) was employed for metal complex separation in this work. Methyl silicone, which has good chemical and thermal stability and offers high solute diffusivity, is a widely used stationary phase for capillary-column GC and SFC [4,14]. The flow was controlled by an 100  $\mu$ m frit restrictor trimmed to give a solvent peak of approximately 5 min at 100°C and 100 atm. All separations were performed at a constant oven temperature of 80°C, FID temperature 390°C and pressure gradients at various ramp rates as indicated. The injection time was 0.025 s time-splitting on a 200 nl loop. Lanthanide-FOD complexes and organophosphorus reagents, tributyl phosphate (TBP), tributyl phosphine oxide (TBPO) and trioctyl phosphine oxide (TOPO) were obtained from Aldrich (Milwaukee, WI, USA). UO<sub>2</sub>(HFA)<sub>2</sub> was synthesized and purified in our laboratory by dissolving UO<sub>3</sub> in a chloroform solution containing 0.2 M HFA followed by recrystallization of the product in chloroform. Solutions of lanthanide and uranyl  $\beta$ -diketonates were prepared with HPLC-grade chloroform in concentrations of 2–10 mg/ml of the specific metal chelates. The adducts of lanthanide-FOD and UO<sub>2</sub>(HFA)<sub>2</sub> complexes with TBP, TBPO, or TOPO were prepared by the addition of an excess amount of the organophosphorus reagent to the chloroform solution containing lanthanide FOD or UO<sub>2</sub>(HFA)<sub>2</sub>. The carbon dioxide used (Air Products, Allentown, PA, USA) was SFC/SFE grade. Hydrogen, air, nitrogen for FID were all obtained

from Liquid Carbonic (Chicago, IL, USA) with 99.99% purity.

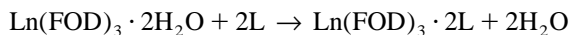
### 3. Results and discussion

#### 3.1. SFC of lanthanide and uranium $\beta$ -diketone adducts with TOPO and TBPO

When lanthanide chelates of FOD were injected into the SFC system, no peak was observed under various SFC conditions. This observation suggests that lanthanide chelates of FOD may decompose and probably are irreversibly adsorbed inside the SFC column. One possible cause of this behavior could be due to the hydration of lanthanide metal chelates or incomplete shielding of center metal ion by ligands. Thermal decomposition of the hydrated  $\beta$ -diketone lanthanide complexes was reported to proceed by the following reaction [16]:



According to this mechanism, the metal chelate may lose a ligand and become attached to the matrix of the column during SFC. When an organophosphorus ligand such as TOPO or TBPO is added to a lanthanide  $\beta$ -diketone solution, adduct formation takes place with the neutral organophosphorus ligand replacing the water molecules coordinated with the metal according to the following equation:



where L is an organophosphorus ligand [5,17–19]. The resulting adduct complex should be better shielded and free of water coordination. Consequently, it may reduce its intermolecular interactions and become thermally stable in SFC. Thus, adduct formation may provide a method of stabilizing lanthanides  $\beta$ -diketonates, making them more soluble in SF CO<sub>2</sub> and separable in SFC.

Fig. 1A and Fig. 1B show the SFC separation of La, Pr, Eu, and Er-FOD organophosphorus adducts with TBPO at 80°C with different initial pressure and pressure ramp. The retention times of the adduct complexes decrease with decreasing radius of the lanthanide ions indicating that the solubility of the

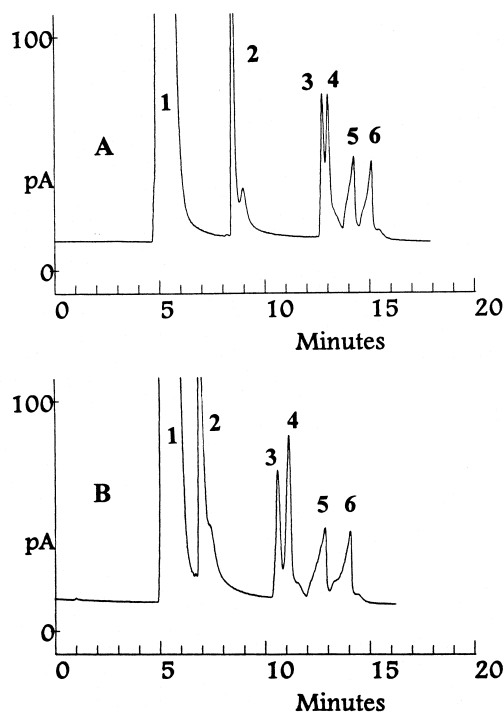


Fig. 1. SFC chromatograms of lanthanide-FOD adducts with TBPO. Conditions: pressure, (A) initial 80 atm; 5 atm/min increase; (B) initial 100 atm; 3 atm/min increase; oven temperature, 80°C; FID, 390°C; samples: chloroform solution containing 5 mg/ml each of Ln(FOD)<sub>3</sub> and excess amount of TBPO. Peaks: (1) chloroform, (2) TBPO, (3) Er(FOD)<sub>3</sub>·2TBPO, (4) Eu(FOD)<sub>3</sub>·2TBPO, (5) Pr(FOD)<sub>3</sub>·2TBPO, (6) La(FOD)<sub>3</sub>·2TBPO.

lanthanide adduct complexes should increase from La to Lu. The enhanced solubility of the heavier lanthanides correlates with the SFE data, where the heavier lanthanides are extracted with higher efficiencies indicating their higher affinities in SF CO<sub>2</sub> [5,11]. This general trend can be attributed to a combination of steric and electronic effects imposed by the lanthanide contraction. With decreasing ionic radius of the Ln<sup>3+</sup> series, the size of the complex decreases and the shielding of the lanthanide ion improves. In addition, the increase in ionic potential of the lanthanide ion probably lowers the polarizability of the  $\beta$ -diketonate ring, reducing their capacity for intermolecular interaction. The overall effect is an increasing volatility and solubility as the atomic number of the lanthanide ion increases.

A satisfactory SFE separation of the Ln-FOD-TBPO adduct complexes can not be achieved under

constant pressure according to our experiments. Therefore, programmed pressures with different pressure ramps and different initial pressures were utilized for the separation of the adduct complexes. Pressure has a significant effect on SFC separation of Ln-FOD-TBPO. When the pressure ramp is lower than 3 atm/min with a initial pressure of 100 atm, the baseline separation of Er(FOD)<sub>3</sub>·2TBPO and Eu(FOD)<sub>3</sub>·2TBPO (peak 3 and 4 in Fig. 1A) can be achieved, but the peak shapes of Pr(FOD)<sub>3</sub>·2TBPO and La(FOD)<sub>3</sub>·2TBPO (peaks 5 and 6 in Fig. 1A) are poor. When pressure ramp increases to higher than 5 atm/min, the peak shapes of Pr(FOD)<sub>3</sub>·2TBPO and La(FOD)<sub>3</sub>·2TBPO become sharper, but the separation of Er(FOD)<sub>3</sub>·2TBPO and Eu(FOD)<sub>3</sub>·2TBPO is worse. To compromise the separation and peak shape of these lanthanide adduct complexes, a pressure ramp of 3 atm/min with a initial pressure of 100 atm was chosen to obtain the chromatogram shown in Fig. 1B. For the separation of Ln-FOD-TOPO adduct complexes, a similar pressures effect was observed.

The effect of temperature on SFC separation of Ln-FOD-TBPO adducts was also investigated and the capacity factor calculated. The changes in rela-

tive capacity factor for Er, Eu, Pr, and La FOD-TBPO adducts as a function of temperature in the range 60–120°C are shown in Fig. 2. The capacity factor is a function of a compound's solubility in the mobile phase and in the stationary phase. The solubility of a solute in supercritical CO<sub>2</sub> is a function of two competing factors, solvation and volatility [20]. The capacity factors of TBPO and the Ln-FOD-TBPO adducts increase with temperature in the range 60–120°C, as shown in Fig. 2. In this temperature range, the solvating power of the supercritical CO<sub>2</sub> should dominate the solubility of TBPO and the lanthanide adducts in supercritical CO<sub>2</sub>, and the SFC behavior of these compounds is LC-like. At 60°C, the capacity factors of the four lanthanides adducts are almost the same; therefore, separation of these adducts would be difficult at this temperature. According to Fig. 2, the best temperature for separating the Ln-FOD adducts is around 80°C, which was used to obtain the chromatograms shown in Fig. 1. SFC separation of the Ln-FOD-TBPO adduct complexes can be tuned by adjusting pressure and column temperature. This is unique for SFC, since temperature and pressure are instrumental rather than

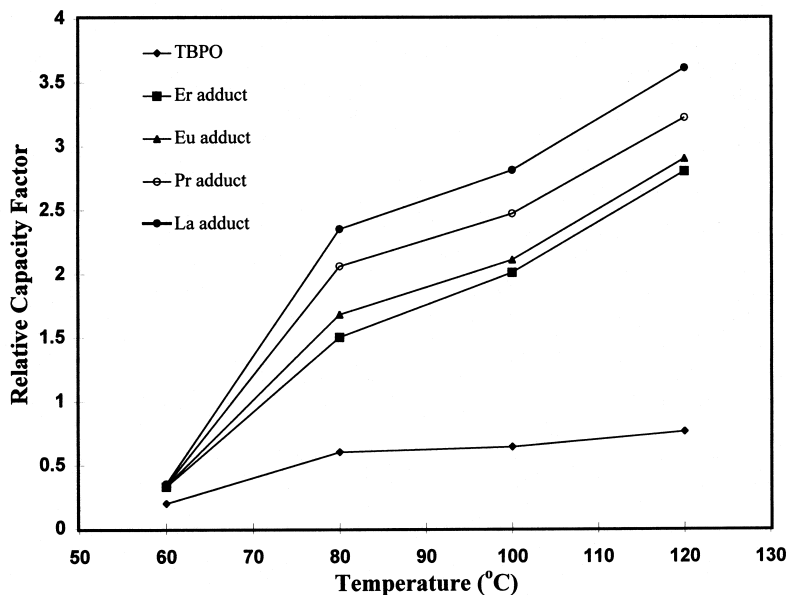


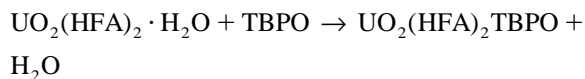
Fig. 2. Effect of temperature on relative capacity factors of TBPO, Er(FOD)<sub>3</sub>·2TBPO, Eu(FOD)<sub>3</sub>·2TBPO, Pr(FOD)<sub>3</sub>·2TBPO and La(FOD)<sub>3</sub>·2TBPO. SFC conditions are the same as in Fig. 1B.

chemical parameters. Thus, SFC separation can be optimized without chemically changing the mobile phase as in the case of LC.

The SFC behavior of  $\text{UO}_2(\text{HFA})_2$  is similar to that of lanthanide  $\beta$ -diketonates. When a chloroform solution containing  $1.0 \times 10^{-2} \text{ M}$   $\text{UO}_2(\text{HFA})_2$  was injected into the SFC system, no  $\text{UO}_2(\text{HFA})_2$  peak was observed. However, when an excess amount of TBPO was added to the solution, a well-defined peak of U-HFA-TBPO adduct was observed as shown in Fig. 3.

The number of L coordinated with the trivalent lanthanide ion in the  $\beta$ -diketonate adduct complex was evaluated by SFC analysis of chloroform solutions containing various molar ratios of L and a Ln  $\beta$ -diketonate,  $\text{Eu}(\text{FOD})_3$ . When a small amount of  $\text{Eu}(\text{FOD})_3$  was added to an excess amount of TOPO in a chloroform solution, the SFC chromatogram showed that the peak height of TOPO decreased and the adduct peak appeared. When the molar ratio of  $\text{Eu}(\text{FOD})_3$ : TOPO equaled 1:2, the TOPO peak disappeared, indicating that TOPO was completely incorporated into the adduct. The results obtained from other lanthanide-FOD adducts with TBPO or TOPO all indicate that the number of TOPO or

TBPO contained in each adduct is 2. Using a similar procedure, we found that the ratio of  $\text{UO}_2(\text{HFA})_2$ : TBPO is 1:1. Therefore the adduct formation reaction for the uranyl  $\beta$ -diketonate can be represented by:



Adduct formation was also observed in solvent extraction [21] and supercritical fluid extraction [5,13] of uranyl ion with a mixed ligand consisting of a  $\beta$ -diketone and an organophosphorus reagent. The crystal structure of uranyl  $\beta$ -diketonate adducts was reported in the literature [22]. The coordination number of uranyl ion is 9 of which four are coordinated with oxygen, four with  $\beta$ -diketone and one with organophosphorus reagent, in agreement with our SFC observation.

The decomposition of metal  $\beta$ -diketonates in SFC system was reported by Jinno et al. [8,23]. According to their study, many metal  $\beta$ -diketonates are unstable in SFC if neat  $\text{CO}_2$  is used as the mobile phase. However, if methanol and a  $\beta$ -diketone ligand are premixed with supercritical  $\text{CO}_2$  and used as the mobile phase, the stability of the metal  $\beta$ -diketonates in SFC can be improved. Methanol and the ligand in the SF phase can cause high background for both FID and UV-Vis detectors and hence a more selective detector, ICP-AES, was used by Jinno et al. ICP-AES is an expensive and complex detector which is not often available in many laboratories. The adduct formation method can greatly improve the stability of metal  $\beta$ -diketonates without addition of methanol and ligand in supercritical  $\text{CO}_2$  and consequently, FID, a commonly used and sensitive detector, can be utilized for SFC of lanthanide and uranium  $\beta$ -diketonates.

### 3.2. Relative stability of lanthanide-FOD adducts

The relative stability of different lanthanide- $\beta$ -diketonate adduct complexes can be evaluated by SFC. Fig. 4A shows a chromatogram of three organophosphorus reagents, TBP, TBPO and TOPO. The retention time of these organophosphorus reagents is inversely correlated to their solubility in SF  $\text{CO}_2$ , which follows the order  $\text{TBP} > \text{TBPO} > \text{TOPO}$

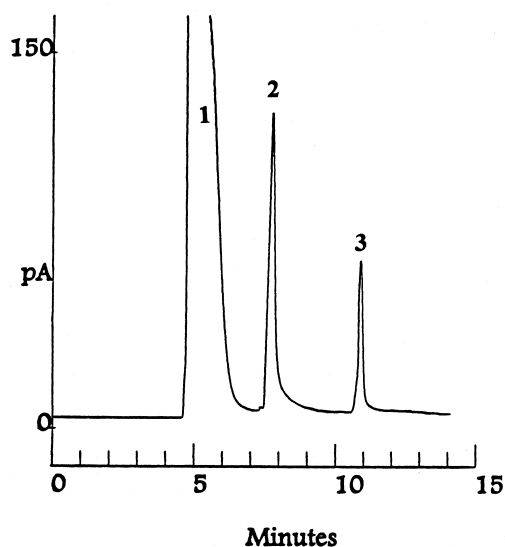


Fig. 3. SFC chromatogram of uranium-HFA-TBPO adduct. Peaks: (1) chloroform, (2) TBPO, (3)  $\text{UO}_2(\text{HFA})_2\text{TBPO}$ . SFC conditions are the same as shown in Fig. 1A.

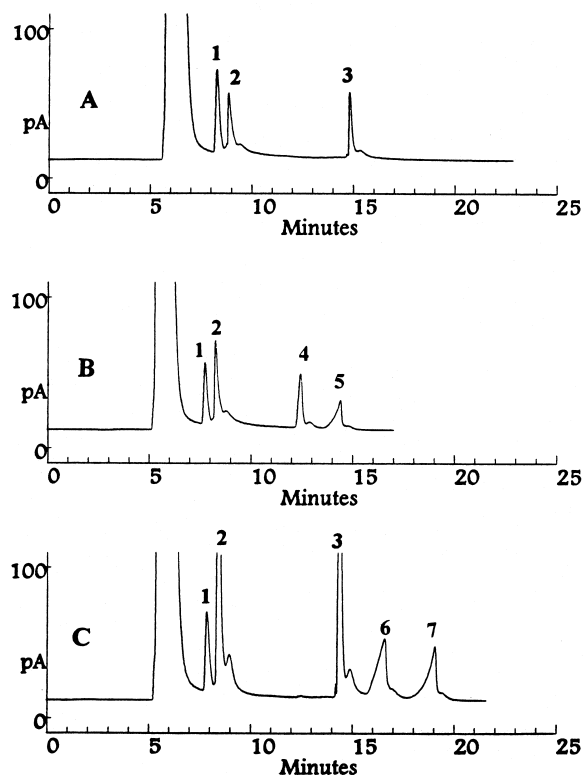


Fig. 4. SFC separation of organophosphorus reagents and their lanthanide-FOD adducts. (A) SF chromatogram of a mixture of TBP, TBPO and TOPO, (B) SF chromatogram of a mixture of  $\text{La}(\text{FOD})_3$ ,  $\text{Eu}(\text{FOD})_3$ , TBP, and TBPO, (C) SF chromatogram of a mixture of  $\text{La}(\text{FOD})_3$ ,  $\text{Eu}(\text{FOD})_3$ , TBP, TBPO, and TOPO. Peaks: (1) TBP, (2) TBPO, (3) TOPO, (4)  $\text{Eu}(\text{FOD})_3 \cdot 2\text{TBPO}$ , (5)  $\text{La}(\text{FOD})_3 \cdot 2\text{TBPO}$ , (6)  $\text{Eu}(\text{FOD})_3 \cdot 2\text{TOPO}$ , (7)  $\text{La}(\text{FOD})_3 \cdot 2\text{TOPO}$ . SFC conditions are the same as indicated in Fig. 1B.

[14]. When 0.02 M TBP and 0.04 M TBPO were simultaneously added to a chloroform solution containing  $5 \times 10^{-3}$  M each of  $\text{La}(\text{FOD})_3$  and  $\text{Eu}(\text{FOD})_3$ , only  $\text{La}(\text{FOD})_3 \cdot 2\text{TBPO}$  and  $\text{Eu}(\text{FOD})_3 \cdot 2\text{TBPO}$  peaks (Fig. 4B, peaks 4 and 5) were observed in SFC. No TBP adduct complexes was detected in the SFC chromatogram indicating that the TBPO adducts are more stable than the TBP adducts. When another ligand TOPO (0.04 M) was added to the mixed solution, the  $\text{La}(\text{FOD})_3 \cdot 2\text{TBPO}$  and  $\text{Eu}(\text{FOD})_3 \cdot 2\text{TBPO}$  peaks disappeared and the height of the TBPO peak increased (Fig. 4C, peak 2). In the same chromatogram, the peaks of  $\text{La}(\text{FOD})_3 \cdot 2\text{TOPO}$  and  $\text{Eu}(\text{FOD})_3 \cdot 2\text{TOPO}$  appeared (Fig. 4C, peaks 6 and 7). These results indicate that

the stability sequence of lanthanide-FOD organophosphorus adducts should follow the order:  $\text{Ln}(\text{FOD})_3 \cdot 2\text{TOPO} > \text{Ln}(\text{FOD})_3 \cdot 2\text{TBPO} > \text{Ln}(\text{FOD})_3 \cdot 2\text{TBP}$ .

Competition experiments involving TBPO and two lanthanide  $\beta$ -diketonates were also performed to investigate the relative stability of the adduct complexes. When  $1.0 \times 10^{-2}$  M of TBPO was added to the chloroform solution containing  $5 \times 10^{-3}$  M each of  $\text{Er}(\text{FOD})_3$  and  $\text{Pr}(\text{FOD})_3$ , followed by injection of the solution into the column, only  $\text{Er}(\text{FOD})_3 \cdot 2\text{TBPO}$  peak was observed in SFC. No  $\text{Pr}(\text{FOD})_3 \cdot 2\text{TBPO}$  or TBPO peak was detected in the SFC chromatogram (Fig. 5A). When the concentration of TBPO was increased to  $3.0 \times 10^{-2}$  M, the peaks of TBPO,  $\text{Er}(\text{FOD})_3 \cdot 2\text{TBPO}$  and  $\text{Pr}(\text{FOD})_3 \cdot 2\text{TBPO}$  appeared on the chromatogram (Fig. 5B). These results indicate that the adduct stability of  $\text{Er}(\text{FOD})_3 \cdot 2\text{TBPO}$  is higher than that of  $\text{Pr}(\text{FOD})_3 \cdot 2\text{TBPO}$ . Based on the results obtained from the competition experiments with Er, Eu, Pr, and La, we conclude that the

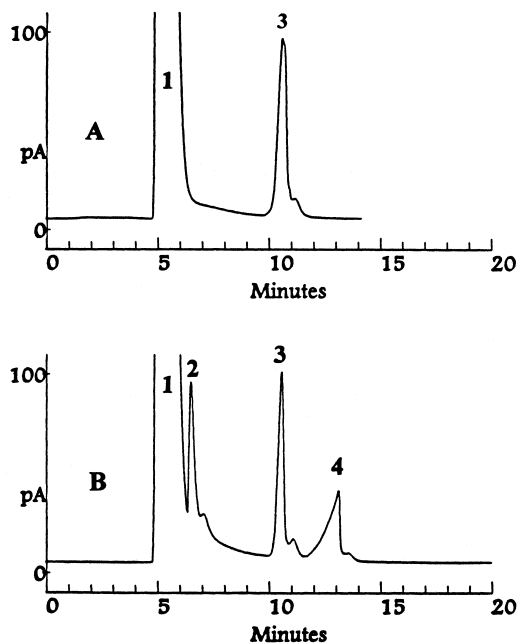


Fig. 5. SFC chromatograms of a mixture of  $5 \times 10^{-3}$  M  $\text{Er}(\text{FOD})_3$ ,  $5 \times 10^{-3}$  M  $\text{Pr}(\text{FOD})_3$ , and 0.01 M TBPO in chloroform (A) and a mixture of  $5 \times 10^{-3}$  M  $\text{Er}(\text{FOD})_3$ ,  $5 \times 10^{-3}$  M  $\text{Pr}(\text{FOD})_3$ , and 0.03 M TBPO in chloroform (B). Peaks: (1) chloroform, (2) TBPO, (3)  $\text{Er}(\text{FOD})_3 \cdot 2\text{TBPO}$ , (4)  $\text{Pr}(\text{FOD})_3 \cdot 2\text{TBPO}$ . SFC conditions are the same as indicated in Fig. 1B.

stability sequence should be in the order  $\text{Er}(\text{FOD})_3\text{2TBPO} > \text{Eu}(\text{FOD})_3\text{2TBPO} > \text{Pr}(\text{FOD})_3\text{2TBPO} > \text{La}(\text{FOD})_3\text{2TBPO}$ . For the Ln-FOD-TBPO system, it appears that the relative stability of the adducts increases with atomic number of lanthanide. The results obtained from this work may have applications for lanthanide separation and purification. By choosing a proper organophosphorus Lewis base, synergistic extraction with a  $\beta$ -diketone and the organophosphorus reagent may greatly improve the separation efficiency of the heavy lanthanides over the light ones in supercritical fluid extraction using a substoichiometric method.

#### 4. Conclusions

Hydrated complexes usually exhibit strong intermolecular interaction or decomposition in SFC. Formation of adducts of the lanthanide and uranium  $\beta$ -diketonates with a neutral organophosphorus donor, which is capable of substituting for  $\text{H}_2\text{O}$  coordinated with the metal, can greatly improve their SFC behavior. This adduct formation method leads to the first successful separation of lanthanide complexes of the same ligand using SFC. Adduct formation/SFE is known to be successful for the extraction of lanthanides and actinides from different matrices [5,11–13]. A hyphenated technique of on-line adduct formation/SFE/SFC may provide a useful separation method for analysis of lanthanides and actinides. SFC can also be used to study the solvation behavior, stability, and stoichiometry of the metal  $\beta$ -diketone adduct complexes in supercritical fluid. Our results show that the molar ratios of the lanthanide-FOD and the uranyl-HFA chelates with an organophosphorus reagent are 1:2 and 1:1, respectively. The stability sequence of lanthanide-FOD organophosphorus adducts follow the order  $\text{Ln}(\text{FOD})_3\text{2TOPO} > \text{Ln}(\text{FOD})_3\text{2TBPO} > \text{Ln}(\text{FOD})_3\text{2TBP}$ . Our results also show that for the Ln-FOD-TBPO system, the relative stability of adduct increases with atomic number of lanthanides.

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