

Supercritical Fluid Extraction of Lanthanides and Actinides from Solid Materials with a Fluorinated β -Diketone

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INTRODUCTION

Supercritical fluid extraction (SFE) offers several advantages over conventional solvent extraction, including the minimization of organic liquid waste generation and exposure of personnel to organic vapors.¹ The high diffusivity, low viscosity, and temperature-pressure dependence of solvent strength are some attractive properties which make supercritical fluids excellent candidates for extraction and recovery of organic compounds from solid materials.² Carbon dioxide is a solvent of choice in SFE because of its moderate critical constants, inertness, and availability in purified form. However, direct extraction of metal ions by supercritical CO₂ is highly inefficient because of the charge neutralization requirement and the weak solute-solvent interactions. One suggested approach of extracting metal ions by supercritical CO₂ is to convert the charged species into metal chelates using a chelating agent in the fluid phase.³ Recently, Wai and co-workers have demonstrated that copper ions (Cu²⁺) in liquid and in solid materials can be extracted by supercritical carbon dioxide containing a fluorinated chelating agent, lithium bis-(trifluoroethyl)dithiocarbamate (LiFDDC).⁴ The choice of the fluorinated ligand was based on the fact that the solubilities of metal-FDDC complexes are significantly higher (2-3 orders of magnitude) than the nonfluorinated analogues.⁵ This in situ chelation-SFE technique may have a wide range of applications, including the preconcentration of trace metals for analytical purposes and the treatment of metal-contaminated waste materials. SFE of lanthanides and actinides are particularly interesting because of its potential applications to nuclear waste analysis and management. The success of this in situ chelation-SFE approach for metal extraction depends largely on the effectiveness of the ligand. A suitable chelating agent should have a reasonable solubility in the supercritical fluid and form stable and extractable chelates with the metal ions of interest. LiFDDC is not an effective ligand for complexation with the f-block elements.⁶ This paper describes a method of extracting lanthanide and uranyl ions from a solid material by supercritical CO₂ containing a fluorinated β -diketone, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (FOD). Potential applications of this SFE method for separating the f-block elements from environmental samples are discussed.

EXPERIMENTAL SECTION

The fluorinated β -diketone FOD was purchased from the Aldrich Chemical Co. and used without further purification. LiFDDC was synthesized in our laboratory according to a

procedure outlined in the literature.⁷ Solutions of La³⁺, Eu³⁺, and Lu³⁺ were prepared from their nitrates, also obtained from Aldrich. Uranyl [(UO₂)²⁺] solutions were prepared from the acetate salt obtained from Baker. Lanthanum and europium FOD complexes were obtained from MTM Research Chemicals (Windham, NH). All other chemicals used were analytical reagent grade. Filter papers used as the sample matrix were obtained from Whatman Ltd. (Maidstone, England). Samples were prepared by spiking 10 μ g each of a mixture of La³⁺, Eu³⁺, and Lu³⁺ solution or 10 μ g of a uranyl acetate solution on prewashed filter papers (Whatman No. 42, 0.5 cm \times 2 cm in size, washed with Ultrex HNO₃ and rinsed with deionized water). The spiked filter papers were allowed to air dry at a room temperature of 23 $^{\circ}$ C.

All experiments were performed with a laboratory-built SFE apparatus. SFC-grade CO₂ or CO₂ with 5 mol % methanol modifier (Scott Specialty Gases, Plumsteadville, PA) was delivered to the SFE system using a Haskel pump (Haskel Inc., Burbank, CA). The system pressure was monitored to ± 5 psi using a Setra system (Acton, MA) pressure transducer. The extractor consisted of an inlet valve (Supelco, Bellefonte, PA) and an outlet valve connected to a commercial extraction cell (Dionex, Sunnyvale, CA) having a volume of 3.5 mL. The extraction cell was placed in an oven with temperature controlled to ± 0.1 $^{\circ}$ C by an Omega (Stamford, CT) CN9000A temperature controller. A fused-silica tubing (Dionex, 50- μ m i.d. and 20 cm in length) was used as the pressure restrictor for the exit gas. The SFE system allows static and dynamic extraction steps to be carried out by closing and opening of the inlet and outlet valves.

A glass tube (0.5-cm i.d. and 3 cm in length) was plugged at one end with a piece of glass wool, previously cleaned with Ultrex nitric acid. To the open end of the glass tube was inserted a spiked filter sample. About 20 μ L (80 μ mol) of FOD was introduced to the sample, and the open end was plugged with a piece of clean glass wool. The sample tube was placed immediately into the extraction cell and installed in the SFE oven. The temperature of the oven was set at 60 $^{\circ}$ C, and the cell was pressurized to 150 atm. The chelation and the extraction processes were allowed to occur under a static SFE condition for 10 min. After that, the exit valve was opened and the sample was extracted and flushed under dynamic condition for 10 min. When the dynamic extraction step was completed, the sample was removed from the SFE system and the filter paper was analyzed by a nondestructive neutron activation analysis (NAA). A standard filter paper containing the same amount of the lanthanide or uranyl ions was irradiated and counted with the sample under identical conditions. The extraction efficiencies were calculated based on the amount of the lanthanide or uranium found in the filter paper before and after the extraction. The extracted lanthanide complexes were also collected in a glass vial containing 5 mL of chloroform. The lanthanides trapped in the chloroform solution were determined by back-extraction with 50% HNO₃ followed by NAA of the acid solution.

The solubilities of La(FOD)₃ and Eu(FOD)₃ in supercritical CO₂ were determined by placing a weighed amount of the lanthanide complex in a glass tube with both ends plugged with glass wool. The sample tube was placed in an extractor of known volume and then installed in the extraction oven. The sample was heated at 60 $^{\circ}$ C and 150 atm for 30 min. After this static heating, the fluid phase was vented into the collection vial containing 5 mL of chloroform and the sample tube was removed from the extraction cell. The empty cell without the sample tube was reinstalled into the oven and the system was flushed

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Table I. Percent Extraction of La³⁺, Eu³⁺, and Lu³⁺ from a Cellulose-Based Filter Paper with Supercritical CO₂ Containing FOD at 60 °C and 150 atm

fluid phase	matrix condition	ligand amt (FOD μ mol)	extraction (%)		
			La ³⁺	Eu ³⁺	Lu ³⁺
(a) Spiked with 10 μ g Each of the Lanthanides at pH 6.5					
CO ₂	dry or wet	0	<1	<1	<1
CO ₂	dry	80	5 \pm 1	10 \pm 2	12 \pm 1
CO ₂	wet ^b	80	11 \pm 1	14 \pm 1	18 \pm 2
CO ₂	wet ^c	80	10 \pm 1	13 \pm 1	19 \pm 1
CO ₂ + MeOH ^a	dry	80	69 \pm 2	76 \pm 2	79 \pm 2
CO ₂ + MeOH ^a	wet ^c	80	91 \pm 2	96 \pm 2	99 \pm 1
CO ₂ + MeOH ^a	wet ^c	8	54 \pm 3	79 \pm 2	90 \pm 2
(b) Spiked with 10 μ g Each of the Lanthanides at pH 1.0					
CO ₂ + MeOH ^a	wet ^c	80	21 \pm 1		82 \pm 2

^a 5 mol % methanol in CO₂. ^b Right after spiking. ^c Dry sample; 10 μ L of water added prior to extraction.

with CO₂ again for 20 min. The lanthanide complex in the second flushing was also collected. The total amount of the lanthanide collected in the chloroform solution was back-extracted with 2 mL of 50% Ultrax HNO₃. Aliquots of 0.5 mL of the acid solution were sealed in polyethylene vials for NAA. The solubility was calculated from the amount of lanthanide dissolved in the fluid phase divided by the volume of the extraction cell. The sample tube was also weighed again after the extraction to measure the decrease in sample weight.

All samples and standards were irradiated for 1 h in a 1-MW Trigar nuclear reactor at a steady flux of 6×10^{12} n cm⁻² s⁻¹. After irradiation, the samples were cooled for 24 h before counting. Each sample was counted for 100 s in a large-volume Ortec Ge(Li) detector with a resolution (fwhm) of ~ 2.3 keV at the 1332-keV ⁶⁰Co peak. The following radioisotopes and their characteristic γ energies were used for the identification and quantification of the lanthanides: ¹⁴⁰La (40.2 h, 328, 487, 815, 1596 keV), ¹⁵²Eu (9.3 h, 121, 344, 841 keV), and ¹⁷⁷Lu (6.7 d, 208 keV). Uranium was determined by the 228-keV γ energies emitted during the decay of its daughter ²³⁰Np (2.36 d). The detailed procedures of NAA are described elsewhere.⁸

RESULTS AND DISCUSSION

The solubilities of La(FOD)₃ and Eu(FOD)₃ complexes in pure CO₂ were determined by the procedures described in the Experimental Section to be $(5.5 \pm 0.2) \times 10^{-2}$ and $(7.9 \pm 0.2) \times 10^{-2}$ M, respectively, at 60 °C and 150 atm. These values are considered high compared with the reported solubilities of other metal chelates in supercritical CO₂. For example, the solubilities of several metal-FDDC complexes in supercritical CO₂ including those of Cu²⁺, Ni²⁺, Co²⁺, and Bi³⁺ are 1–2 orders of magnitude lower than the lanthanide-FOD values given above.⁵ It is known that FOD forms thermally stable complexes with trivalent lanthanides which are extractable by organic solvents.^{9,10} The FOD complexes are also the most volatile lanthanide β -diketone complexes known. These properties make FOD a good candidate for in situ chelation-SFE of lanthanides.

The results of extracting La³⁺, Eu³⁺, and Lu³⁺ from the cellulose-based filter paper by supercritical CO₂ under various conditions are given in Table I. Without the chelating agent, less than 1% of the spiked lanthanides could be extracted from the filter paper by supercritical CO₂ after 10 min of static extraction and 10 min of dynamic flushing at 60 °C and 150 atm. This would suggest that, within the experimental error, free trivalent lanthanide ions cannot be extracted by supercritical CO₂. In the presence of the fluorinated ligand

FOD, the spiked lanthanides became extractable by CO₂ but the extraction efficiencies were poor (5–12%) when the sample was dry. In our SFE experiments, the ligand was present in large excess relative to the lanthanides and the amounts of the lanthanide ions spiked in the filter paper ($\sim 5 \times 10^{-8}$ mol) were much lower than the solubility limits for the FOD complexes in CO₂. The low extraction efficiencies observed with the dry samples cannot be explained by the solubility of the lanthanide complexes in supercritical CO₂. Other factors, including the matrix interactions and the transport of the metal chelates from the solid matrix to the fluid phase, must also be important for the extraction of the lanthanide ions in this system. The extraction efficiencies for the lanthanides could be increased to 11–18% when the spiked filter papers were still wet before the extraction. The same results were observed when a small amount of water (10 μ L) was added to a dry sample prior to the extraction. Water molecules apparently can facilitate the extraction of lanthanides, probably by reducing the interactions between the solutes and the cellulose matrix and thereby enhancing the migration of the metal chelates from the matrix into the fluid phase. Water appears to function like a matrix modifier in this system.

The addition of methanol to CO₂ modifies the polarity of the fluid phase, which should generally result in an enhanced extraction of polar compounds in supercritical CO₂. The extraction efficiencies for La³⁺, Eu³⁺, and Lu³⁺ were significantly enhanced when 5% methanol was present in the fluid phase. The critical temperature and pressure of the methanol (5 mol %) modified CO₂ ($T_c = 41.8$ °C, $P_c = 73.6$ atm) are higher than the pure CO₂.¹¹ Our experimental temperature and pressure conditions for the SFE experiments were kept significantly higher than the T_c and P_c of the modified fluid phase to assure that the extraction occurred in the supercritical region. About 69%, 76%, and 79% of the spiked La³⁺, Eu³⁺, and Lu³⁺, respectively, were extracted from the dry filter paper by the methanol-modified CO₂ at 60 °C and 150 atm. When the paper was extracted wet with the addition of 10 μ L of water, the extraction efficiencies were found even higher, reaching 91 \pm 2%, 96 \pm 2%, and 99 \pm 1% for La³⁺, Eu³⁺, Lu³⁺, respectively. It is interesting to note that even though the solubility of lanthanide-FOD complexes in supercritical CO₂ is high, water and methanol are needed in order to extract the lanthanide complexes effectively from the filter paper. The trivalent lanthanide ions and their FOD complexes obviously interact strongly with the cellulose matrix. The Ln(FOD)₃ complexes are known to form adducts with water and other Lewis bases, a property which makes them useful as lanthanide shifting agents.¹⁰ Water molecules in the system probably compete with the active sites of the cellulose matrix to release the lanthanide-FOD complexes as water adducts. The enhanced polarity of the methanol-modified CO₂ probably can further enhance the removal of the Ln(FOD)₃-H₂O adducts from the matrix.

The in situ FOD chelation-SFE process shows a preference for the extraction of heavy lanthanides over the light ones. When the amount of the chelating agent in the system was reduced by a factor of 10 (from 80 to 8 μ mol), the extraction efficiencies for the lanthanides at 60 °C and 150 atm were lowered to 54 \pm 3%, 79 \pm 2%, and 90 \pm 2% for La³⁺, Eu³⁺, and Lu³⁺, respectively. Since the SFE experiments were performed with a mixture of equal amounts of La³⁺, Eu³⁺, and Lu³⁺, the system resembles competition experiments in conventional solvent extraction under substoichiometric conditions. The relative partition coefficients (the amount of lanthanide in the fluid phase over that in the solid phase) for La³⁺/Eu³⁺/Lu³⁺ in this competition experiment are roughly

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Table II. Extraction of Uranyl Ions from a Cellulose-Based Filter Paper by Supercritical CO₂ Containing FOD at 60 °C and 150 atm

fluid phase	matrix condition	ligand (μmol)	extraction (%)
(a) Spiked with 10 μg of Uranyl Acetate at pH 6.5			
CO ₂	wet	0	<1
CO ₂	dry	80	12 ± 1
CO ₂	wet	80	40 ± 1
CO ₂ + MeOH ^a	dry	80	95.2 ± 2.0
CO ₂ + MeOH ^a	wet	80	99.1 ± 1.0
(b) Spiked with 10 μg of Uranyl Acetate at pH 1.0			
CO ₂ + MeOH ^a	wet	80	99.2 ± 1.4

^a 5% methanol in CO₂.

in the order of 1:4:9. The observed selectivity of Lu³⁺ over La³⁺ may be useful for the selective separation of lanthanides by this SFE method.

The rate of extraction of lanthanides from the filter paper by methanol-modified supercritical CO₂ is fast. Steady-state concentrations of the lanthanide-FOD in the fluid phase were essentially reached after 5 min of static extraction and 5 min of flushing. To guarantee that saturation values were obtained in our SFE experiments, the samples were all extracted for 10 min followed by 10 min of dynamic flushing. Under these experimental conditions, quantitative recovery of the extracted lanthanides was observed. For example, in the case of methanol-modified CO₂ extraction of 10 μg each of the three lanthanides with 80 μmol of FOD listed in Table I, the amounts of La³⁺, Eu³⁺, and Lu³⁺ recovered from the chloroform trapping solution were 9.2 ± 0.2, 9.4 ± 0.2, and 9.8 ± 0.2 μg, respectively. These recoveries agree with the 91%, 96%, and 99% extraction of La³⁺, Eu³⁺, and Lu³⁺, respectively, found in the spiked filter paper.

The results for the extraction of uranyl ions from the cellulose-based filter papers are given in Table II. The experiments were conducted at 60 °C and 150 atm with 10 μg of uranium (from an uranyl acetate solution) spiked on Whatman No. 42 filter paper. The SFE behavior for uranyl ions is similar to those observed from the lanthanide experiments. Free uranyl ions cannot be extracted (<1%) by supercritical CO₂ even with 5% methanol in the fluid phase. With FOD (80 μmol) present in the fluid phase, ~12% of the uranyl ions can be extracted when the paper is dry and up to 40% of the uranyl ions can be extracted when the paper is wet by the addition of 10 μL of water. Using 5% methanol-modified CO₂, ~95% of the spiked uranyl ions can be extracted from the dry filter paper. If the paper is wet, quantitative removal of uranyl ions from the cellulose matrix can be achieved at 60 °C and 150 atm with 10 min of static extraction followed by 10 min of flushing. The rapid and efficient removal of uranyl ions by supercritical CO₂ using this in situ chelation technique with FOD as a ligand may have significant application for analysis and treatment of uranium-contaminated materials.

In solvent extraction, uranyl ions can only be extracted quantitatively by FOD into an organic solvent such as benzene

in a very narrow pH range approximately between 6 and 7. Below pH 3, uranyl ions cannot be extracted into benzene by FOD at all.¹² The uranyl ions in the SFE experiments described above were spiked to the filter paper using an acetate solution at pH 6.5. If the uranyl ions were introduced to the filter paper with a solution of pH 1, quantitative extraction of uranium was still observed in our SFE experiments (Table II). This pH range for SFE is very different from the pH range for solvent extraction of uranyl ions by FOD. The results imply that effective extraction of uranyl ions by the modified supercritical CO₂ can be extended to solutions with pH as low as 1. The much wider pH range for uranyl extraction by supercritical fluid is definitely an advantage of the SFE approach. Similar observations were made with the SFE experiments with the lanthanides. Solvent extraction experiments indicate that Lu³⁺ and Eu³⁺ cannot be extracted by FOD at pH less than 3 and 4, respectively.⁹ In SFE with FOD, the trivalent lanthanide ions can still be extracted from the filter paper spiked with lanthanide solutions at pH 1, although the efficiencies of extraction are lowered to 82% for Lu³⁺ and 21% for La³⁺ (Table I).

Two other types of ligands, LiFDDC and a fluorinated crown ether carboxylic acid, *sym*-difluorobenzo-16-crown-5-oxyacetic acid, were also tested for SFE of lanthanides and uranyl ions. The synthesis and the extraction characteristics of the fluorinated macrocycle for lanthanides and actinides have been reported recently.¹³ Crown ether carboxylic acids such as *sym*-dibenzo-16-crown-5-oxyacetic acid and its analogues are effective extractants for the trivalent lanthanide ions in solvent extraction.⁸ In our SFE experiments, insignificant extraction (<1%) of La³⁺ and Lu³⁺ from the wet filter papers was observed with 5% methanol-modified supercritical CO₂ containing a saturated amount of LiFDDC (~1 × 10⁻³ M) at 60 °C and 150 atm. Uranyl ions can be extracted by the modified CO₂ containing a saturated amount of LiFDDC (~5 × 10⁻⁴ M) in the presence of water with an efficiency of ~83%. In the case of the fluorinated crown ether carboxylic acid, only a small fraction (<7%) of the trivalent lanthanide and uranyl ions was extracted with 5% methanol-modified supercritical CO₂ containing a saturated amount of the ligand (~1 × 10⁻⁴ M) at 60 °C and 150 atm with water present in the matrix. Although the crown ether carboxylic acid is very effective for solvent extraction of the f-block elements, the nonvolatile complexes it forms with the lanthanides and actinides are unfavorable for SFE. The fluorinated β-diketone FOD, which forms volatile and thermally stable complexes with the f-block elements, appears to be a suitable ligand for SFE of the lanthanide and actinide ions from solid and liquid materials.

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