Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

STUDIES ON *IN-SITU* CHELATION/SUPERCRITICAL FLUID EXTRACTION OF LANTHANIDES AND ACTINIDES USING A RADIOTRACER TECHNIQUE

Yuehe Lin[a]; Hong Wu[a]; Neil G. Smart[b]; Chien M. Wai[c]
[a] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, U.S.A. [b] Research and Technology, Sellafield, Cumbria, UK [c] Department of Chemistry, University of Idaho, Moscow, Idaho, U.S.A.

To cite this Article Lin, Yuehe , Wu, Hong , Smart, Neil G. and Wai, Chien M.(2001) 'STUDIES ON *IN-SITU* CHELATION/SUPERCRITICAL FLUID EXTRACTION OF LANTHANIDES AND ACTINIDES USING A RADIOTRACER TECHNIQUE', Separation Science and Technology, 36: 5, 1149 — 1162

To link to this Article: DOI: 10.1081/SS-100103642

URL: http://dx.doi.org/10.1081/SS-100103642

SEPARATION SCIENCE AND TECHNOLOGY, 36(5&6), 1149–1162 (2001)

STUDIES ON *IN-SITU* CHELATION/SUPERCRITICAL FLUID EXTRACTION OF LANTHANIDES AND ACTINIDES USING A RADIOTRACER TECHNIQUE

Yuehe Lin[1,*], Hong Wu[1], Neil G. Smart[2], and Chien M. Wai[3]

[1] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, PO Box 999, MS: K8-93, Richland, Washington 99352, USA
[2] Research and Technology, BNFL, Sellafield, Cumbria, CA20 1PG, UK
[3] Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, USA

ABSTRACT

Radioisotope tracer techniques were used to study the process of *in-situ* chelation / supercritical fluid extraction (SFE) of La^{3+} and Lu^{3+} from a solid matrix using mixed ligand hexafluoroacetylacetone (HFA) and tributylphosphate (TBP) as chelating agents. A lab-built SFE extractor was used in this study and the extractor design was optimized based on the experimental results. Quantitative recovery of La and Lu was achieved when the extractor design was optimized. Extraction of uranium from real world samples was also investigated to demonstrate the feasibility of this chelation /

---

*Corresponding author. E-mail: yuehe.lin@pnl.gov

SFE technology for environmental remediation applications. A novel on-line back extraction technique for the recovery of metal ions and regeneration of ligands is also reported.

INTRODUCTION

Chelation combined with solvent extraction is one of the most widely used techniques for separating metal ions and organometallic compounds from aqueous and solid samples for analytical and processing purposes (1,2). Solvent extraction procedures, however, are usually time- and labor-intensive. In some cases, solvent extraction requires the use of toxic organic liquids, creating environmental difficulties related to spent solvent handling and disposal. Recently, supercritical fluid extraction (SFE) has become an attractive alternative to conventional solvent extraction for the recovery of metal ions and organometallic compounds from liquid and solid samples (3-19). One approach for extracting metal ions by supercritical fluid (SF) CO_2 is to convert the charged metal ions into neutral metal chelates by introducing a suitable CO_2-soluble ligand into the sample matrix. Conversion of metal ions into metal chelates can be performed by two methods. One method is on-line chelation, which is performed by first dissolving ligands into SF CO_2 then flowing the SF CO_2 through the sample matrix. Another method involves adding the ligands directly to the sample matrix prior to the supercritical fluid extraction. Both methods have been found to be successful for metal ion extraction using SF CO_2. A variety of organic complexing reagents including dithiocarbamates (4,5,8,9), β-diketones (3,6-8,18), organophosphorus reagents (14,15), crown ethers (12), and thioglycolic acid methylester (19), have been used in the chelation-SFE of metal species. In recent reports, synergistic extraction of lanthanides and actinides in SF CO_2 was demonstrated using a mixture of two ligands such as a fluorinated β-diketone with tributyl phosphate (TBP) (6,7) or trioctylphosphine oxide (TOPO) (8). Several uranium-containing samples, including mine water and contaminated soils, were studied using mixed ligands in SF CO_2 (7,8). High extraction efficiencies for uranium were observed when a β-diketone such as HFA, thenoytrifluoroacetone (TTA) or heptafluorobutaboylpivaroylmethane (FOD) was used in conjunction with either TBP or TOPO in a SF CO_2 solvent.

Compared with simple extraction of organic compounds from different matrices with SF CO_2, the process of chelation/SFE to extract metal ions is more complicated. SFE of metal ions involves an additional step to chelate the metal ions followed by diffusion of the metal chelates into the SF CO_2. The extracted metal chelates are typically transported to a restrictor and collected in a collection vessel, where they are often back-extracted with nitric acid solution and analyzed by atomic absorption, emission, or neutron activation techniques. Analyte extracted by this method can potentially be lost by a variety of mechanisms. These include: (i) decomposition of metal chelates in SF CO_2 (9,20,21) during the extraction and transportation; (ii) precipitation of metal chelates on the walls or end fittings of the extraction vessel, outlet valve, and connection tubing due to dead volume; and (iii) deposition of metal chelate in the outlet valve or restrictor due to solubility decrease in depressurized CO_2. Choosing a suitable technique to study the whole process of chelation / SFE is important for optimizing the extractor design, and for optimizing experimental conditions for metal ion extraction.

Radiotracer techniques offer a convenient way of studying many physical and chemical processes that often cannot be examined by any other methods (22,23). In this study, radioisotopes ^{140}La and ^{177}Lu were used as tracers to follow the process of in-situ chelation/SFE of La^{3+} and Lu^{3+} from solid matrices using mixed HFA and TBP as the chelating agents. An on-line back extraction device is described and results obtained using this device are compared with the results obtained by collection after depressurization at the exit of a restrictor.

EXPERIMENTAL

SFE/on-line back-extraction experiments were performed with a lab-built SFE apparatus as shown in FIG. 1. SFC grade CO_2 with a 5 mol% methanol modifier (Scott Specialty Gases, Plumsteadville, PA) was cooled by a coolant circulator and delivered to the SFE system using a Haskel Pump (Haskel Inc., Burbank,CA). The system pressure was monitored and controlled to ±5 PSI using a

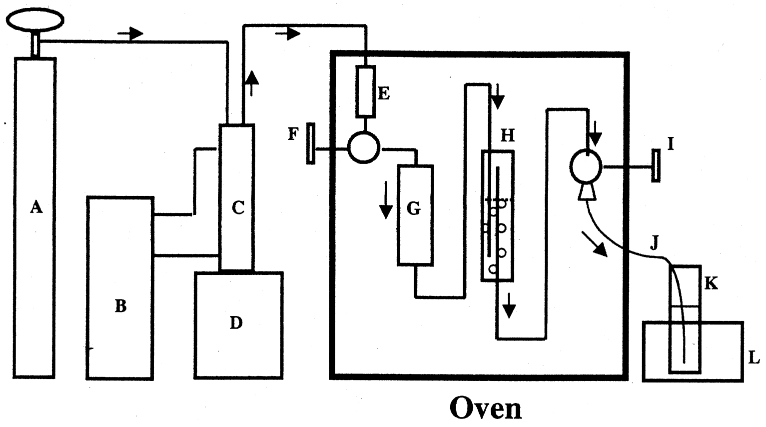

Figure 1. Supercritical fluid extraction apparatus with an on-line back-extraction device. (A) CO_2 cylinder; (B) circulator coolant; (C) liquid CO_2 reservoir; (D) Haskel pump; (E) temperature equilibration device; (F) inlet valve; (G) extraction vessel; (H) liquid vessel for on-line back-extraction; (I) outlet valve; (J) restrictor; (K) collection vessel; (L) water bath.

Setra System (Acton, MA) pressure transducer and a microprocessor-based controller. The extractor consisted of a temperature controlled oven, a temperature equilibration vessel, an inlet valve, a sample extraction vessel, a liquid vessel for on-line back extraction, an outlet valve, a restrictor, and a collection vessel. The temperature equilibration and sample extraction vessels, both having volumes of 3.5 mL, were purchased from Dionex (Sunnyvale, CA). Other experiments, such as optimization of extractor design, extraction rate measurement, and extraction of uranium samples, were perform in the same SFE system as shown in FIG. 1 except that the liquid back-extraction vessel was not installed.

The liquid vessel used for the on-line back-extraction study was modified from a commercial SFE vessel (Dionex, 1.0 cm i.d. and 13 cm in length) having a volume of 10 mL. The modified vessel was used as shown in FIG. 1. The 1/16 in. stainless steel inlet tubing was extended to the bottom of the vessel cavity, forcing the SF CO_2 to flow through the liquid in the vessel before exiting through the outlet tubing at the top. The sample extraction vessel, liquid back-extraction vessel, and outlet valve were placed in an oven controlled to ±0.1°C by a BS5001J1-A bench top temperature controller (Omega, Stamford, CT).

Three different kinds of restrictors were used to maintain the extraction pressure. The first was a stainless steel restrictor with 50 μm i. d. and 48 cm in length (Isco Inc). The second was made from 50 μm i. d. x 375 μm o. d. fused-silica capillary tubing (J&W Scientific; Folsom, CA). The third was made from 50 μm i. d. x 375 μm o. d. fused-silica capillary tubing inserted into a 0.020 in i. d. x 1/16 in o. d. PEEK tubing (Upchurch Scientific, Oak Harbor, WA). The flow rate of the SF CO_2 through the system using any of the restrictors was about 1.4 mL/min at 60°C and 200 atm. The SFE system used in this study allowed either static (extraction vessel pressurized with SF CO_2 with no flow through the cell) or dynamic (SF CO_2 flowed through the cell continuously) extraction to be carried out by use of the outlet and inlet valves.

Reagents and Sample Preparation

Reagents, HFA and TBP, were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. Solutions of La^{3+} and Lu^{3+}, prepared from their nitrates, were also purchased from Aldrich. All other chemicals used were analytical reagent grade. The radioisotopes ^{140}La ($E\gamma$ $=487$ KeV, $t_{1/2}=40.2$ h) and ^{177}Lu ($E\gamma$ $=208$ KeV, $t_{1/2}=6.7$d) were produced by neutron activation. A solution containing 2.0×10^{-3} M each of La^{3+} and Lu^{3+} in 0.01 M HNO_3 was irradiated for 1 hr in a 1 MW Trigar nuclear reactor at a steady flux of 6×10^{12} n cm^{-2} s^{-1}. After irradiation, pH of the solution was adjusted to about 4.0 by addition of NaAc. Filter paper samples were prepared by spiking 5 μL each of 2.0×10^{-3} M La^{3+} and Lu^{3+} solution containing ^{140}La and ^{177}Lu radioisotopes on filter paper (Whatman, Maidstone, England) strips. Soil samples were prepared by spiking 25 μL each of irradiated La^{3+} and Lu^{3+} solution on 500 mg of topsoil collected from northern Idaho. The spiked soil samples were allowed to dry at room temperature, then mixed thoroughly. About 100 mg of soil sample was used for each extraction

Procedures

A glass tube (0.5 cm i. d. and 3 cm in length) was plugged at one end with a piece of glass wool. To the open end of the glass tube, a spiked filter paper or 100 mg soil sample was inserted. For the filter paper experiments, 10 μL water, 30 μL HFA, 20 μL TBP, and 20 μL methanol were introduced sequentially to the sample. For Lu^{3+} and La^{3+} spiked soil samples, 20 μL water, 50 μL HFA, 25 μL TBP and 50 μL methanol were added to the sample sequentially. The open end was then plugged with a piece of clean glass wool. The sample tube was placed immediately into the extraction vessel and installed in the SFE oven upstream from a previously installed liquid back-extraction vessel which contained 6 mL 50% HNO_3. The temperature of the oven was set at 60°C, and the sample and liquid vessels were pressurized to 200 atm. The chelation and the extraction processes were allowed to occur under a static SFE condition for 10 min. The outlet valve was then opened and the sample was extracted and flushed under dynamic condition for 15 min. During the dynamic extraction step, metal chelates were extracted from the sample and flushed through the liquid vessel containing 6 mL 50% HNO_3 placed inside the oven. On-line back extraction occurred as SF CO_2 containing solute diffused through nitric acid solution. Metal chelates were decomposed into ligands and metal ions, which were insoluble in CO_2 and were separated from the protonated ligands. A collection vessel containing 6 mL methylisobutylketone (MIBK) solvent was placed at the exit restrictor to trap undecomposed metal chelates from the system. After extraction, the sample (filter paper or soil) was removed from the extraction vessel and the remaining radioisotopes were counted using a large-volume Ortec Ge(Li) detector with a resolution (fwhm) of ~ 2.3 KeV at the 1332 KeV ^{60}Co peak. A filter paper strip or 100 mg soil containing the same amount of the radioactive $^{140}La^{3+}$ and $^{177}Lu^{3+}$ ions was used as a standard and counted under identical conditions. The extraction efficiencies (percent removal) were calculated based on the amount of the lanthanides found in the filter paper or soil before and after extraction. Nitric acid solution in the liquid vessel and MIBK solvent in the collection vessel were transferred to PEEK bottles and counted with the same Ge(Li) detector. A 6 mL HNO_3 solution containing 5 μL each of the same amount of $^{140}La^{3+}$ and $^{177}Lu^{3+}$ ions as the sample was used as a standard for comparison. The recovery in 50% HNO_3 solution was calculated based on the amount of lanthanide activity found in the acid solution in comparison with the standard. The amounts of the un-decomposed metal chelates were calculated based on the lanthanide activities found in the MIBK solution in the collection vessel. After each extraction, a portable Geiger-Muller Counter (Model PUG-1, Technical Associates, Burbank, CA) was used to trace the radioactivity in each component of the extractor. The extractor was disconnected and the radioactivity remaining in the sample extraction vessel, connection tubing, liquid vessel, outlet valve and restrictor was measured both with the Geiger-Muller Counter and the Ge(Li) detector. The detailed counting procedures using Ge(Li) detector were described elsewhere (24).

RESULTS AND DISCUSSION

Restrictor Construction and Location

For SFE of metal ions from solid samples, a small amount of water is usually added to the solid matrices to improve the extraction efficiencies. Water probably facilitates the formation and migration of metal chelates by blocking the active sites in solid matrices holding the metal ions (3,6,7). In some cases, SFE has been applied to the extraction of metal ions from aqueous samples (6-8). However, restrictor plugging due to ice formation often occurs during dynamic extraction or the depressurization step. To prevent restrictor plugging from ice formation, different restrictor arrangements were tested. The most satisfactory arrangement was to connect the restrictor directly with the outlet valve, which was located inside the oven. Half of the restrictor capillary remained inside the heated oven while the other half penetrated a small hole in the oven wall and was unheated. The unheated portion of the restrictor was inserted into a collection vessel immersed in a water bath maintained at room temperature to prevent the collection solvent temperature from dropping below 0°C. In this manner, restrictor plugging was minimized.

The breakage of the fused-silica restrictor can be another problem in SFE when methanol modifier is used (25). In this study, a simple, robust, flexible restrictor was constructed by securing the fused-silica capillary restrictor inside a PEEK tube. For an unprotected fused-silica restrictor, the capillary became brittle and usually broke after 40 min to 1 hr when the polar CO_2-methanol (95:5) continuously flowed through a liquid vessel containing 6 mL 50% HNO_3 solution. The location of the breaking point in the fused-silica restrictor was frequently at the position about 3-5 cm from the exit end and was caused by vibration of the restrictor during expansion of SF CO_2. However, when the fused-silica restrictor was secured inside a PEEK tube, restrictor breakage did not occur during a 6-hr test. When the protected fused-silica capillary eventually broke, it could be easily removed by inserting a stainless steel capillary through the PEEK tube. A new fused-silica capillary was then inserted into the PEEK tube and the system was returned to operation without changing the ferrule used for holding the restrictor.

Optimization of Extractor Design

One major consideration in the design of an analytical procedure for the extraction and preconcentration of metal species is that losses of metals are minimized during the transport and collection procedures. Metal chelates are usually non-volatile and can easily be trapped using an organic solvent, such as MIBK or chloroform. In this study, MIBK was chosen. Deposition of metal chelates during their extraction and transportation could be a potential factor resulting in low metal recovery. To study this possibility, a Lu^{3+} solution containing $^{177}Lu^{3+}$ was spiked onto a filter paper for the SFE experiments using a mixture of HFA and TBP as chelating agents. Following the SFE of ^{177}Lu, a Geiger-Muller counter was passed along the length of the apparatus. Radioactivity could still be detected within the extraction cell and outlet valve, and to a lesser extent within the transfer tubing and restrictor. This external assessment of the extraction process was undertaken within minutes of completing the SFE step and could be used as a screening technique to qualitatively ascertain if the metal had been successfully transferred to the collection device.

To quantitatively determine the concentration of ^{177}Lu remaining in the apparatus after SF extraction, the system was dismantled and the various components sequentially flushed with organic (MIBK) and aqueous (50% nitric acid) solvents. Our results indicated that the effects of extraction vessel orientation and outlet valve orientation and location were very important factors determining the recovery of the metal chelates. When the extraction vessel was placed horizontally and the outlet valve was also placed horizontally outside the oven (for ease of installation and operation), recovery was not quantitative. Surveying the experimental system using a portable Geiger-Muller counter showed that a small portion of radiotracer still remained inside the extraction vessel and the outlet valve, as well as in the fittings of the outlet valve and the restrictor. When the extraction vessel, outlet valve, connection fittings, tubing and restrictor were all disconnected and washed with MIBK and nitric acid solution, the washed radiotracer was counted with Ge(Li) detector and the percentage of radiotracer remaining in each part was calculated. The results showed that most of the remaining radiotracers were deposited inside the extraction vessel (8%) and outlet valve (6%). Radiotracers remaining in the extraction vessel and outlet valve were mostly in the metal chelate form because they could be rinsed from the dismantled system using MIBK. About 1% of the radiotracer remained inside the sample extraction vessel and the outlet valve as inorganic metal species (insoluble in MIBK, but soluble in 50% HNO_3), which were probably formed by thermal decomposition or ligand exchange reactions.

When the extraction vessel was placed vertically and the outlet valve was moved into the oven and installed vertically (Fig. 1), recovery improved greatly. However, a small amount of radiotracer (~2%) was still deposited inside the outlet valve and its fittings. A similar trend was found for the supercritical fluid extraction of organic analytes, which have a slower rate of extraction from a horizontal vessel than from a vertical vessel (26). Based on the results obtained from radiotracer technique, the optimum extractor design should have the extraction vessel and the outlet valves placed vertically and heated inside the oven.

Back-Extraction of Lanthanides

All commercially available extractants of the chelating or acidic type available today are monobasic in nature, and thus release one hydrogen ion for every molecule which combines with a metal. The number of molecules of extractant involved in the formation of an extracted species depends on the oxidation state and coordination number of the metal ion. In this study, the extraction of La^{3+} or Lu^{3+} by mixed ligands HFA + TBP can be represented by the following equation (27):

$$Ln^{3+} + 3\,HHFA + 2\,TBP \rightarrow Ln(HFA)_3 \cdot 2\,TBP + 3\,H^+ \tag{1}$$

Stripping, or back-extraction, is the reverse reaction of extraction. The back-extraction of the chelated species involved in our tests should be possible in an acid solution sufficiently concentrated to shift the equilibrium far to the left of equation (1) to drive the metal into the aqueous phase. In this study, both off-line and on-line back-extractions were investigated**.**

Off-Line Back-Extraction of La^{3+} and Lu^{3+} from MIBK Trapping Solution

For conventional metal ion analysis with neutron activation analysis (NAA), atomic absorption spectrometry (AAS), or inductively coupled plasma-mass spectrometry (ICP-MS), it is convenient to prepare the sample in aqueous solution. Therefore, it is necessary to quantitatively back extract metal ions from the MIBK trapping solution. To test the back-extraction efficiency, 5 mL MIBK solution containing ^{140}La and ^{177}Lu radiotracers trapped from extraction of spiked filter paper were back-extracted with 5 mL 50% HNO_3 solution for a 5-min shaking time. The results are summarized in Table 1. The results showed quantitative back-extraction of La^{3+} and Lu^{3+} from MIBK solvent with 50% HNO_3.

Table 1. Back Extraction of La^{3+} and Lu^{3+} from MIBK Collection Solution With 50% HNO_3

	γ—Activity (Counts / 5 min)	
	La (487KeV)	Lu (207 KeV)
Organic Phase before Back Extraction (MIBK Collection Solution)	7943	2744
Organic Phase after Back Extraction (MIBK)	151	36
Aqueous Phase after Back Extraction (50% HNO_3)	7788	2662
Percent Back Extraction	La = 98	Lu = 97

Recovery of Metal Ions by On-Line Back-Extraction

Although optimization of the extractor design was performed, there typically remained a small amount of radiotracer deposited inside the outlet valve and its fittings after extraction. To further prevent the loss of metal chelates due to the deposition and decomposition during the transportation and to avoid using an organic solvent as a trapping solution, an on-line back-extraction technique was used. This was achieved by installing a liquid back-extraction vessel between the extraction vessel and the outlet valve. A 6 mL aliquot of 50 % HNO_3 was loaded in the liquid vessel as back-extraction solution. La^{3+} and Lu^{3+}in the solid samples were first extracted into SF CO_2 and then back-extracted into nitric acid solution when SFE solution flowed through the liquid vessel. For comparison, radiotracers collected in MIBK trapping solution both from spiked filter paper or spiked soils without installation of the liquid back-extraction vessel were also investigated. The results are summarized in Table 2.

As can be seen from Table 2, most of the La and Lu (about 90%) were recovered in the liquid back-extraction vessel. About 5-7% of the La and Lu broke through the liquid vessel without being back-extracted and was trapped in MIBK solvent at the restrictor exit. Break-through of La and Lu metal chelates from the liquid vessel was probably due to insufficient contact time of metal chelates in SF CO_2 with the nitric acid solution. The recovery of metal ions might be improved by increasing contact time of SF CO_2 with the nitric acid solution by decreasing the flow rate of SF CO_2 or by increasing the height of nitric acid solution (i.e., using a “narrower and higher” liquid vessel). Modification of the liquid vessel configuration by adding a porous solvent filter normally used for helium sparging in HPLC would improve the contact area between the CO_2 fluid and the bulk nitric

Table 2. Extraction and Recovery of La^{3+} and Lu^{3+} from Filter Paper and Soil With or Without On-Line Back-Extraction System

	Percent Removal		On-Line Recovery with 50% HNO_3		Percent Collection with MIBK	
Sample No.	La	Lu	La	Lu	La	Lu
Paper #1	99	99	88	90	7	6
Paper #2	99	99	90	86	5	7
Paper #3	99	100	NO*	NO*	87	90
Paper #4	99	100	NO	NO	85	91
Soil #1	98	98	NO	NO	90	92
Soil #2	98	96	NO	NO	89	90

Conditions: Supercritical CO_2 with 5% MeOH at 60°C and 200 atm; ligands: HFA+TBP; extraction times: 10 min static followed by 10 min dynamic extraction.
* Extractions were conducted without an on-line extraction device.

acid solution, and hence increase the recovery efficiency of the back-extraction process.

One potential advantage of an on-line back-extraction technique is the prevention of restrictor plugging when samples containing very high concentration of metal ions are being extracted. Due to the solubility decrease of metal chelates at lower fluid pressures, the restrictor sometimes becomes plugged with extracted metal chelates as the supercritical CO_2 is decompressed along the length of the restrictor. Usually metal chelates are solid, having fairly high melting-points. Based on our experience, the conventional technique of heating the restrictor at high temperature to remove blockages often causes the thermal decomposition of metal chelates into inorganic metal species, resulting in irreversible plugging of the restrictor. The on-line back-extraction technique offers a convenient method for recovering the metal ions before they reach the restrictor, and thereby reducing the restrictor plugging issue.

For industrial scale application of chelation/SFE technology, the capability to recycle the CO_2 and the ligand is very important. On-line back-extraction can regenerate the ligands and the CO_2 containing the ligands can be recycled without depressurizing the system. This has the potential to make a process more convenient and more economic. Although only the β-diketone ligand was investigated in this study, the principle demonstrated in this work can be extended to other chelation / SFE systems using extractants of the chelating or acidic type.

Kinetics of Extraction of Lu^{3+} from Soil Sample

The kinetic data of metal extraction are very important for optimization of both analytical and industrial-scale SFE. The rate of metal extraction is affected by several factors including affinity of ligands and metal chelates to supercritical CO_2 and the kinetics of the chelation reaction. Therefore, the selection of a suitable ligand system requires not only the formation of stable metal chelates, but also the fast kinetics of chelate formation and sufficient solubility of both ligand and metal chelate in supercritical CO_2. To evaluate the kinetics of metal extraction from solid matrices using ligands of HFA plus TBP, the extraction rate of Lu (containing ^{177}Lu) from the soil sample using in-situ chelation / SFE was measured using CO_2 modified with 5% methanol. The extraction process consisted of a static extraction step, followed by a dynamic extraction step. Extracted solute was trapped by 5 mL MIBK at the exit of the restrictor at varying time intervals, and was quantified by counting the proportion of radioactivity collected. The percent collection was calculated based on percent collection of radiotracer spiked in the soil sample.

The effect of static extraction time on extraction efficiency was investigated by varying static extraction time (5-20 min) with a constant dynamic extraction time (20 min). It is observed that the static phase of the extraction process played little part in increasing extraction efficiencies. This indicates that the rate of metal ion complexation was not rate limiting under the conditions of this study. The effect of dynamic extraction time was observed by varying the amount of dynamic extraction time after a constant static extraction time (10 min). The results are shown in Fig. 2. As indicated from Fig. 2, extraction was rapid, with about 88%

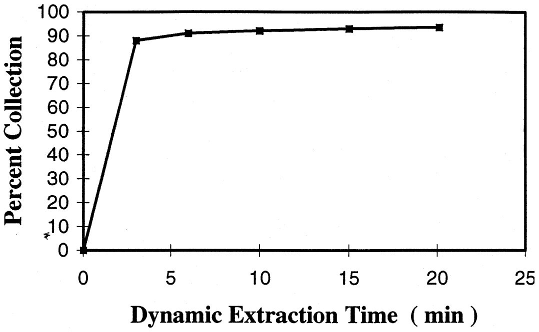

Figure 2. Rate of extraction of Lu^{3+} from spiked soil sample using 5 % methanol-modified supercritical CO_2 containing HFA and TBP at 60 °C and 200 atm. Extraction conditions: 100 mg soil sample spiked with Lu^{3+} containing radiotracer ^{177}Lu; 20 μL water, 30 μL HFA, 25 μL TBP and 50 μL methanol were added to the sample sequentially; 10 min static extraction followed by 20 min dynamic extraction.

of Lu^{3+}collected within 5 min, and about 93% collected at the end of 15 min. After 15 min, the percent collection of Lu^{3+} increased only slightly with increasing dynamic extraction time.

Extraction of Uranium from Contaminated Soil Sample

The fast extraction of spiked Lu^{3+} has been demonstrated as discussed above. However, the extraction of metal ions from "real" environmental matrices could be different. To demonstrate the capability of chelation/SFE technology for the environmental remediation application, extraction of uranium-contaminated soil samples collected from a spent uranium mine in the Northwest of the United States was investigated using the synergistic ligand system of HFA plus TOPO. TOPO is a stronger Lewis base than TBP and has shown stronger synergistic effect than TBP for the SFE of uranium (7). The experimental procedures used for uranium extraction from soil and NAA analysis of uranium in soil were the same as reported previously (3,7). The results are summarized in Table 3. The extraction of uranium from these samples was not as rapid as the extraction of spiked Lu^{3+} from soil. The difference is most likely due to the differing chemical nature and accessibility to the SF for the naturally occurring sample (uranium speciation and matrix effects). Additionally, concentrations of uranium in the soil samples were higher than Lu^{3+} concentrations in the spiked soil samples. Although quantitative extraction of uranium from contaminated soil has not been achieved, the results obtained from this study were promising. With 10 min of static extraction followed by 20 min of dynamic extraction, 72-88% uranium was extracted from

Table 3. Extraction of Uranium from Contaminated Soils with Supercritical CO_2 (5% methanol) Containing HFA and TOPO at 60°C and 200 atm

Sample*	U Conc. (mg/g)	Percent Removal**
#1	0.48	80 ± 3
#2	0.66	81 ± 4
#3	1.76	72 ± 4
#4	0.14	88 ± 5
#5	34.5	82 ± 3

* Soil samples collected from different spots of a spent U mine.

** Average data of three runs

Conditions: 100 mg soil was used for extraction; 100 μL HFA + 50 mg TOPO + 30 μL H_2O; 10 min static extraction followed by 20 min dynamic extraction for each sample.

the soil samples. The extraction efficiency may be further improved by adding more ligands or by increasing extraction times**.** Characterization of uranium speciation and matrix effects for soil samples needs to be performed in order to further optimize the extraction conditions.

CONCLUSIONS

Radioisotopes ^{140}La and ^{177}Lu were used as radiotracers to monitor the process of *in-situ* chelation / SFE of La^{3+} and Lu^{3+} from solid matrix using mixed HFA plus TBP as chelating agents. The choice of a robust restrictor was found to be very important for *in-situ* chelation / SFE for metal ions or organomatallic compounds when the polar modifier, methanol was added to CO_2. Optimal orientation and location of the outlet valve, as well as the orientation of the extraction vessel was necessary to achieve quantitative recovery of metal chelates. The new approach of on-line back-extraction improved metal ion recovery, minimized restrictor clogging and eliminated the need for an organic trapping solvent. On-line recovery of metal ions allowed the regeneration of ligands, and consequently CO_2 containing ligands can be recycled without depressurizing the system.

ACKNOWLEDGMENTS

The authors would like to thank Drs. Dean Matson and David Holman at PNNL for reviewing the manuscript. This work was supported by BNFL and by NSF-Idaho EPSCoR Program under NSF Cooperative Agreement OSR-9350539. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under a Reactor Program supported by DOE. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. DOE under Contract DE-AC06-76RLO 1830.

REFERENCES

1. J. Minczewski, J. Chwastowska, and R. Dybczynski, in *Separation and Preconcentration Methods in Inorganic Trace Analysis*, Elis Horwood, Ed., Halsted Press, Chichester, 1982, p. 97-282.
2. C. M. Wai in *Preconcentration Techniques for Trace Elements*, Z. B. Alfassi and C.M. Wai, Eds., CRC Press, Boca Raton, FL, 1991, p.101-32.
3. Y. Lin, R. D. Brauer, K. E. Laintz, and C.M. Wai, *Anal. Chem. 65,* 2549 (1993).

4. K. E. Laintz, C. M. Wai, C. R. Yonker, R. D. Smith, *Anal. Chem. 64*, 2875 (1992).
5. C. M. Wai, Y. Lin, R. D. Brauer, S. Wang, and W. F. Beckest, *Talanta 40,* 1325 (1993).
6. Y. Lin and C. M. Wai, *Anal. Chem. 66,* 1971 (1994).
7. Y. Lin, C. M. Wai, F. M. Jean, and R. D. Brauer, *Environ. Sci. Technol. 28,* 119 (1994).
8. Y. Lin, N.G. Smart, and C. M. Wai, *Trends in Anal. Chem. 14,* 123 (1995).
9. J. Wang and W.D. Marshall, *Anal. Chem. 66,* 1658 (1994).
10. Y. Liu, V. Lopez-Avila, M. Alcaraz, and W. F. Beckert, *J. High Resolut. Chromatogr. 16,* 106 (1993).
11. Y. Cai, R. Alzaga, and J. M. Bayona, *Anal. Chem. 66,* 1161 (1994).
12. S. Wang, S. Elshani, C. M. Wai, *Anal. Chem. 67,* 919 (1995).
13. J. W. Oudsema and C. F. Poole, *J. High Resolut. Chromatogr. 16,* 198 (1993).
14. K. E. Laintz and E. Tachikawa, *Anal. Chem. 66,* 2190 (1994).
15. Y. Lin, N. G. Smart, and C. M. Wai, *Environ. Sci. Technol. 29,* 2706 (1995).
16. Y. Liu, V. Lopez-Avila, M. Alcaraz, W. F. Beckert, and E. M. Heithmar, *J. Chromatogr. Sci. 31,* 310 (1993).
17. N. G. Smart, Y. Lin, and C. M. Wai, *American Environ. Lab.*, *2*, 38 (1996).
18. K. G. Furton, L. Chen, and R. Jaffe, *Anal. Chim. Acta 304,* 203 (1995).
19. B. W. Wenclawiak and M. Krah, *Fresenius J. Anal. Chem. 351,* 134 (1995).
20. C. Fujimoto, H. Yoshita, and K. Jinno, *J. Microcol. Sep. 1,* 19 (1989).
21. K. Jinno, H. Mae, and C. Fujimoto, *J. High Resolut. Chromatogr. 13,* 13 (1990).
22. D. Ehmann and D. E. Vance, in *Radiochemistry and Nuclear Methods of Analysis*, John Wiley & Sons, Inc., New York, 1991, p 313-345.
23. H. J. Arnikar, *Isotopes in the Atomic Age,* John Wiley & Sons, Inc., 1989.
24. J. Tang and C. M. Wai, *Anal. Chem. 58,* 3233 (1986).
25. M. D. Burford, S.B. Hawthorne, D. J. Miller, and J. Macomber, *J. Chromatogr. 648,* 445 (1993).
26. S. B. Hawthorne, D. J. Miller, M. D. Burford, J. J. Langenfeld, S. Eckert-Tilotta, and P. K. Louie, *J. Chromatogr. 642,* 301 (1993).
27. Y. Lin, H. Wu, N. G. Smart, and C. M. Wai, *J. Chromatogr. A 793*, 107 (1998).

Downloaded At: 10:49 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100103642