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Review

Supercritical fluid extraction: metals as complexes

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Abstract

Metal species in solid and liquid materials can be extracted by supercritical CO₂-containing organic ligands. This SFE technique converts charged metal species into neutral metal complexes which become soluble in CO₂. The efficiency of metal extraction using the in situ chelation–SFE method depends on a number of factors including (1) stability and solubility of ligand, (2) solubility of metal chelate, (3) water and pH, (4) temperature and pressure, (5) chemical form of metal species, and (6) matrix. Several different types of chelating agents including dithiocarbamates, β-diketones, organophosphorus reagents and macrocyclic compounds have been tested for their ability to extract heavy metals, lanthanides, and actinides from different sample matrices. With proper selection of ligands, separation of organic and inorganic metal species may be achieved using this SFE technique. Metal species extracted by the SFE method probably represent the leachable metals present in solid matrices. © 1997 Elsevier Science B.V.

Keywords: Supercritical fluid extraction; Reviews; Metals; Dithiocarbamates; β-Diketones; Organophosphorus compounds; Macrocyclic compounds

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1. Introduction

Chelation combined with solvent extraction is one of the most widely used techniques for preconcentration and separation of metal ions from aqueous samples for analytical purposes [1]. These solvent extraction procedures, however, are usually time consuming, especially for solids where leaching procedures are needed to release the metal ions before complexation and solvent extraction. In many cases, solvent extraction requires the use of toxic organic liquids, generating environmental problems for handling and disposal of used solvents. Supercritical fluid carbon dioxide is an alternative solvent for extraction of metal species from environmental samples. Carbon dioxide is widely used in supercritical fluid extraction (SFE) because of its moderate critical constants ($T_c=31.1^\circ\text{C}$, $P_c=72.8$ atm, $\varphi_c=0.471$ g/ml), inertness, low cost and availability in pure form. A major advantage of utilizing supercritical CO_2 as a solvent is the minimization of organic solvent waste generation. The high diffusivity and low viscosity of supercritical CO_2 also allows direct extraction of solutes from solid matrices.

Until recently, little information was available in the literature regarding SFE of metal species. Direct extraction of metal ions is highly inefficient because of charge neutralization requirement and the weak solute–solvent interactions. However, when metal ions are chelated with organic ligands, they may become quite soluble in supercritical CO_2 [2]. This in situ chelation–SFE technique appears to have a wide range of applications including the treatment of metal contaminated waste materials and mineral processing. The success of this SFE technique for metal extraction depends largely on the effectiveness of the ligand. A suitable chelating agent should have a reasonable solubility in supercritical fluid and form

stable and extractable chelates with metal ions of interest. For large scale applications, the extractant should also be commercially available and inexpensive.

Quantitative measurements of metal chelate solubilities in supercritical CO_2 were first made by Wai and coworkers in 1991 using a high pressure view cell and UV–Vis spectroscopy [3]. In this report, the authors showed that the solubility of metal dithiocarbamates depends on metal coordination and that fluorine substitution can greatly enhance their solubility in supercritical CO_2 . The demonstration of copper extraction from solid and liquid materials using supercritical CO_2 containing the fluorinated ligand bis(trifluoroethyl)dithiocarbamate (FDDC) was reported in 1992 [4]. Since then there are over 50 papers reported in the literature regarding SFE of metal species from different sample matrices. A variety of chelating agents, including dithiocarbamates, β -diketones, organophosphorus reagents, macrocyclic compounds, fluorinated surfactants, etc. have been tested for SFE of metals [2–13,15–19]. The feasibilities of extracting organometallic compounds, heavy metals, lanthanides and actinides from solid and liquid materials using the in situ chelation–SFE method have been evaluated by a number of research groups from different countries. These studies provide a basis for understanding the nature of metal chelation and extraction in supercritical fluids. According to the literature, the important parameters controlling SFE of metal species appear to be: (1) solubility and stability of chelating agents, (2) solubility of metal chelates, (3) water and pH, (4) temperature and pressure, (5) chemical form of metal species, and (6) matrix. This article summarizes the literature information in the past five years concerning SFE of metal species for analytical applications.

2. Parameters controlling SFE of metals

2.1. Solubility and stability of chelating agents in supercritical CO₂

The solubility of free ligands in supercritical CO₂ depends on the chemical nature of the ligand and varies significantly from one type to another. The solubility and stability of some commonly used chelating agents for SFE of metal species are described in this section.

2.1.1. Dithiocarbamates

One ligand system which has been extensively studied for SFE of metal species in the literature is the derivatives of dithiocarbamic acid of the general form R₂NCS₂X, where R is an alkyl group and X is a cation which can be an alkali metal ion, an ammonium ion or an alkyl ammonium ion [3–7]. Dithiocarbamate derivatives are effective extractants for preconcentration of trace elements from aqueous solutions by solvent extraction [1]. A widely used dithiocarbamate reagents for this purpose is sodium diethyldithiocarbamate (NaDDC) which is able to extract over 40 metal species from aqueous solutions into organic solvents. The alkali metals, the alkaline earth metals, the halogens and the lanthanides are not extractable by NaDDC. The dithiocarbamate reagents used in metal extractions are usually as alkali metal or ammonium salts [3–6,15,16]. The solubility of NaDDC in neat CO₂ is about 1.5 × 10⁻⁴ M (mol/l) at 50°C and 100 atm. Fluorination can enhance the solubility of the free ligand in supercritical CO₂. For example, sodium bis(trifluoroethyl)dithiocarbamate (NaFDDC), a fluorinated analogue of NaDDC, has a solubility of 4.7 × 10⁻⁴ M in neat CO₂ at 50°C and 100 atm [3]. Pressure has a significant effect on the solubility of dithiocarbamate reagents in CO₂. The solubility of NaDDC in neat CO₂ at 60°C and 200 atm is increased to 1.5 × 10⁻³ M [11]. The alkylammonium salts of dithiocarbamate reagents show very high solubilities in CO₂ [11,15]. For example, diethylammonium diethyldithiocarbamate (Et₂NH₂DDC) has a solubility of 4 × 10⁻² M in CO₂ at 60°C and 200 atm, which is an order of magnitude higher compared to the solubility of the sodium salt (NaDDC) under the same temperature and pressure. Formation of metal chelates depends on the forma-

tion constants and the concentration of the ligand. Metal dithiocarbamate chelates generally have extremely large formation constants [1]. Complexation of trace metals with dithiocarbamate ligands usually will take place, as long as the ligands are present in sufficient amounts in supercritical CO₂. The limiting factor of metal extraction is probably determined by the solubility of the metal chelates formed in supercritical CO₂.

The structures of the dithiocarbamate reagents tested for metal ions extraction in supercritical CO₂ are given as follows:

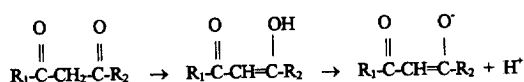
	R = -CH ₂ CF ₃	FDDC	Bis-trifluoroethylthiocarbamate
	R = -C ₂ H ₅	DDC	Diethyldithiocarbamate
R \	R = -C ₃ H ₇	P3DC	Dipropyldithiocarbamate
N-CS ₂	R = -C ₄ H ₉	BDC	Dibutyldithiocarbamate
R /	R = -C ₅ H ₁₁	P5DC	Dipentyldithiocarbamate
	R = -C ₆ H ₁₃	HDC	Dihexyldithiocarbamate
	R + R = -CH ₂ (CH ₂) ₂ CH ₂ -	PDC	Pyrrolidinedithiocarbamate

Increasing alkyl chain length of the alkylammonium dithiocarbamate salts can also increase their solubility in supercritical CO₂. For example, in a dynamic supercritical CO₂ system the solubilities of (C₄H₉)₄N[SC(S)N(C₄H₉)₂] and (C₄H₉)₄N[SC(S)N(C₂H₅)₂] were reported by Wang and Marshall to be 23.24 and 2.91 g/(min/ml), respectively, at 45°C and 170 atm. Increasing the carbon chain length by two units can increase the solubilities about 8 times [15].

One problem of using dithiocarbamate reagents as extractants is their instability in water especially in acidic solutions [1]. It is well known that when water is in contact with supercritical CO₂, its pH at equilibrium is less than 3 because of the formation and dissociation of carbonic acid in water [17]. Thus, in the presence of water, dithiocarbamate reagents tend to decompose in supercritical CO₂ extraction systems. Because of this, an excess amount of dithiocarbamate reagents is usually required in order to achieve good metal extraction efficiencies in SFE.


2.1.2. β-diketones

β-diketones react with metal ions to form neutral chelates through the enolate anions shown by the following equilibria:



Except TTA, other β-diketones listed in Table 1 are

Table 1
Structure of fluorinated β -diketonates tested for lanthanides and actinides extraction in supercritical carbon dioxide

β -Diketone	Abbrev.	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}_1\text{-C-CH}_2\text{-C-R}_2 \end{array}$		Mol. Wt.	B.P. ($^\circ\text{C}$)
		R ₁	R ₂		
Acetylacetone	AA	CH ₃	CH ₃	100.12	139 ^o (760 Torr)
Trifluoroacetylacetone	TFA	CH ₃	CF ₃	154.09	107 ^o
Hexafluoroacetylacetone	HFA	CF ₃	CF ₃	208.06	70-71 ^o
Thenoyltrifluoroacetone	TTA		CF ₃	222.18	103-104 ^o (9 Torr)
Heptafluorobutanoyl-pivaloyl-methane	FOD	C(CH ₃) ₃	C ₃ H ₇	296.18	33 ^o (2.7 Torr)

all liquids at room temperature under atmospheric pressure. Little information is available in the literature concerning the solubility of β -diketones in supercritical CO₂. Some preliminary data obtained from our laboratory show that the solubility of AA in CO₂ at 600 $^\circ\text{C}$ and 130 atm is about 4×10^{-4} mole fraction. At the same temperature and pressure, the solubility of TTA in CO₂ is about 2.3×10^{-2} mole fraction. The solubilities of fluorine-containing liquid β -diketones in supercritical CO₂ are probably comparable to that of tributylphosphate (TBP) judging from their high volatility. Under normal SFE conditions all of these liquid β -diketones show high miscibility with CO₂. Recent NMR studies show that the fluorinated β -diketones (HFA and TTA) are almost exclusively in the enol form under the high temperature and pressure conditions relevant to SFE systems [18]. The non-fluorinated ligand AA is found to be partly in each form in supercritical CO₂ [19]. The acidity of the ligand originates from the enol form and the deprotonated β -diketone involved in the metal complexation process. It has shown that the presence of electron-withdrawing fluorine substituents can significantly increase ligand acidity [20]. There is no report in the literature regarding decomposition of β -diketones in supercritical CO₂. Free β -diketones are assumed to be stable in CO₂ under normal SFE conditions.

2.1.3. Organophosphorus reagents

The structures of some organophosphorus reagents tested for SFE of metals are given as follows:

RO \		
RO - P = O	TBP (R = <i>n</i> -C ₄ H ₉)	Tributylphosphate
RO /		
R \		
R - P = O	TBPO (R = <i>n</i> -C ₄ H ₉)	Tributylphosphine oxide
R /	TOPO (R = <i>n</i> -C ₈ H ₁₇)	Trioctylphosphine oxide
	TPPO (R = -C ₆ H ₅)	Triphenylphosphine oxide
R \		
R - P = O	Cyanex 272 (R = (CH ₃) ₃ CCH ₂ -CH(CH ₃)-CH ₂ -)	
HO /	Bis(2,4,4-trimethylpentyl)phosphinic acid	
R \		
R - P = S	Cyanex 301 (R = (CH ₃) ₃ CCH ₂ -CH(CH ₃)-CH ₂ -)	
HS /	Bis(2,4,4-trimethylpentyl)dithiophosphinic acid	
R \		
R - P = S	Cyanex 302 (R = (CH ₃) ₃ CCH ₂ -CH(CH ₃)-CH ₂ -)	
HO /	Bis(2,4,4-trimethylpentyl)monothiophosphinic acid	
RO \		
RO - P = O	D2EHPA (R = CH ₃ (CH ₂) ₂ CH(CH ₂ CH ₃)-CH ₂ -)	
HO /	Di(2-ethylhexyl)phosphoric acid	

Organophosphorus reagents such as tributylphosphate (TBP) and phosphine oxides such as tributylphosphine oxide (TBPO), trioctylphosphine oxide (TOPO) and triphenylphosphine oxide (TPPO) have long been established for use as extractive ligands for actinide elements [21]. Recently, these compounds have been used in supercritical CO₂ extraction of U and Th from solid and liquid matrices [12]. A number of organophosphorus reagents are commercially available and widely used for metal extraction in conventional solvent extraction processes. Such reagents have great technological importance within the nuclear industry. In particular, TBP is extensively used in the extraction and separation of U and Pu in the 'Purex' process [22,23].

TBP is a viscous liquid at room temperature (b.p. 289 $^\circ\text{C}$). The phosphine oxides TBPO, TOPO and TPPO are solids with melting points 64–69 $^\circ\text{C}$, 50–54 $^\circ\text{C}$, and 156–158 $^\circ\text{C}$, respectively. These organophosphorus reagents are known to form coordinatively solvated salts with lanthanides and actinides through the P=O group.

According to Page et al. about 11% of TBP is miscible with CO₂ at 60 $^\circ\text{C}$ and 120 atm [24]. The solubilities of different phosphine oxides have been measured by Schmitt et al. [25] and by Lin et al. [12]. The solubility of TBPO in supercritical CO₂ at

60°C and 200 atm is rather high, about 0.85 mol/l [12]. The solubility of TOPO in supercritical CO₂ is 6.6×10^{-2} M, at 45°C and 200 atm, an order of magnitude lower compared with TBPO (Table 2). A much lower solubility (7.7×10^{-3} M) is observed for the phenyl substituted phosphine oxide, TPPO. Aromatic substituent groups such as phenyl usually have a negative effect upon solubility of organic compounds in supercritical CO₂ [26].

The solubility of bis(2,4,4-trimethylpentyl)-monothiophosphinic acid under the trade name Cyanex 302 was determined using a high pressure view cell. The sulfur-containing organophosphorus reagent is very soluble in CO₂ and forms extractable complexes with transition metals and heavy metals. The solubilities of Cyanex 302 in supercritical CO₂ at 60°C under different pressures are 8 g/l, 40 g/l, 60 g/l, and 108 g/l, for 110 atm, 200 atm, 240 atm and 280 atm, respectively [26]. The ligand solubility increases rapidly with pressure. If a ligand is very soluble in CO₂ at high pressure, deposition of the free ligand within the extraction system may take place during depressurizing. This may cause plugging of the restrictor during dynamic flushing. Therefore, using this type of chelating agents for metal extraction it is important that the solubility of the ligand is not exceeded in designing a dynamic extraction process.

The phosphorus-containing reagents appear stable in supercritical CO₂. The IR spectra of Cyanex 302 were studied before and after treatment in a supercritical CO₂ vessel at 60°C and 300 atm for 20 min. No change in the IR spectra was observed between the treated and the untreated reagent. For the phosphorus-containing metal complexes, ³¹P NMR was

utilized to determine the amount of degradation before and after treatment in supercritical CO₂. No changes in the main features of the spectra were observed and importantly no new peaks appeared, indicating that the amount of degradation of the complex in the supercritical CO₂, under normal SFE conditions, is below the detection limits of the ³¹P NMR technique used [26].

2.1.4. Macrocyclic ligands

Macrocyclic polyethers (crown ethers) are a class of selective ligands which form stable complexes with metal ions based primarily on the ionic radius–cavity size compatibility concept. Modification of crown ether structure by attaching negatively charged functional groups to the host can eliminate the need for counteranions that are required for the transport of charged complexes into an organic phase. One type of ionizable crown ethers containing triazole groups (Fig. 1) has been studied for selective extraction of mercury in supercritical CO₂. The triazolocrown systems tested contain two triazole subcyclic units, which are suitable for complexation with divalent metal ions [14]. The solubilities of triazolocrown ethers 1 and 2 are in the range of $1\text{--}1.3 \times 10^{-5}$ M in CO₂ at 60°C and 200 atm [13]. Substitution of a tertiary butyl group at the benzene ring can significantly increase the solubility of the macrocyclic ligand in CO₂. The *tert.*-butyl substituted triazolocrown 3 has a solubility about 40 times greater than the ones without *tert.*-butyl substitution. The solubility of these triazolocrowns also increases

Table 2
Solubility of solid phosphine oxides in supercritical CO₂

Compound	MW	P (atm)	T (°C)	Solubility	
				(g/l)	(mol/l)
TBPO	218	200	60	184.9	8.5×10^{-1}
TOPO ^a	387	150	40	20.18	5.2×10^{-2}
TOPO ^a	387	200	45	25.35	6.6×10^{-2}
TPPO	278	200	60	2.127	7.7×10^{-3}

^a m.p. of TOPO is around 50–54°C. Experiments were performed at 40 and 45°C for solid TOPO. Data from Ref. [12].

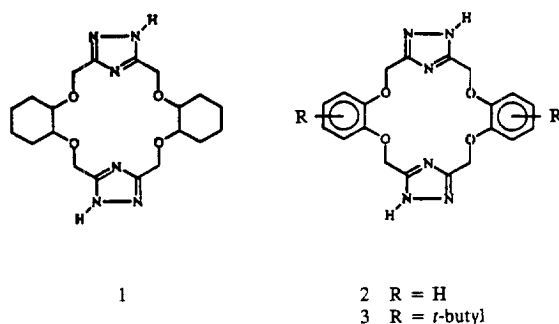


Fig. 1. Structures of the triazolocrowns tested for SFE of metals (Ref. [13]).

in MeOH modified CO₂ [13]. The increase in solubility for each crown ether system is about an order of magnitude from neat CO₂ to 5% MeOH modified CO₂.

The feasibility of SFE of metals using calixarene-based chelating agents was reported recently by Graham et al. [27]. Calixarenes are macrocyclic chelating agents that possess a lipophilic moiety (upper rim) and a metal coordinating moiety (lower rim). Most metals can form highly lipophilic complexes with the deprotonated forms of the simplest phenolic calixarenes. Experimental metal SFE data using calixarene based reagents are preliminary at the present time.

2.1.5. Other chelating agents

Designing chelating agents which are highly soluble in CO₂ is of interest to developing efficient metal extraction processes. It is well established that fluorinated compounds usually exhibit high solubilities in supercritical CO₂. Molecules which contain functional groups such as fluoroether and fluoroalkyl are considered CO₂-philic. Yazdi and Beckman [28] reported the synthesis of chelating agents containing a perfluoropolyether tail with average molecular weight of 2500 (DuPont Krytox) and chelating heads such as dithiocarbamate, dithiol, and picolyl amine. As much as 5–10 weight percent of these fluoroethyl ligands can be dissolved in CO₂. In terms of molarity, their solubility is in the range 10⁻²–10⁻³ M.

In general, it can be seen that many chelating agents show relatively high supercritical CO₂ solubilities. For analytical applications the fluorine substituted systems are clearly most favorable because of their high solubilities in CO₂ [2–4]. However, the high cost of fluorine-substituted ligands will probably limit their use in SFE. For hydrocarbon based ligands, aliphatic substituted systems show solubilities approaching those of fluorine substituted systems and these may have potential for larger scale applications [15]. *tert*-Butyl substitution appears to be an effective means of increasing solubility of ligands. Phenyl substituted ligands show the lowest solubilities and are not likely to find many supercritical fluid applications [12,25].

2.2. Solubility of metal chelates in supercritical fluids

Solubility of metal chelates in supercritical CO₂ is an important factor in determining the efficiency of metal extraction using this *in situ* chelation–SFE method. The solubilities of different types of metal chelates in supercritical CO₂ are discussed as follows.

2.2.1. Metal dithiocarbamate complexes

The solubility of metal–DDC chelates in supercritical carbon dioxide is generally low, typically in the range of 10⁻⁵ to 10⁻⁶ mol/l under normal SFE conditions [3,5,15]. Fluorination of DDC as in the case of FDDC can enhance the solubilities of the resulting metal chelates in supercritical CO₂ by 2–3 orders of magnitude [3–5]. Wang and Marshall showed that increasing the chain length of the R group, e.g. by substituting the two ethyl groups in DDC with two butyl groups, can also increase the solubility of the resulting metal chelates in supercritical CO₂ [15]. The solubilities of a number of metal dithiocarbamate chelates in supercritical CO₂ have been measured recently [16]. The experimental solubility data of metal dithiocarbamate in CO₂ were found to correlate with the Hildebrand solubility parameters of the free ligands calculated using a group contribution method [16] (Fig. 2). The solubility parameter of the ligands may provide a simple method for predicting the solubility of the resulting metal chelates in supercritical fluids. According to Fig. 2, the fluorinated metal complexes M(FDDC)₂ are always more soluble in supercritical CO₂ than the non-fluorinated ones. The least soluble ones are the PDC metal complexes with a ring structure associated with the ligand. The other linear alkyl substituted dithiocarbamate metal complexes show a general trend of increasing solubility in supercritical CO₂ with respect to increase in chain length. The solubility of each metal dithiocarbamate system follows the order M(FDDC)₂ > M(HDC)₂ > M(P5DC)₂ > M(BDC)₂ > M(P3DC)₂ > M(DDC)₂ > M(PDC)₂ [16] (Fig. 2). However, as the chain length increases, other properties of the ligand must be considered. Long chain dithiocarbamate ligands are difficult to synthesize. Experimental results also

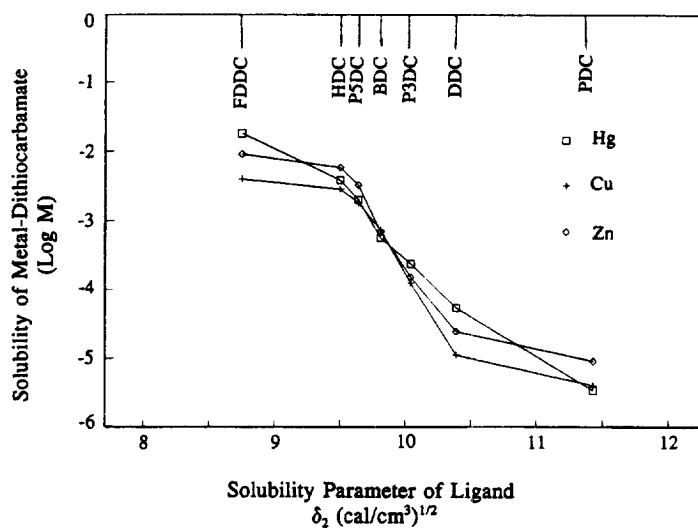


Fig. 2. Solubilities of metal dithiocarbamate complexes in supercritical CO_2 (60°C, 230 atm) versus the solubility parameters of ligands (Ref. [16]).

indicate that the SFE efficiency of FDDC for some metals in solid samples is usually better than those of large dithiocarbamate reagents with long alkyl chain substitutions. The small ligands are probably easier to diffuse into the solid matrix to form metal complexes which are also easier to migrate out of the solid-phase. The use of methanol modified CO_2 can further enhance the solubility of metal chelates, as shown in the case of $\text{Hg}(\text{FDDC})_2$ [5].

Changes in density (pressure) of supercritical CO_2 at a given temperature can significantly enhance the solubility of metal dithiocarbamate chelates. As shown in Fig. 3, the solubility of $\text{Cu}(\text{FDDC})_2$ increases from $0.35 \times 10^{-3} \text{ M}$ to $1.75 \times 10^{-3} \text{ M}$ as density increases from 0.18 to 0.55 g/cm^3 [3]. Metal dithiocarbamate complexes are much more stable in supercritical CO_2 relative to the free ligands. When $\text{Cu}(\text{FDDC})_2$ is placed in supercritical CO_2 at 60°C and 200 atm for 20 min, quantitative recovery of the metal complex can be achieved by dynamic extraction.

2.2.2. Metal- β -diketonates

β -diketonates are extensively used in the SFE of lanthanides, actinides and some transition metals. The fluorinated β -diketonates usually form very soluble metal complexes in supercritical CO_2 and thus

are more effective extractants especially for SFE of the f-block elements [7–10].

Hamdi et al. have studied the solubility of a range of different metal-AA and metal-HFA complexes in supercritical CO_2 [29]. The solubilities of $\text{Cu}(\text{AA})_2$ and $\text{Y}(\text{AA})_3$ in supercritical CO_2 were found to be 0.37 and 0.082 g/l , respectively, at 170°C and at a CO_2 density around 0.330 g/ml . The effect of fluorine substitution upon solubility of metal β -diketonates can be seen from the yttrium complex $\text{Y}(\text{HFA})_3$ which has a solubility of 4.06 g/l at the same temperature and density, about 50 times greater than $\text{Y}(\text{AA})_3$. Ashraf-Khorassani et al. also reported more than 40-fold enhancement in solubility for $\text{Cr}(\text{HFA})_3$ relative to $\text{Cr}(\text{AA})_3$ in supercritical CO_2 at 60°C and 200 atm [30].

Saito et al. have studied acetylacetonate complexes of different metals including Ga, In, Zn, Mn, Co, Cu, and Li at 60°C and 290 atm [31]. The solubilities are 3.01, 2.63, 1.26, 1.01, 0.62, 0.40, 0.25, 0.21, and 0.01 mg/l for $\text{Ga}(\text{AA})_3$, $\text{In}(\text{AA})_3$, $\text{Mn}(\text{AA})_3$, $\text{Zn}(\text{AA})_2$, $\text{Co}(\text{AA})_3$, $\text{Mn}(\text{AA})_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{AA})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{AA})_2$, and $\text{Li}(\text{AA})$, respectively, at the specified temperature and pressure. The solubility of the metal complexes at 60°C is much lower than those observed at 170°C. The poorest solubility was observed for Li complex and this can be interpreted in terms

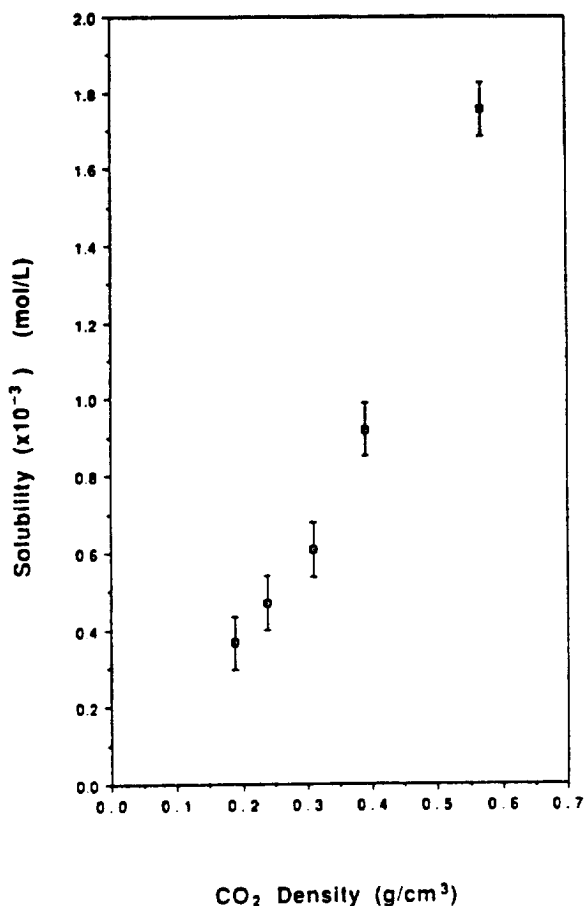


Fig. 3. Solubility of $\text{Cu}(\text{FDDC})_2$ in supercritical CO_2 as a function of density at 50°C (Ref. [3]).

of the inability of the single AA ligand to shield the ionic Li from the supercritical CO_2 . The highest solubility was observed for the elements In and Ga, which may be related to their chemical behavior lying between metallic and non-metallic systems. For elements which exist in the oxidation states 2^+ and 3^+ (Mn and Co), it was observed that the higher oxidation state complex shows an enhanced solubility. This can be correlated to a more complete shielding of the 3^+ metal ion center with a greater number of ligands so that the solvation of the resulting complex is enhanced due to the increase in solute/solvent interactions between the supercritical CO_2 and the organic part of the complex.

Lagalante et al. have studied the solubility of copper β -diketone and chromium β -diketone systems

with 9 different types of β -diketone ligands [32]. A direct correlation was observed between the metal complex solubility and the Hildebrand solubility parameter of the free ligands (Fig. 4). These authors also noted that the metal complexes of the fluorinated β -diketones always have high solubilities, with the HFA complexes having the highest values. The lowest solubility was observed for the benzyl substituted β -diketone system, correlating with the general observation for organic compounds.

β -diketones form quite soluble lanthanide complexes in supercritical CO_2 . For example, the solubilities of $\text{La}(\text{FOD})_3$ and $\text{Eu}(\text{FOD})_3$ in CO_2 at 60°C and 150 atm were reported to be 5.5×10^{-2} and 7.9×10^{-2} mol/l, respectively [8].

2.2.3. Metal complexes with organophosphorus reagents

Recently, organophosphorus reagents have been utilized for metal extraction in supercritical CO_2 . The solubilities of some Cu complexes with Cyanex reagents at 60°C and different pressures are given in Table 3. The solubilities of these Cu complexes with Cyanex reagents in CO_2 all increase with pressure. At 300 atm, the solubility of the Cu-Cyanex 301 complex is 7.83 g/l or 0.011 mol/l, about an order of magnitude higher than that at 200 atm. Generally speaking, gram quantities of these metal complexes can be dissolved per liter of CO_2 . For environmental samples, metal contamination is often in the range 1 to 2000 mg/l [33]. The solubilities of the metal

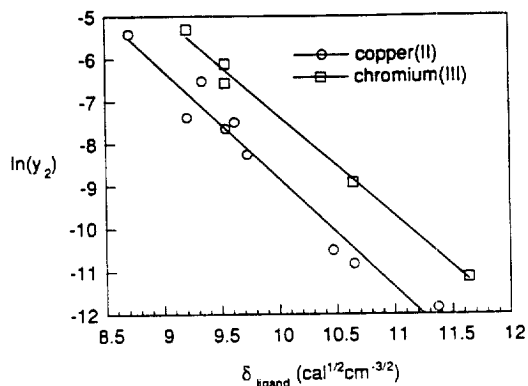


Fig. 4. Plot of $\ln(y_2)$ solubility in supercritical CO_2 at a density of 0.874 g ml^{-1} versus Fedors' calculated solubility parameter of the free ligand (Ref. [32]).

Table 3
Solubility of Cu complexes with cyanex reagents in supercritical CO₂ at 60°C and different pressures

Complex	MW	Solubility (g/l)		
		100 atm	200 atm	300 atm
Cu–Cyanex 272	642	–	0.083	0.51
Cu–Cyanex 301	706	0.022	2.65	12.06
Cu–Cyanex 302	674	–	0.9	7.83

complexes shown above would therefore be reasonable for achieving effective extractions and would unlikely be a rate limiting aspect of the extraction processes.

2.2.4. Metal complexes with macrocyclic compounds

The solubility of crown ether metal complexes has not been reported. This is partly due to the nature of the complexes that are formed, usually in ion-pairs, which are difficult to obtain in a purified crystal form. The solubility of *tert*-butyl-substituted dibenzobistriazolone crown ether in methanol-modified CO₂ is apparently high enough to permit its use for the extraction of ppm level of Hg²⁺ from sand, cellulose filter paper and liquid samples at 60°C and 200 atm [13].

2.2.5. Organometallic compounds

Only one organometallic compound, ferrocene, has been extensively studied for its solubility in supercritical CO₂ [34]. Ferrocene shows high solubility and the effect of increasing density upon solubility is almost independent of temperature. The high solubility of ferrocene is probably due to the nature of the bonding in the ferrocene compound. Ferrocene is a system in which the metal's 3d, p and s orbitals are filled so that no free coordination sites are available for interaction with the solvating CO₂, resulting in ferrocene having properties resembling an aromatic compound.

Generally speaking, the maximum metal complex solubilities observed in a supercritical CO₂ system are in the range 30 g/l to 60 g/l for both non-fluorinated and fluorinated systems [32,34,35]. This corresponds to dissolution of approximately between 5 g/l to 10 g/l of metals into the supercritical system. For analytical purposes, it is unlikely that

this level of metal ion loading of the supercritical CO₂ would be required, however, for larger scale applications this may limit some processes.

2.3. Effects of water and pH

The efficiency of metal extraction using the in situ chelation–SFE method generally increases significantly when a small amount of water is added to a solid matrix such as filter paper, sand, soil or wood. The presence of water probably facilitates metal chelation. The water may also serve as a modifier for the solute/matrix interactions by blocking the active sites of the matrix, thus reducing the adsorption of the solute by the active sites of the polar matrix [36]. Water can also substitute for metal in matrix coordination site and facilitate the migration of the metal complex from the solid matrix into the fluid phase.

Another factor that should be considered in the SFE of metals is pH. A recent report shows that when water is in equilibrium with CO₂ under normal SFE conditions, the pH of the water is around 2.9 due to the formation and dissociation of carbonic acid [17]. Metal chelate formation generally depends on pH. For example, dithiocarbamate reagents usually can extract metal ions in water from pH 2–8 [1]. Thus, the pH of unbuffered aqueous systems will fall directly to that range favored for efficient extraction. β -diketones also form extractable complexes with metal ions from neutral to slightly acidic solutions. The triazolocrown ethers extract mercury in slightly acidic solutions (pH 2.5 to 6) and other divalent metal ions in neutral solutions. Thus, they are selective for SFE of Hg²⁺ in systems containing water. The Cyanex reagents and other organophosphorus extractants are effective for extraction of metals from acidic media [12]. They are potential extractants for metal recovery from acid solutions by SFE. Information on pH dependence of specific ligands for metal extraction in supercritical fluid can be obtained from relevant solvent extraction experiments [1].

2.4. Temperature and pressure

The supercritical fluid pressure in the extraction cell has a decisive effect on the efficiency of extraction. The behavior of an extraction system as a

function of pressure is quite similar no matter what kind of supercritical fluid is used. With increase in pressure, the density of supercritical fluid CO_2 will increase, thus enhancing the solubilities of ligands and metal chelates, consequently the extraction efficiency of metals [3,5,16]. Changing the temperature of the extraction cell also has a large effect as it alters the analyte volatility, extraction kinetics and supercritical fluid density. The effects can be different since, while the analyte volatility and extraction kinetics are usually favored by increased temperatures, the resulting decreased density gives rise to varying effects on the extraction process.

2.5. Chemical forms of metal species

Metals can exist in natural environments as organometallic compounds, ionic species, and inorganic compounds such as oxides, sulfides, etc. SFE of metals is therefore more complicated than that of organic compounds. Some forms of metal species or compounds may not be extractable by the ligands utilized in SFE. Thus with proper selection of ligands, SFE may provide a means of metal speciation in natural samples. Organometallic compounds usually are soluble in supercritical fluid, therefore they may be extracted without a ligand. Wai et al. demonstrated that methylmercuric chloride and dimethylmercury spiked in water or solid materials can be effectively extracted by supercritical CO_2 at 50°C and 100 atm [5]. After removing the organomercurial compounds, a dithiocarbamate reagent can be introduced to extract Hg^{2+} ions in CO_2 . Using this kind of sequential extraction, separation of the organic and inorganic mercury species may be achieved. Arsenic speciation is another example. Arsenic can exist in natural samples as As^{3+} , As^{5+} , monomethylarsinic acid (MMA) and dimethylarsonic acid (DMA). A method for speciation of these arsenic species was reported by Wenclawiak and Kraha who developed a reactive SFE and chromatographic method for separating the organic DMA, MMA, and the inorganic arsenic species in solid samples [37]. Thioglycolic acid methyl ester (TGM) was used to react with the arsenic compounds. Derivatization with TGM was done during SFE. A capillary-SFC method was used for the analysis of the TGM derivatives of organic and inorganic arsenic species

and a comparison was made with GC. The resulting recoveries for DMA and MMA were more than 90%.

2.6. Matrix

The nature of the solid matrix plays an important role in determining the efficiency of extracting organic compounds as well as metal complexes by supercritical CO_2 . When metal ions are spiked onto solid supports such as filter papers or sand, high extraction efficiencies are usually observed using the in situ chelation-SFE method. This may not be true when metal ions are spiked in real soil samples. The active sites and natural ligands present in real soil systems may bind strongly to certain metal ions hindering their complexation with added ligands. In real environmental samples native metals can also be in highly insoluble forms such as oxides and sulfides. Dissolution and extraction of these insoluble metal compounds from solid matrices depend upon the chelation ability of the ligand and the accessibility of the compound sites. Consequently, a certain fraction of native metals in solid samples such as soil may not be extractable by this SFE method [26]. The metal fraction which is not extractable by supercritical CO_2 probably represents the unextractable metal in soil. This implies that the in situ-SFE technique may be used to evaluate the amounts of leachable metals in solid matrices [26].

3. SFE of organometallic compounds

Organic bound metal species in natural samples can be charge neutral or in ionic forms. Ionic compounds such as organotin ($\text{R}_m\text{SnX}_{4-m}$, $m = 1-3$) from aqueous and solid samples cannot be directly extracted with neat CO_2 because of the charge neutralization requirement. However, when ionic compounds are bound to organic ligands or form ion-pairs, their solubility in supercritical CO_2 is significantly increased, enabling the extraction of ionic organometallic compounds from liquid or solid matrices [4,38,39]. For the determination of organotin in aqueous and solid matrices, Bayona and Cai investigated ethylation of ionic organotins by sodium tetraethylborate, enrichment of the in situ derivatized organotins on a C_{18} disc, and then acid-

modified extraction with supercritical CO₂ [40]. Alzaga and Bayona utilized these methods to extract dibutyltin and tributyltin and the degradation products from seawater [41]. They also demonstrated the extraction of these compounds from aqueous matrices using C₁₈ liquid–solid extraction discs, followed by *in situ* Grignard ethylation and SFE of the derivatized liquid–solid extraction discs. Using static plus dynamic extraction mode at 40°C and 100 atm, the optimum extraction efficiency of dibutyltin and tributyltin from synthetic seawater at pH 2 exceeded 92% [41]. Bayona et al. also developed a procedure for the simultaneous speciation of butyl-, phenyl-, and cyclohexyltin in sediment samples at 40°C and 350 atm [42] as well as a SFE procedure for tributyltin in the same matrix at 60°C and 350 atm [43]. This study and the other related work relevant to SFE of organotin compounds in aquatic sediments were reviewed recently by Bayona [44]. A comparison of SFE with improved tropolone solvent extraction method for determining butyltin species from sediments was reported by Chau et al. [45]. With the addition of NaDDC as a chelating agent, both the dibutyltin and tributyltin species can be quantitatively recovered by SFE from the sediments [45]. An off-line complexation–SFE method for 13 organotin compounds was reported by Liu et al. [46]. These authors also reported the determination of organotin compounds in environmental samples by SFE and GC–AED [47]. Amended with a chelating agent diethylammonium diethyldithiocarbamate, soil and sediment samples were extracted with 5% methanol modified CO₂ at 60°C and 450 atm by these authors. The extracted materials were treated with pentylmagnesium bromide to convert the ionic organotin into their neutral derivatives, which are amenable to GC–AED [46]. A determination of the organotin compounds by on-line SFE–SFC using formic acid-modified CO₂ with flame ionization detection was developed and evaluated by Oudsema and Poole [48,49].

A method for the SFE of ionic alkyllead species from sediment and urban dust was reported by Johansson et al. [50]. The results indicated that methanol was an optimal modifier comparing with other modifiers such as water and acetone. The ionic alkylleads were extracted as DDC complexes into hexane, propylated using a Grignard reagent, and

quantified by GC–MS. At 80°C and 450 atm, extraction recoveries are more than 96% for trimethyllead, and triethyllead, and 80% for diethyllead from spiked sediment samples. An urban dust sample was also analyzed using the developed procedure [50].

The extraction of alkyllead and alkyltin compounds in soil and in polyvinyl chloride plastic samples was investigated by Li using supercritical chlorodifluoromethane as the solvent [51]. The separation and determination of extracts from solid samples was performed using micellar electrokinetic capillary chromatography.

The extraction of dimethylmercury and methylmercuric chloride from solid materials by neat CO₂ at 50°C and 100 atm was demonstrated by Wai et al. [5]. A small amount of water is required to achieve quantitative extraction of methylmercuric chloride from filter paper by supercritical CO₂. Simon reported the extraction of methylmercury from biological tissues (dogfish muscle and liver) using supercritical CO₂ modified with methanol [52]. Calcium chloride and water were added to the samples to facilitate the partitioning of methylmercury from the sample matrix to the supercritical fluid CO₂.

4. SFE of toxic metals

Using FDCC as a chelating agent, metal ions including As³⁺, Au³⁺, Cd²⁺, Cu²⁺, Ga³⁺, Hg²⁺, Pb²⁺, Pd²⁺, Sb³⁺, and Zn²⁺ spiked in solid materials such as filter papers and sand can be effectively extracted by methanol modified supercritical CO₂ [2,7,11,26]. Wang and Wai recently reported that bioaccumulated mercury in aquatic plants can also be extracted by the *in situ* chelation–SFE process. Dithiocarbamate reagents are most effective for removing the bioaccumulated mercury in supercritical CO₂ [53]. Other commercially available chelating agents such as thiourea, EDTA, HFA, and Tris are not as effective as the dithiocarbamate reagents. Fluorinated β-diketones (TFA, HFA, and TTA) can also effectively extract heavy toxic metals from solid matrices including sand, filter paper, and real soil samples, although not as effective as FDCC [11].

The feasibility of extracting toxic metals (As, Cd,

Cr, Cu, and Pb) from real contaminated soil and wood samples using the Cyanex reagents as extractants in supercritical CO₂ was evaluated recently [26]. The extractions were performed at 60°C and 200 atm using neat CO₂ or 5% methanol modified CO₂. A significant fraction of the toxic metals in these contaminated samples can be removed by methanol modified CO₂-containing Cyanex 302. The amounts of the metals removed by SFE appear to correspond to the leachable metals determined by the Toxicity Characteristics Leaching Procedure (TCLP) [54].

The in situ chelation–SFE technique was also used by Liu et al. for the extraction of Cu²⁺, Co²⁺, Cd²⁺, and Zn²⁺ from filter papers, sand, and silica gel [38]. LiFDDC was used as a chelating agent and the extracted metal complexes were determined by GC–AED. The recoveries ranged from 70% to 100% [38]. In order to avoid contamination from stainless steel, polyetheretherketone (PEEK) components were used to modify the apparatus in Liu's experiments. Coupling metal SFE with on-line detection by AAS was reported by Wang and Marshall [55]. The system was able to operate at normal extractor flow-rates and to provide sensitivities equivalent to conventional flame AAS. Heavy metals including As, Cd, Cu, Mn, Pb, Se, and Zn in aqueous solutions were derivatized by in situ complexation with tetrabutylammonium dibutylthiocarbamate and the complexes formed were mobilized into supercritical CO₂ for the AAS. Wang and Marshall also used the SFE method to separate and characterize the Cd, Zn, and Cu bound to metallothionein (MT) isolated from rabbit liver samples [56]. Without a complexing reagent, approximately 12, 13 and 15% of the MT bound Cd, Zn, and Cu, respectively, were mobilized

in supercritical CO₂ from a 0.1 M NaHCO₃ solution. In the presence of tetrabutylammonium dibutylthiocarbamate in CO₂, quantitative recovery of Cd was obtained if the MT had been dissolved in water. This approach of SFE with and without the added complexing reagent coupled with on-line detection of metals by AAS may be a speciation technique for analyzing protein bound heavy metals.

5. SFE of lanthanides and actinides

Lanthanides and actinides in solid and liquid materials can be extracted with β-diketones dissolved in supercritical CO₂ [2,7,9,57]. Fluorine-containing β-diketones such as HFA, TTA, and FOD are more effective than the non-fluorinated AA for SFE of the f-block elements.

A strong synergistic effect was observed for the extraction of lanthanides from solid samples when a mixture of TBP and a fluorinated β-diketone was used in neat CO₂ [8,10]. Tributylphosphate alone is ineffective for SFE of lanthanides from solids as shown in Table 4. This result is expected because TBP is neutral and trivalent lanthanide ions are not extractable by supercritical CO₂ without counteranions. However, when TBP is mixed with TTA, the extraction efficiencies of the mixed ligands for the lanthanides are drastically increased with respect to each individual ligands (Table 4). Synergistic extractions of lanthanides with mixed ligands are known in conventional solvent extraction experiments [58]. The coordination number of trivalent lanthanide ions is usually large, up to 8 or 9. TBP probably replaces the coordinated water molecules by forming adducts with the Ln(TTA)₃ complexes

Table 4

Percent extraction and recovery of La³⁺, Eu³⁺ and Lu³⁺ from sand with neat CO₂-containing TTA, TBP and mixed TTA+TBP at 60°C and 150 atm

Ligand	Amt.	Extraction (%)			Recovery (%)		
		La ³⁺	Eu ³⁺	Lu ³⁺	La ³⁺	Eu ³⁺	Lu ³⁺
TTA	80	40±3	51±3	65±4	29±3	40±3	60±4
TBP	80	4±3	3±1	5±2	2±1	2±1	3±1
TTA+TBP	40+40	91±3	92±4	95±4	91±3	89±4	91±4

^a Each sand sample (300 mg by weight) contains 10 μg each of La³⁺, Eu³⁺ and Lu³⁺. 10 min of static extraction followed by 20 min of dynamic extraction. Data from ref. [8].

which become more soluble in supercritical CO₂, making them easier to move from solid-phase into the fluid phase.

Uranium and thorium in solid and liquid materials can also be extracted by supercritical CO₂-containing fluorinated β-diketones. For example, spiked UO₂²⁺ and Th⁴⁺ in sand can be extracted by supercritical CO₂-containing TTA with efficiencies around 70–75%, at 60°C and 150 atm. Using a mixture of TTA and TBP, the extraction efficiencies of UO₂²⁺ and Th⁴⁺ are increased to >93% [10]. The feasibility of extracting uranyl ions from natural samples using the mixed ligand approach was tested using mine wastes collected from an abandoned uranium mine in the Northwest region, USA. The uranium concentrations in two mine waters tested were 9.6 g/ml and 18 g/ml, respectively. The mine waters were extracted with a 1:1 mixture of TTA and TBP in neat CO₂ at 60°C and 150 atm for a static time of 10 min followed by 20 min of dynamic extraction. Under the specific experimental conditions, the percent extraction of uranium from these samples were 81±4% and 78±5%, respectively. The mine waters were also added to a top soil sample collected from northern Idaho. The contaminated soil samples were dried at room temperature. The results of extraction of uranium from the contaminated soil samples with a 1:1 mixture of TTA/TBP or HFA/TBP in supercritical CO₂ at 60°C and 150 atm are given in Table 5 [10,57]. The percent extraction of uranium with HFA/TBP for both soil samples A and B is about 90%, whereas TTA/TBP shows lower percent extractions (77–82%) of uranium under the same conditions. HFA/TBP appears to be more effective

Table 5

Extraction of uranyl ions from mine waters and from contaminated soils

Sample	U concentration	Ligand	(%) Extraction
Mine Water A	9.6 g/ml	TTA + TBP	81±4
Mine Water B	18.0 g/ml	TTA + TBP	78±5
Soil A	6.3 g/100 mg	HFA + TBP	91±4
		TTA + TBP	82±5
Soil B	15.4 g/100 mg	HFA + TBP	89±5
		TTA + TBP	77±4

^a For mine water experiments: 4-ml sample, 200 μmole each of TTA and TBP; for soil experiments: 100-mg sample, 200 μmole each of TTA and TBP or HFA and TBP. Data from Ref. [10].

than TTA/TBP for synergistic extraction of uranium from soil samples in supercritical CO₂.

In highly acidic solutions (1–6 M HNO₃), organophosphorus reagents such as TBP and TBPO in supercritical CO₂ can extract uranyl ions (UO₂²⁺) and thorium ions (Th⁴⁺) effectively [12]. The extraction efficiencies for UO₂²⁺ and Th⁴⁺ using TBP-saturated supercritical CO₂ are comparable to those observed in solvent extraction with kerosene containing 19% v/v TBP [12]. Uranyl in nitric acid solutions is probably extracted as (UO₂)(NO₃)₂·2TBP in supercritical CO₂. When the stronger Lewis base TBPO or TOPO is used as the extracting reagent in supercritical CO₂, the extraction efficiencies of uranyl and thorium ions are higher than that of TBP (Table 6). These results suggest that supercritical CO₂ may be used to replace the organic solvents conventionally utilized in the Purex process.

Tributylphosphate modified CO₂-containing TTA was used to extract lanthanides from an acidic aqueous matrix by Laintz et al. [59]. Near-quantitative extraction of Sm³⁺, Eu³⁺, Gd³⁺, and Dy³⁺ from a 6 M HNO₃ + 3 M LiNO₃ solution by TBP-modified supercritical CO₂ was observed.

Extractions of Yb, Ho, and La from aqueous solutions using TBP-modified CO₂ and TBP-modified CO₂ containing di(2-ethylhexyl)phosphoric acid (D2EHPA) were studied by Dehghani et al. [60]. With D2EHPA, extraction of the trivalent lanthanide

Table 6

Percent extraction of uranyl and thorium ions from nitric acid solutions with supercritical CO₂-containing organophosphorus reagents at 60°C and 200 atm

Sample matrix	Extraction reagent	Extraction (%)	
		UO ₂ ²⁺	Th ⁴⁺
6 M HNO ₃	TBP	91	80
	TBPO	99	98
	TOPO	99	98
1 M HNO ₃	TBP	52	26
	TBPO	99	99
	TOPO	98	98
0.1 M HNO ₃	TBP	12	20
	TBPO	97	91
	TOPO	89	93

^a Extraction conditions: 15 min static followed by 15 min dynamic at 60°C and 200 atm. Sample volume: 4 ml containing 50 μg/ml each U and Th. Data from Ref. [12].

ions is more effective than that without D2EHPA in the TBP-modified CO₂.

Furton et al. evaluated the extraction and spectrophotometric determination of UO₂(NO₃)₂·6H₂O from different solid matrices by liquid ethanol and by supercritical CO₂ using FOD and TBP as extractants [61]. The highest recoveries were observed with supercritical CO₂ modified with FOD (0.1 M), TBP (0.1 M), and ethanol (5% v/v). Comparing with liquid ethanol extraction, SFE method required a shorter extraction time and produced higher recoveries and greater precision.

6. Summary

The in situ chelation–SFE technique described in this paper provides a new method for extracting trace metals, lanthanides, and actinides directly from solid and liquid samples. This sample preparation method avoids the use of acid leaching and organic solvent extraction required for separation and concentration of trace metals in conventional methods. A variety of ligands, including dithiocarbamates, β-diketones, organophosphorus reagents and macrocyclic compounds, can be utilized for SFE of metal species. Some of them are general complexing agents and others are selective for certain metals. Experimental data indicate that fluorinated ligands usually form highly soluble metal complexes in supercritical CO₂ and thus are very effective for SFE applications. Alkyl substitution in ligands, especially tert-butyl substitution, can also enhance the solubility of metal complexes in supercritical CO₂. In some cases, SFE efficiencies for metal species can be enhanced using a mixture of ligands. With proper selection of ligands, separation of organic and inorganic metal species can also be achieved. Most of the SFE experiments reported in the literature deal with simulated samples with simple matrix. In real samples, the matrix plays an important role in determining the efficiency of metal extraction by supercritical CO₂. Metal ions in aqueous samples usually can be quantitatively extracted by supercritical CO₂ containing suitable ligands. In real soil samples, certain fractions of metals are not extractable by this SFE method. It is possible that the metal species extracted

by supercritical CO₂ may represent the leachable metals in solid matrices.

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