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Review

Supercritical fluid extraction of metal ions and metal chelates from different environments

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Abstract

Metal ions and metal chelates have been extracted from both solid and aqueous matrices using both pure and modified supercritical fluid CO₂. It has been demonstrated that fluorinated chelates have higher solubility in the supercritical fluid which can cause enhanced extraction efficiency. Stability of the neutral metal chelate under supercritical conditions plays an important role in the extraction of metal ions from water. Also, it has been demonstrated that the matrix can have a major effect on extraction of both metal ions and metal chelates. Addition of modifier to both matrix and supercritical fluid can increase extraction efficiency of analytes. © 1997 Elsevier Science B.V.

Keywords: Reviews; Metal ions; Metal chelates

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1. Introduction

One of the most common methodologies for the extraction of metal ions from aqueous and solid matrices is the reaction of a metal ion with a specific ligand to form a neutral metal complex followed by solvent extraction. Extraction procedures for metal ions and organometallics from solid matrices usually

require leaching procedures to release the metal ions from the matrix before complexation and solvent extraction. The organic extraction solvent, often toxic and in relatively large volume, creates environmental concerns in terms of both solvent handling and disposal.

Supercritical fluids have become an attractive alternate extraction medium in the past decade. The high diffusivity, low viscosity and variable solvent strength are some of the attractive features of

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supercritical fluids (SF). Carbon dioxide (CO_2) is the most common fluid for supercritical fluid extraction (SFE). The moderate critical temperature (31°C) and critical pressure (73 atm; 1 atm=101 325 Pa), chemical inertness, low cost and wide availability in pure form are a few of the advantages of supercritical CO_2 . Most of the studies in the literature (>95%) regarding SFE have dealt with organic compounds. However, the number of publications dealing with SFE of metal ions, metal chelates and organometallic compounds from various matrices are limited. We wish therefore to review here the literature as it relates to these topics.

2. Solubility of metal complexes

The experimental techniques for measuring the solubility of a compound in a supercritical fluid are either dynamic or static. In the dynamic case, solute is continuously but slowly swept with SF. The solubility is measured based on weight of the analyte dissolved in an exact volume of fluid. In this case solubility would be expressed in moles of analytes per liter of SF at the given density. Solubility is also commonly reported as mole fraction of analyte wherein moles of fluid can be obtained from volume and density. In this technique, solubility depends on the flow of fluid passing by the analyte. Fig. 1 shows the solubility of ethyl centralite (Fig. 2) in supercritical CO_2 (w/w) using different flow-rates [1]. As can be observed solubility of the analyte was a function

of the CO_2 flow-rate through the flow cell. At low flow-rates, solubility increased because the system is closer to equilibrium conditions, while at higher flow-rate solubility was lower.

In the static mode, the cell is loaded with a known amount of solute and SF at a known density. Usually equilibrium between solute and SF is obtained using either re-circulation or diffusion to homogenize the fluid. In the re-circulation technique, a circulating pump is used to recirculate the SF in a closed system after system pressurization which allows equilibrium to be established between the undissolved solute and the solute solvated by SF. Analysis in this case is usually accomplished by using a spectroscopic method such as ultraviolet spectroscopy. This technique is more convenient since the analysis is in situ, and equilibrium can be obtained easily, however the effect of the SF on the spectral absorption properties of the analyte and the band shape of the solute complicate these measurements. In addition, adsorption of solute on to the UV or IR cell window from the saturated solution may occur, which would yield incorrect results. In the static diffusion mode, after the system pressurization the equilibrium between the solute and SF is attained by allowing the solubilized solute to diffuse into the SF for a certain period of time. After attainment of equilibrium, the cell is depressurized and the analyte dissolved is collected in an organic solvent. The solubility of an analyte in this case can be measured using either gravimetric or spectroscopic methods. This technique has several pitfalls: (A) equilibration by diffusion

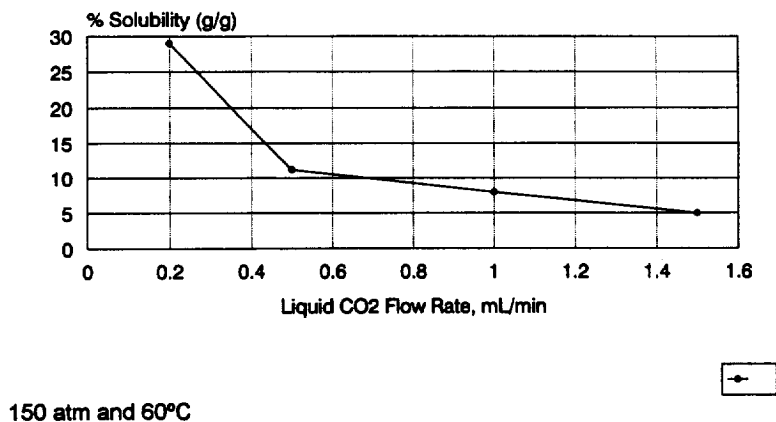


Fig. 1. Effect of liquid CO_2 flow-rate on % solubility of ethyl centralite.

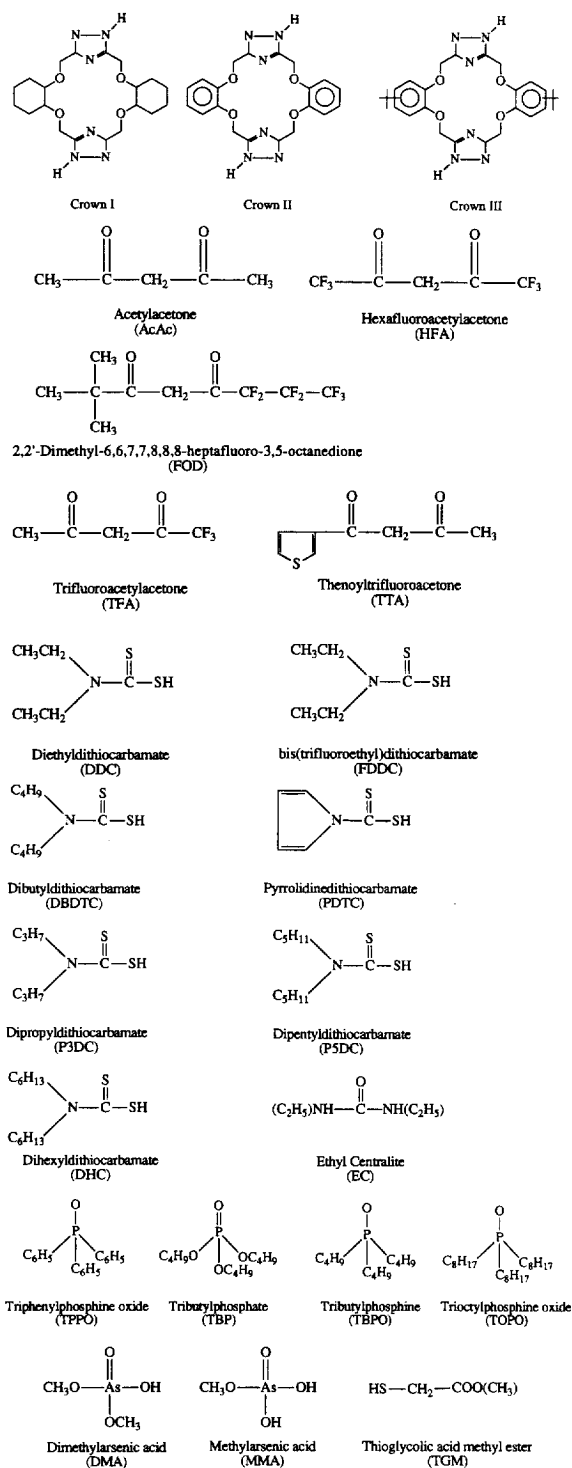


Fig. 2. Structure of different ligands.

may take more than 1 or 2 h, (B) precipitation of the analyte on the top and inside of the extraction tube during the depressurization may occur and (C) the restrictor may plug due to the high concentration of analytes in the decompressing fluid.

It is known that cationic metal ions are not soluble in pure CO₂ due to weak interactions between the positively charged metal ion and the non-polar CO₂ [2]. Therefore, one can conclude that extraction and separation of metal ions via supercritical CO₂ is not feasible. However, metal ions may be solubilized, extracted and separated via binding them to an organic ligand which results in the formation of a neutral stable metal complex that often exhibits considerable solubility in supercritical fluids. Rapid complexation kinetics between metal ion and ligand and a high stability constant for the resulting neutral complex can obviously enhanced the extraction process.

A key factor in supercritical CO₂ extraction of metal complexes from different matrices is a reasonable solubility for the metal chelate in supercritical CO₂. In this regard, different types of ligands have been used for complexation and extraction of trace metals in supercritical CO₂. The literature, however, regarding the solubility of metal chelates in supercritical CO₂ is very limited. In 1991, M'Hamdi et al. [2] measured the solubility of β -diketonate complexes of Cu⁺², Y⁺³ and Ba⁺² [i.e., the β -diketonate was either acetylacetonate anion (AcAc) or hexafluoroacetylacetonate anion (HFA), Fig. 2] in supercritical CO₂ at different pressures and temperatures. Solubility measurements were based on the weight of solute lost from the extraction cell and the mass of CO₂ which passed through the extraction system. In this study, hexafluoroacetylacetonate complexes showed higher solubility in supercritical CO₂ than the acetylacetonate complexes.

Lin et al. used the static mode with a 30 min equilibrium time to measure the solubility of lanthanide and europium 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (FOD), Fig. 2, (La(FOD)₃ and Eu(FOD)₃) in supercritical CO₂ [5]. Analysis of the collected material was obtained via neutron activation analysis. The reported solubility of La(FOD)₃ was approximately two to three orders of magnitude higher than that obtained for metal-AcAc complexes. The high solubility of La(FOD)₃ in supercritical

CO₂ was related to the fact that FOD forms thermally stable and highly volatile complexes with trivalent lanthanides [La(FOD)₃=(5.5±0.2)·10⁻² M and Eu(FOD)₃=(7.9±0.2)·10⁻² M].

Recently Ashraf-Khorassani et al. [7] used on-line SFE-HPLC to measure the solubility of different metal β-diketonate complexes in supercritical CO₂. Fig. 3 shows a schematic of the system used to determine the solubilities. In each measurement, the 0.5 ml extraction vessel was filled with a metal chelate. Next, the system was pressurized to 200 atm using pure CO₂. After pressurization of the system, the three-way valve was closed and a recirculating pump was activated (Fig. 3A). The function of the recirculating pump was to ensure complete saturation of supercritical fluid with the metal chelate of interest. After 30 min of equilibration, the 4 port-2 position valve with a 1 μl sample loop was rotated such that the solubilized chelate in supercritical CO₂ was directed from the 1 μl loop to the HPLC system

(Fig. 3B). The HPLC flow then washed the chelate from the injection loop through the column to a variable-wavelength UV absorbance detector operated at 280 nm. By employing a second valve (6 port-2 position valve), a stream of carbon dioxide or air could then pass through the sample loop to remove the chromatographic mobile phase from the loop, thus avoiding modification of supercritical fluid composition (Fig. 3C). The 4 port-2 position valve could then be rotated back to the load position and the procedure repeated (Fig. 3D).

This system had several advantages compared to systems used previously. First, solubility measurements were obtained in an organic solvent not under SF conditions. Second, complete equilibration between solute and supercritical fluid was achieved via a re-circulation pump. Finally, replicate measurements can be obtained without recharging the vessel with CO₂ or analyte. The solubility of metal hexafluoroacetylacetonates were found to be two to three

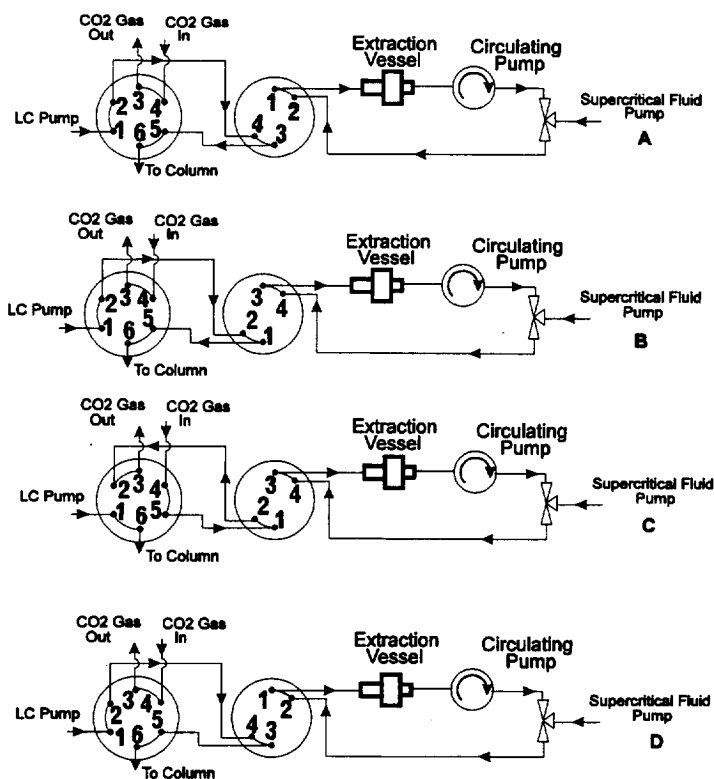


Fig. 3. Schematic of solubility measurement device.

Table 1
Solubility of different metal β -diketone complexes in supercritical CO₂

Metal	Acetylacetonone	Hexafluoroacetylacetonone	Ref.
Cu ⁺²	^a 6.20·10 ⁻⁶ , 119 atm, 150°C	^b (8.7±0.2)·10 ⁻² , 200 atm, 60°C	[2]
Cu ⁺²	^a 4.75·10 ⁻⁵ , 168 atm, 150°C	^b (8.6±0.2)·10 ⁻² , 400 atm, 60°C	[2]
Cu ⁺²	^a 7.25·10 ⁻⁵ , 218 atm, 150°C		[2]
Y ⁺³	^a 1.65·10 ⁻⁵ , 119 atm, 150°C	^a 7.25·10 ⁻⁴ , 119 atm, 150°C	[2]
Y ⁺³	^a 1.80·10 ⁻⁵ , 168 atm, 150°C	^a 8.35·10 ⁻⁴ , 168 atm, 150°C	[2]
Y ⁺³	^a 3.40·10 ⁻⁵ , 218 atm, 150°C	^a 9.30·10 ⁻⁴ , 218 atm, 150°C	[2]
Ba ⁻²		^a 7.90·10 ⁻⁵ , 119 atm, 150°C	[2]
Ba ⁻²		^a 2.20·10 ⁻⁴ , 168 atm, 150°C	[2]
Ba ⁻²		^a 2.40·10 ⁻⁴ , 218 atm, 150°C	[2]
Ni ⁺²		^b (8.0±0.1)·10 ⁻³ , 200 atm, 60°C	[7]
Ni ⁺²		^b (9.9±0.2)·10 ⁻³ , 400 atm, 60°C	[7]
Cr ⁺³		^b (>8.0·10 ⁻²), 200 atm, 60°C	[7]
Cr ⁺³		^b (>8.2·10 ⁻²), 400 atm, 60°C	[7]
Cr ⁻³	^b (2.0±0.1)·10 ⁻³ , 200 atm, 60°C		[7]
Cr ⁻³	^b (3.5±0.2)·10 ⁻³ , 400 atm, 60°C		[7]

^a Mol fraction.

^b Mol/l.

orders of magnitude higher than the solubility of metal acetylacetonates in keeping with the earlier study of M'Hamdi et al. (Table 1).

Laintz et al. [3] measured the solubility of different metal diethyldithiocarbamate (DDC) and bis-(trifluoroethyl)dithiocarbamate (FDDC) complexes (Fig. 2) in supercritical CO₂ [e.g., Ni(DDC)₂, Ni(FDDC)₂, Co(DDC)₃, Co(FDDC)₃, Cu(DDC)₂, Cu(FDDC)₂, Na(DDC), Na(FDDC), Bi(DDC)₃ and Bi(FDDC)₃]. A high pressure view cell connected to a UV-Visible spectrometer was used to measure the solubility of the metal chelates. In order to assure equilibrium between the analyte in the supercritical fluid and the free analyte, a magnetic stirrer coated with PTFE was placed in the view cell. After

pressurization of both the view cell and transfer line, the system was equilibrated by stirring for one hour. UV-Vis spectroscopic measurements were obtained under static supercritical conditions. The FDDC metal chelates were found to have approximately 2–3 orders of magnitude higher solubility than the comparable DDC metal chelates in supercritical CO₂ (Table 2).

In another study, Wai and coworkers [4,5] used a known amount of metal complex placed in a glass tube where both ends were plugged with glass wool. The sample tube was then placed in an extraction cell and pressurized to 150 atm. The cell was heated for 30 min at 60°C under static conditions. Following this period, the fluid and dissolved analyte were

Table 2
Solubility of different metal metal-diethyldithiocarbamate chelates in supercritical CO₂.

Chelate	Ligand=DDC	Ligand=FDDC	Ref.
Cu ⁺²	(1.1±0.2)·10 ⁻⁶ M, 100 atm, 50°C	(9.1±0.3)·10 ⁻⁴ M, 100 atm, 50°C	[3]
Na ⁺	(1.5±0.1)·10 ⁻⁴ M, 100 atm, 50°C	(4.7±0.1)·10 ⁻⁴ M, 100 atm, 50°C	[3]
Co ⁺³	(2.4±0.4)·10 ⁻⁶ M, 100 atm, 50°C	(8.0±0.6)·10 ⁻⁴ M, 100 atm, 50°C	[3]
Bi ⁺³	(1.3±0.1)·10 ⁻⁶ M, 100 atm, 50°C	<10 ⁻⁷ M, 100 atm, 50°C	[3]
Hg ⁻²	(8.2±0.6)·10 ⁻⁶ M, 100 atm, 50°C	(5.0±0.4)·10 ⁻³ M, 100 atm, 50°C	[4]
Hg ⁺²	(3.0±0.5)·10 ⁻⁵ M, 150 atm, 50°C, 5% MeOH	(1.2±0.4)·10 ⁻³ M, 150 atm, 50°C, 5% MeOH	[4]
Ni ⁺²	(8.5±1.0)·10 ⁻⁷ M, 100 atm, 50°C	(7.2±1.0)·10 ⁻⁴ M, 100 atm, 50°C	[4]
Zn ⁺²	1.1·10 ⁻⁶ M, 100 atm, 60°C	9.5·10 ⁻⁴ M, 100 atm, 60°C	[19]
Hg ⁺²	6.8·10 ⁻⁶ M, 100 atm, 60°C	3.0·10 ⁻³ M, 100 atm, 60°C	[19]

removed from the extraction cell by decompressing the fluid into a collection vial containing 5 ml of chloroform. After complete depressurization of the extraction cell, the glass tube containing the undissolved analytes was removed from the cell. Next, the empty extraction cell was flushed with excess high density CO₂. Any metal complex that may have been flushed out of the cell during this process was also collected. The solubility of the metal complex was measured based on the amount of metal complex dissolved in a volume of known density CO₂ equal to that of the extraction cell. Using this technique they measured the solubility of Hg(FDDC)₂ and Hg(DDC)₂ in both pure and 5% methanol modified CO₂ (Table 3). The solubility of Hg(FDDC)₂ increased from 5.0·10⁻³ M in pure CO₂ to 1.2·10⁻² M in 5% methanol modified CO₂ [4].

Wang and Marshall [6] used a similar technique, but without the use of any in situ glass tube, to measure the solubility of zinc dibutyl dithiocarbamate (Zn-DBDTC), Zn(DDC)₂ and Zn pyrrolidine dithiocarbamate (Zn-PDTC) complexes (Table 3 and Fig. 2). In this study, 0.5 to 0.8 g of test complexing agent contained in a cardboard thimble was placed inside the extraction cell. After 30 min under no-flow conditions, the cell was decompressed and analyte was trapped in methanol which was

subsequently analyzed spectrophotometrically at 298 nm. The solubility of the zinc chelates in most cases increased with increasing hydrocarbons chain length. The solubility of the metal complexes was found to decrease in the order of DBDTC>DDC>PDTC.

Recently Wai et al. [19] performed a similar study to measure the solubilities of Cu⁺², Hg⁺² and Zn⁺² complexes with seven different dithiocarbamate ligands (PDTC; DBTDC; DDC; P3DC which is dipropyl dithiocarbamate; P5DC which is dipentyl dithiocarbamate; DHC which is dihexyl dithiocarbamate; and FDDC) in supercritical CO₂ at 60°C and two different pressures (100 and 230 atm). They found that dithiocarbamate ligands with a small Hildebrand solubility parameter value yielded metal complexes that exhibited higher solubilities in supercritical CO₂ (Table 3). For example, PDTC with a solubility parameter of 11.43 cal^{1/2}/cm^{3/2} formed a copper complex [Cu(PDC)₂] which had a solubility of 4.1·10⁻⁷ M in supercritical CO₂ at 60°C and 100 atm, while FDDC with a solubility parameter of 8.75 cal^{1/2}/cm^{3/2} formed a copper complex [Cu(FDDC)₂] which had a solubility of 9.1·10⁻⁴ M under identical conditions (1 cal=4.184 J).

Wang et al. [9] used the same static technique to measure the solubility of three different bistriazolocrown ethers ligands (Fig. 2) in both pure and 5%

Table 3
Solubility of dithiocarbamate metal complexes in supercritical CO₂

Metal Chelates	Solubility	Solubility	Ref.
Zn[SC(S)N(C ₄ H ₉) ₂] ₂		5.3·10 ⁻⁴ M, 237 atm, 55°C	[6]
Zn[SC(S)N(C ₂ H ₅) ₂] ₂		3.3·10 ⁻⁵ M, 237 atm, 55°C	[6]
Zn[SC(S)NC ₄ H ₈] ₂		5.0·10 ⁻⁵ M, 237 atm, 55°C	[6]
Zn(PDC) ₂	3.2·10 ⁻⁷ M, 100 atm, 60°C	9.0·10 ⁻⁶ M, 230 atm, 60°C	[19]
Zn(P3DC) ₂	7.9·10 ⁻⁶ M, 100 atm, 60°C	1.5·10 ⁻⁴ M, 230 atm, 60°C	[19]
Zn(BDC) ₂	8.2·10 ⁻⁶ M, 100 atm, 60°C	6.9·10 ⁻⁴ M, 230 atm, 60°C	[19]
Zn(P5DC) ₂	1.6·10 ⁻⁴ M, 100 atm, 60°C	3.2·10 ⁻³ M, 230 atm, 60°C	[19]
Zn(HDC) ₂	3.2·10 ⁻⁴ M, 100 atm, 60°C	5.8·10 ⁻³ M, 230 atm, 60°C	[19]
Hg(PDC) ₂	3.5·10 ⁻⁷ M, 100 atm, 60°C	3.4·10 ⁻⁶ M, 230 atm, 60°C	[19]
Hg(P3DC) ₂	1.2·10 ⁻⁵ M, 100 atm, 60°C	2.3·10 ⁻⁴ M, 230 atm, 60°C	[19]
Hg(BDC) ₂	5.6·10 ⁻⁵ M, 100 atm, 60°C	5.6·10 ⁻⁴ M, 230 atm, 60°C	[19]
Hg(P5DC) ₂	1.0·10 ⁻⁴ M, 100 atm, 60°C	2.0·10 ⁻³ M, 230 atm, 60°C	[19]
Hg(HDC) ₂	1.6·10 ⁻⁴ M, 100 atm, 60°C	3.8·10 ⁻³ M, 230 atm, 60°C	[19]
Cu(PDC) ₂	4.1·10 ⁻⁷ M, 100 atm, 60°C	4.0·10 ⁻⁶ M, 230 atm, 60°C	[19]
Cu(P3DC) ₂	6.3·10 ⁻⁶ M, 100 atm, 60°C	1.2·10 ⁻⁴ M, 230 atm, 60°C	[19]
Cu(BDC) ₂	1.3·10 ⁻⁵ M, 100 atm, 60°C	7.2·10 ⁻⁴ M, 230 atm, 60°C	[19]
Cu(P5DC) ₂	9.0·10 ⁻⁵ M, 100 atm, 60°C	1.8·10 ⁻³ M, 230 atm, 60°C	[19]
Cu(HDC) ₂	2.1·10 ⁻⁴ M, 100 atm, 60°C	2.8·10 ⁻³ M, 230 atm, 60°C	[19]

Table 4
Solubility of miscellaneous ligand and metal chelates in supercritical CO₂

Metal complex and ligand	Solubility	Ref.
Crown 1	1.3·10 ⁻⁵ M, 200 atm, 60°C	2.1·10 ⁻⁴ M, 200 atm, 60°C, 5% MeOH [9]
Crown 2	1.0·10 ⁻⁵ M, 200 atm, 60°C	2.0·10 ⁻⁴ M, 200 atm, 60°C, 5% MeOH [9]
Crown 3	4.3·10 ⁻⁴ M, 200 atm, 60°C	1.3·10 ⁻³ M, 200 atm, 60°C, 5% MeOH [9]
Ferrocene	2.6·10 ⁻³ M, 134 atm, 40°C	[18]
Ferrocene	4.9·10 ⁻³ M, 244 atm, 40°C	[18]
Ferrocene	6.5·10 ⁻³ M, 335 atm, 40°C	[18]
5,7,12,14-Tetramethyl-2,3:9,10-dibenzo[<i>b,i</i>][1,4,8,11]tetraaza-cyclotetradecine nickel (II)	1.05·10 ⁻⁵ g/ml, 160 atm, 40°C, 10% MeOH 1.00·10 ⁻⁵ g/ml, 160 atm, 50°C, 10% MeOH 8.02·10 ⁻⁶ g/ml, 160 atm, 60°C, 10% MeOH 7.21·10 ⁻⁶ g/ml, 160 atm, 70°C, 10% MeOH	[18]
5,7,12,14-Tetramethyl-2,3:9,10-dibenzo[<i>b,i</i>][1,4,8,11]tetraaza-cyclotetradecine nickel (II)	1.70·10 ⁻⁵ g/ml, 250 atm, 40°C, 10% MeOH 2.01·10 ⁻⁵ g/ml, 250 atm, 50°C, 10% MeOH 2.44·10 ⁻⁵ g/ml, 250 atm, 60°C, 10% MeOH 3.44·10 ⁻⁵ g/ml, 250 atm, 70°C, 10% MeOH	[18]
5,7,12,14-Tetramethyl-2,3:9,10-dibenzo[<i>b,i</i>][1,4,8,11]tetraaza-cyclotetradecine nickel (II)	2.20·10 ⁻⁵ g/ml, 340 atm, 40°C, 10% MeOH 2.45·10 ⁻⁵ g/ml, 340 atm, 50°C, 10% MeOH 2.44·10 ⁻⁵ g/ml, 340 atm, 60°C, 10% MeOH 5.77·10 ⁻⁵ g/ml, 340 atm, 70°C, 10% MeOH	[18]

methanol modified CO₂. Solubilities of these crown ethers increased by an order of magnitude in 5% methanol modified CO₂ over 100% CO₂ (Table 4). These ligands were used for direct in-situ chelation of Hg⁺² and Au⁺³ from both solid and liquid matrices. Solubility of the metal chelates was not measured.

Cowey et al. [18] used dynamic conditions to measure the solubility of 5,7,12,14-tetramethyl-2,3,9,10 - dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine-nickel(II) in supercritical CO₂ and 10% methanol modified CO₂ at different pressures (160, 250 and 340 atm) and temperatures (40, 50, 60 and 70°C). The solubility of each analyte was measured by comparing the amount of collected analyte which was extracted with a certain volume of pure or methanol modified supercritical CO₂. The Ni complex solubility in 10% methanol modified CO₂ was varied from 7.2·10⁻⁶ to 5.77·10⁻⁵ g/ml depending on the pressure or temperature of the operation (Table 4). Cowey et al. [18] also measured solubility of ferrocene in pure and 10% methanol modified CO₂. The ferrocene solubility varied from 4.77·10⁻³

to 1.1·10⁻² g/ml depending on the pressure and temperature of the operation (Table 4).

3. SFE of metal ions and metal chelates

3.1. Solid matrices

Extraction of metal ions from various solid matrices have been demonstrated by several research groups. Laintz et al. [8] have extracted Cu⁺² spiked onto Celite. Extraction efficiency of Cu⁺² using FDDC, however, did not exceed 80% at a CO₂ density of 0.70 g/ml and 35°C. Later, Wai et al. [4] reported extraction of mercuric ion (Hg⁺²) from cellulose-based filter paper using LiFDDC as a chelating agent. In this experiment 10 µg of Hg⁺² was spiked onto filter paper. Then 10 mg of LiFDDC was added directly to the extraction vessel, thus creating a large excess of ligand relative to the mercuric ion. Extraction efficiency of Hg⁺² was less than 12% for a dry sample. The low extraction efficiency of mercuric ion was thought to be due to a

strong interaction between Hg^{+2} and the cellulose matrix. However, the addition of a small amount of water (10 μl) onto the matrix increased the extraction efficiency of mercuric ion to 84%. The extraction efficiency of Hg^{+2} was further increased from 84 to 95% with the use of 5% methanol modified CO_2 . This increase in extraction efficiency was stated to be mostly due to enhanced interaction between Hg^{+2} and the solvent modifier. In the same report, the extraction efficiency of spiked methylmercury and dimethylmercury onto filter paper was reported. Extraction efficiency of greater than 99% was reported for both compounds using pure CO_2 when filter paper was spiked with 10 μl of water.

Besides LiFDDC, other ligands such as bis-triazolo-crown ethers (Fig. 2) have been used for extraction of Hg^{+2} [9]. 5% methanol modified CO_2 saturated with tetrabutyl-substituted dibenzobis-triazolo-crown ether (Crown III) was found to extract only 78% of Hg^{+2} from sand, while, the same fluid in the presence of 10 μl of water improved extraction efficiency to more than 95%. The high extraction efficiency of Hg^{+2} in the presence of water was related to a higher modified fluid–solute interaction. Tetra-butyl-substituted dibenzobis-triazolo-crown ether was also used for extraction of similar heavy metal ions (Cd^{+2} , Co^{+3} , Pb^{+2} , Ni^{+2} , Mn^{+2} , Au^{+3} and Zn^{+2}) from sand and filter paper [9]. Extraction efficiencies of most metal ions besides Au^{+3} from wet matrices, were less than 4% even when using 5% methanol modified CO_2 . The efficiency of extracted Au^{+3} from wet filter paper using 5% methanol modified CO_2 was 79%.

Extraction of other heavy metal ions has been achieved using LiFDDC as a chelating agent. Liu et al. [10] reported extraction of Co^{+3} , Cd^{+2} , Zn^{+2} and Cu^{+2} from solid matrices (sand, soil and filter paper) using supercritical CO_2 saturated with LiFDDC. Metal ion recovery ranged from 70 to 100%. Extraction efficiencies were determined using gas chromatography–atomic emission detection. They reported that metal impurities in the stainless-steel extraction vessel can react with the ligand and positively affect the percent recovery of analyte. They suggested using a non-metal containing vessel such as polyether ether ketone (PEEK) which cannot affect extraction efficiency of metal ions.

Wai [11] has reported extraction of both divalent

and trivalent metal ions from spiked cellulose based filter and sand. Extraction efficiencies of greater than 90% were reported for Cd^{+2} , Cu^{+2} , Pb^{+2} , Pd^{+2} , Zn^{+2} , As^{+3} , Au^{+3} , Ga^{+3} and Sb^{+3} from sand and filter paper using LiFDDC ligand. Wang and Marshall [12] have separated and characterized Cd^{+2} , Zn^{+2} and Cu^{+2} bound to metallothionein (MT), isolated from rabbit liver samples, using supercritical CO_2 saturated with tetrabutylammonium dibutylthiocarbamate (TDBDTC) ligand. Quantitative recovery of Cd^{+2} was obtained if MT was dissolved in water.

Extraction of lanthanides and actinide series ions from a solid environmental sample has been investigated by several research groups. The first SFE of lanthanides and actinides was reported by Lin et al. [5] at the University of Idaho. In their report, the extraction of La^{+3} , Eu^{+3} , Lu^{+3} and uranyl [$(\text{UO}_2)^{+2}$] ions was performed from both wet and dry cellulose base filter paper using pure and methanol modified CO_2 . In each extraction, filter paper was spiked with 10 μg of lanthanide or actinide ion and 20 μl (80 mmol) of FOD was placed in the extraction cell. The chelation and solubilization processes were allowed to occur under static SFE conditions for 10 min. A wet sample was prepared by spiking 10 μl of water onto the filter paper. Following extraction, decompression and collection of analyte in chloroform, the lanthanides were back-extracted with 50% HNO_3 solution followed by Neutron Activation Analysis of the acid solution. Extraction efficiency of less than 20% was obtained for La^{+3} , Eu^{+3} and Lu^{+3} using pure CO_2 from a wet matrix. However, the recoveries increased to above 65 and 90% from dry and wet matrix, respectively, using 5% methanol modified CO_2 . In a similar fashion the extraction efficiency of uranyl ion spiked onto filter paper was studied. The extraction of [$(\text{UO}_2)^{+2}$] using 5% methanol-modified CO_2 containing FOD at 60°C and 150 atm from either dry or wet matrix yielded recoveries above 95%.

Different types of chelating agents such as LiFDDC and fluorinated crown ether carboxylic acid (sym-difluorobenzene-crown-5-oxyacetic acid) have also been used for SFE of lanthanide and uranyl ion [5]. Extraction efficiency of uranyl ion was greater than 80% using 5% methanol modified CO_2 saturated with LiFDDC in the presence of water, while

recoveries of La^{+3} and Lu^{+3} using the same fluid and ligand were less than 1%. Supercritical fluid extraction of lanthanides and uranyl ion using 5% methanol-modified CO_2 saturated with sym-di-fluorobenzo-16-crown-5-oxyacetic acid in the presence of water at 60°C and 150 atm was less than 7%.

Lin and coworkers [14,15] have used other fluorinated β -diketones [e.g., HFA, thenoyltri-fluoroacetone (TTA), trifluoroacetylacetone (TFA) and AcAc] for extraction of lanthanides and actinides using both pure and 5% methanol modified CO_2 . The extraction efficiency of La^{+3} , Eu^{+3} and Lu^{+3} from cellulose based filter paper using pure supercritical CO_2 saturated with different fluorinated β -diketones was less than 25%, while extraction efficiency of the same lanthanides using 5% methanol modified CO_2 saturated with the same fluorinated ligands varied from 11 to 95% depending on the ligand.

Similar results were obtained for the extraction of Th(IV) and U(VI) spiked onto cellulose-based filter paper. The recovery was less than 70% using pure CO_2 and greater than 95% when 5% methanol modified CO_2 used. From this study, it was concluded that extraction efficiency of both lanthanides and actinides depend on the structure of the ligand, following approximately the order; $\text{TTA} \approx \text{FOD} > \text{HFA} > \text{TAA} > \text{AA}$. They also evaluated the synergistic effect of tributyl phosphate (TBP, Fig. 2) for the extraction of lanthanides and actinides using both pure and modified supercritical CO_2 . Significant increases in the extraction efficiency of lanthanides and actinides from sand and filter paper (>90%) were observed when an equimolar amount of TBP and ligand (HFA, TTA or FOD) were added to the supercritical CO_2 . However, the extraction efficiency of the same lanthanides and actinides from the same matrices using supercritical CO_2 saturated with only ligand or TBP was not greater than 65%.

The effect of the matrix on lanthanide extraction was also investigated. A topsoil sample was spiked with 10 μg of La^{+3} , Eu^{+3} and Lu^{+3} each. The sample was extracted with neat CO_2 containing a mixture of TBP and one of the fluorinated β -diketones, HFA, TTA or FOD. Results showed that the best extraction efficiency of lanthanides (80, 88 and 92%) was obtained using a mixture of TBP and HFA. Recently, Furton et al. [17] determined the

extraction efficiency of uranium spiked onto solid matrices (e.g., polyester, glasswool, cotton and K-olin) via synergistic in-situ chelation using pure and modified CO_2 . They were able to conclude that SFE yielded higher recovery than conventional liquid extraction. In their study, high extraction recovery of uranium was obtained via 5% ethanol with 0.10 M FOD and 0.10 M TBP modified supercritical CO_2 .

Triorganotin compounds have been used for several years in agriculture science (a) as a biocide to combat fungal growth, (b) in wood preservative formulation to reduce fungal rot and (c) in marine plants as an antifoulant against barnacles [21]. Diorganotins have routinely been used as heat and light stabilizers in the polymer and food packing industries [22]. Oudsema and Poole [23,24] studied coupled on-line SFE and supercritical fluid chromatography (SFC) of organotin compounds using 0.3% formic acid modified supercritical CO_2 . Separation of twelve organotin compounds was obtained using Deltabond methyl column using 0.3% formic acid modified CO_2 . In another experiment, on-line SFE–SFC was used to extract and separate different organotin compounds from marine paint and spiked into a potato or almond matrices. This study was focused mainly on SFC rather than SFE.

Liu et al. [25] studied extraction of six tetraalkyltin and seven additional ionic organotin compounds from spiked topsoil using both pure and 5% methanol-modified CO_2 . All tetraalkyltin compounds were extracted from topsoil with recoveries of 90 to 110% using either fluid at 100 atm and 40°C. However, recoveries of ionic organotin compounds ranged from 70 to 90% when NaDDC was added to the sample matrix in order to neutralize the change. The addition of 5% methanol as a modifier did not increase extraction efficiencies of ionic organotin compounds. Later, the same group extended their study to extract different ionic organotin compounds from clay and sediments. All soil and sediment samples were treated with diethylammonium DDC prior to extraction. Extractions were performed using both pure and 5% methanol modified CO_2 . Results showed that most dialkyltin, trialkyltin and tetraalkyltin compounds can be quantitatively extracted from most of the matrices, while the recovery of monoalkyltin compounds from all matrices was less than 20% [26].

Extraction efficiency of greater than 80% was obtained [29] for tributyltin from both spiked and Certified Reference Material (CRM) sediment using 347 atm, 60°C and 20% methanol modified CO₂. The same group also studied in-situ derivatization of butyltin and phenyltin from sediment using hexylmagnesium bromide as a derivatizing agent and supercritical CO₂ as an extraction fluid. Once again, the recovery of monobutyltin was less than 20%, while recovery of di- and tributyltin was greater than 80%. Recoveries of monophenyltin, diphenyltin and triphenyltin were 40, 106 and 114%, respectively [30]. Chau et al. [31] compared extraction efficiencies of butyltin spiked in sediment and a CRM. Their results showed monobutyltin could be extracted up to 60% from a spiked sediment, while, the same analyte from the CRM using pure CO₂ was not detected in the extract. Extraction of the same analyte from the CRM using NaDDC modified CO₂ increased the extraction efficiency of monobutyltin to 148%. Extraction efficiency of di- and tributyltin from CRM using NaDDC modified CO₂ was 79 and 85%, respectively.

SFE of alkyltin and alkyllead from solid samples [e.g., soil and polyvinyl chloride (PVC) plastic] using both supercritical and subcritical chlorodifluoromethane was investigated [32]. Quantitative recoveries of triethyllead and triethyltin were obtained, while, low recoveries of trimethyltin and trimethyllead were obtained. Addition of NaDDC as a complexing agent to the extraction vessel increased extraction efficiencies of the two trimethylmetallic compounds to above 89%. They also demonstrated that the addition of NaDDC decreased extraction time by half. In addition, the extraction efficiencies of alkyltin and alkyllead compounds were improved using subcritical chlorofluoromethane instead of supercritical chlorofluoromethane. Higher extraction efficiency of dibutyltin stabilizer from PVC was also obtained via subcritical chlorofluoromethane than dichloromethane liquid–solvent extraction.

Johansson et al. [33] extracted ionic alkyllead from both sediment and urban dust using modified supercritical CO₂. They used different modifiers (methanol, water and acetone) to optimize extraction efficiencies. Methanol provided the most favorable recoveries. At the optimum extraction conditions (80°C, 446 atm and 10% methanol added to the cell)

recovery of trimethyllead, triethyllead and diethyllead were 96, 106 and 80%, respectively.

Recently, Wenclawiak et al. [34] measured the extraction efficiencies of dimethylarsenic acid (DMA) and monomethylarsenic acid (MMA) from a solid sample using supercritical CO₂, Fig. 2. The DMA and MMA were derivatized under supercritical CO₂ conditions using thioglycolic acid methylester (TGM), Fig. 2. After 10 min of static extraction, the valve between the restrictor and extraction vessel was opened and the derivatized analytes were collected in a solvent. Extraction efficiencies of both DMA and MMA were greater than 90% at 400 atm. Temperature did not effect the extraction efficiencies of the derivatized analytes.

3.2. Aqueous matrices

Laintz et al. [8] has been able to quantitatively extract Cu⁺² ion from an aqueous sample using supercritical CO₂ saturated with LiFDDC. In their experiment, supercritical CO₂ was passed through a 10 ml stainless-steel vessel filled with solid LiFDDC, which functioned as the ligand extraction vessel. Next, the supercritical CO₂ saturated with LiFDDC was introduced into a high pressure view cell filled with 5 ml of the aqueous Cu⁺² solution. The reaction of Cu⁺² ion with LiFDDC was monitored via UV–Vis spectroscopy as a function of time at 416 nm [e.g., the charge transfer absorbance band of Cu(FDDC)₂]. The rate of extraction of Cu⁺² at different densities (constant temperature, 35°C) and different temperatures (constant density, 0.22 g/ml) was studied. This was the first report of direct extraction of a metal ion from an aqueous solution using in-situ chelation SFE. The extraction efficiency of Cu⁺² ion was greater than 95% at densities above 0.35 g/ml and 35°C. Extraction of Hg⁺² ion from water was achieved with 5% methanol modified CO₂ and tetrabutyl-substituted dibenzobistriazolocrown ether (Crown III) at 200 atm and 60°C [9]. Extraction efficiency of Hg⁺² was dependent on the amount of ligand placed in the ligand extraction vessel. It was determined that at least 10 mg of ligand is necessary for the extraction of 5 ppm Hg⁺² from 4.5 ml of contaminated water.

Wai [11] has reported extraction of both divalent and trivalent metal ions with CO₂ from an aqueous

matrix using Li(FDDC) as a ligand. Extraction efficiency of greater than 90% percent was reported for Cd^{+2} , Cu^{+2} , Pb^{+2} and Zn^{+2} from aqueous solution. In their study, after SFE the metal chelates were back extracted from the collection solvent (chloroform) using nitric acid and analyzed via inductively coupled plasma mass spectrometry (ICP-MS).

Recently Wang and Marshall [6] used tetra-butylammonium dibutylthiocarbamate (TDBDTC) ligand for in-situ chelation SFE of Zn^{+2} , Cd^{+2} and Pb^{+2} from aqueous media. Again supercritical CO_2 was passed through a vessel which was filled with the dithiocarbamate. The saturated supercritical CO_2 then passed through the aqueous phase contaminated with heavy metals. Following extraction and collection of the metal chelates, flow injection analysis coupled with atomic absorption spectroscopy (FIA-AAS) was used to analyze and quantify the metals. Recoveries of ions from aqueous solution were >73% and >94% within 5 to 15 min, respectively. Different dithiocarbamates such as TDBDTC, DDC and PDTC were compared for extraction of Zn^{+2} ion. The extraction efficiency of Zn-DBDTC was much greater than Zn-DEDTC or Zn-PDTC. The high extraction efficiency of Zn-DDC was related to the high solubility of the chelate, since the solubility ratio of Zn-DBDTC/Zn-DEDTC and Zn-SDDTC/Zn-PDTC were 20 and 139, respectively.

Recently Ashraf-Khorassani et al. [7] demonstrated extraction of different metal acetylacetonates (AcAc), metal hexafluoroacetylacetonates (HFA), metal DDC and metal FDDC from an aqueous environment. Both metal AcAc and metal HFA complexes had lower extraction efficiency than metal DDC and metal FDDC, although DDC and FDDC complexes exhibited lower solubility in supercritical CO_2 using identical extraction conditions. They demonstrated that the extraction of metal DDC complexes is solubility dependent, while, extraction of metal ions via in-situ chelation is not only solubility dependent, but also depends on the stability of chelate under supercritical conditions. Toews et al. [13] studied the influence of pH on the SFE extraction efficiency of metals and ionizable organic species in water. They concluded that metal extraction by in-situ chelation is pH dependent. The pH of water ranged between 2.80 and 2.95 at pressures

of 70 to 200 atm CO_2 and temperatures between 25–70°C. Therefore, any ligand which forms a stable neutral complex with metal ions at pH 3 should be useful in SFE.

SFE of lanthanides from a liquid environment has also been investigated. Lin and Wai [14] studied extraction of La^{+3} , Eu^{+3} and Lu^{+3} from a buffered acetate solution at pH 4.0. Maximum extraction efficiencies of lanthanides (ranging from 75 to 89%) were obtained with supercritical CO_2 containing TTA and TBP at 150 atm and 60°C. Extraction efficiencies of ions with supercritical CO_2 containing only TTA or TBP were poor. Extraction of uranyl and thorium ions from water was also performed [15]. In this study, the addition of 80 μmol TTA to pure supercritical CO_2 increased extraction efficiencies of uranyl and thorium ions from water to 38 and 70%, respectively. The synergistic effect on extraction of each ion by using TBP and TTA mixed with pure supercritical CO_2 was investigated. Extraction efficiencies of ions increased to 70 and 87%, respectively. Addition of 5% methanol as a modifier and TTA as a ligand to the extraction fluid increased extraction efficiencies of both ions to greater than 85%.

A similar study was reported by Laintz and Tachikawa [16] investigating the synergistic effect of 10, 20 and 30% TBP modified CO_2 saturated with TTA for the extraction of Sm^{+3} , Eu^{+3} , Gd^{+3} , Dy^{+3} , Yb^{+3} , La^{+3} , Ce^{+3} , Yb^{+3} and Lu^{+3} from an aqueous environment. Quantitative extraction of Sm^{+3} , Eu^{+3} , Gd^{+3} and Dy^{+3} (>90%) was achieved using 30% TBP modified CO_2 saturated with TTA while recovery of La^{+3} , Ce^{+3} , Yb^{+3} and Lu^{+3} using the same extraction conditions was less than 70%. Extraction of the same lanthanide ions from acidic solution (6 M HNO_3 –3 M LiNO_3) using 30% TBP modified CO_2 yielded extraction efficiencies of greater than 85% for Sm^{+3} , Eu^{+3} , Gd^{+3} and Dy^{+3} , while, less than 70% recovery of La^{+3} , Ce^{+3} , Yb^{+3} and Lu^{+3} was obtained. The log of the SFE distribution coefficient was plotted as a function of percent TBP in the extraction fluid. The slope of the line for Sm^{+3} , Gd^{+3} , Eu^{+3} and Dy^{+3} suggested that not only was TBP forming a 3:1 adduct with $\text{Ln}(\text{NO}_3)_3$ during extraction but it was also forming a 3:1 adduct with $\text{Ln}(\text{TTA})_3$ during the extraction.

Later Lin et al. [20] studied the extraction of

uranium (UO_2^{+2}) and thorium (Th^{+4}) from nitric acid solutions using different organophosphorus reagents [i.e., TBP, tributylphosphine oxide (TBPO), tri-*n*-octylphosphine oxide (TOPO) and triphenylphosphine oxide (TPPO), Fig. 2]. In all extractions, supercritical CO_2 was saturated by passing it through a cell filled with an organophosphorus compound. Then the saturated CO_2 with organophosphorus compound was bubbled through the solution in the extraction vessel. Results showed that extraction efficiencies of both UO_2^{+2} and Th^{+4} using TBP are directly dependent on the concentration of nitric acid solution. Extraction efficiencies of both ions decreased from 91% for UO_2^{+2} and 80% for Th^{+4} in 6 M nitric acid solution to 12% for UO_2^{+2} and 20% for Th^{+4} in 0.1 M nitric acid solution. Addition of LiNO_3 to the 6 M nitric acid solution increased extraction efficiencies of both ions to 98% and 93%, respectively. Extraction efficiencies of both UO_2^{+2} and Th^{+4} using supercritical CO_2 modified with TBP were greater than 90% regardless of the concentration of nitric acid solution (6 M, 1 M or 0.1 M).

Bayona and coworkers [27,28] studied SFE of butyl-, phenyl- and cyclohexyltin compounds from aqueous matrices using C_{18} solid-phase extraction (SPE) discs. The analytes were first concentrated via SPE discs. Next, the organotin compounds that were trapped on the SPE disc were derivatized via Grignard ethylation followed by SFE at 100 atm. Extraction efficiencies of both di- and tributyltin were above 90%; while, SFE recovery of monobutyltin was less than 70%.

4. Conclusion

Direct extraction of metal ions and metal chelates via SFE from both solid and liquid matrices have been accomplished. Different ligands such as β -diketones, dithiocarbamates, crown ethers and organophosphorous reagent can be utilized for extraction of metal ions. Results from different studies have demonstrated that fluorinated ligands have higher metal complex solubility in supercritical CO_2 which makes them more effective for extraction of metal ions. One should consider that the stability of ligands in supercritical CO_2 is an important factor.

Most of the SFE experiments reported in the literature to date deal with solid matrices (filter paper, sand, water) that are spiked with metal ions or metal chelates. Extraction of different metal ions from liquid matrices can be obtained quantitatively.

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