Extraction of Chromium(III) and Chromium(VI) Species from Solid Matrices Using Green Solvent Supercritical Carbon Dioxide

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Supercritical fluid extraction (SFE) provides an environmentally green technique to decontaminate chromium species from solid matrices using supercritical fluid carbon dioxide (ScCO_2). Methanol and a small amount of water were found to significantly improve the extraction efficiency. The fluorinated chelating agent lithium bis(trifluoroethyl)-dithiocarbamate (LiFDDC) was effective in removing Cr ions in methanol-modified CO_2 via *in situ* chelation/SFE technique. This paper indicates that the extraction efficiencies of Cr(III) and Cr(VI) from solid matrices can be greatly increased to more than 92% in the presence of a small amount of water, using 5% methanol-modified CO_2 containing LiFDDC as an extractant. Chromium species in a wood waste sample in the form of chromated copper arsenate (CCA) can be extracted, but the extraction efficiency is not as good as expected, possibly due to the complications of the chemistry of Cr species in different oxidation states and to matrix effects.

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Determination and removal of heavy metals from natural samples are the essential requirements in a variety of environmental investigations.¹ Chromium speciation has attracted great attention in scientific communities due to the toxic nature of Cr(VI) relative to Cr(III).² Hexavalent chromium is considered to be extremely toxic and carcinogenic. In aqueous solution, trivalent chromium is difficult to extract due to its strong hydration by water molecules. This strong hydration prohibits the access of chelating agents to the metal centers in conventional solvent extraction.^{3,4} With a selective chelating agent and under specific conditions, Cr(VI) and Cr(III) can be separated from aqueous solutions by solvent extraction.⁵ For example, EPA methods 218.3 and 218.4 indicate that Cr(VI) can be extracted by ammonium pyrrolidinedithiocarbamate (APDC) into isobutyl methyl ketone (IBMK) at pH 2.8.⁶ In the EPA's methods, Cr(III) is initially oxidized to Cr(VI) by KMnO_4 , followed by extraction with APDC. The amount of Cr(III) is calculated based upon the difference of total Cr minus Cr(VI) removed. Studies also indicate that Cr(VI) reacts with ammonium pyrrolidinedithiocarbamate ligand to form two products, $\text{Cr(PDC)}_2(\text{OPDC})$ and Cr(PDC)_3 . The former involves coordination with two normal dithiocarbamate ligands and one dithioperoxycarbamate ligand. The latter was formed with three PDC ligands.⁵ The complexes formed by Cr(VI) and Cr(III) individually with sodium diethyldithiocarbamate (NaDDC) give different chemical structures. For example, Tande *et al.*³ and Hope *et al.*⁸ reported that Cr(III) forms a Cr(DDC)_3 complex with NaDDC, whereas Cr(VI) is first reduced by the ligand and then forms two different complexes Cr(DDC)_3 and $\text{Cr(DDC)}_2(\text{ODDC})$, where ODDC represents an oxygen atom inserted between the

metal ion and one of the sulfur atoms.^{3,8} These two complexes formed by Cr(VI) with NaDDC can be separated by HPLC.^{3,9} Extraction of Cr(III) by APDC occurs at higher pH but appears to have a very low efficiency at room temperature. The non-extractability of Cr(III) by solvent extraction is ascribed to the fact that Cr(III) is strongly hydrated and the displacement of coordinated water molecules by dithiocarbamate ligand is kinetically difficult.^{3,7} The complexes formed by Cr(VI) or Cr(III) with NaDDC have different chemical structures. Of particular interest to analytical chemists is the possibility of applying *in situ* chelation/SFE technique for the extraction metal species Cr(VI) and Cr(III) from solid materials. Only a few papers have been reported regarding the investigation of Cr extraction with ScCO_2 . Supercritical fluid extraction has become an attractive alternative to conventional solvent extraction from environmental samples. There are several advantages from an environmental standpoint, rooted in the characteristics of carbon dioxide being nontoxic, nonflammable, and having the potential for recycling.¹⁰⁻¹² The *in situ* chelation/SFE technology presented here shows advantages over conventional solvent extraction methods, in which it greatly minimizes the organic solvent generation in decontamination processes. Carbon dioxide is an excellent solvent for SFE due to its moderate critical constants (Temp. = 31°C and $P_c = 7.4\text{ MPa}$), inertness, and tunable solvating strength. Solutes can often be separated from the supercritical fluid by simply venting the benign CO_2 into the atmosphere, leaving pure solutes behind. Moreover, supercritical CO_2 can easily penetrate and diffuse into small pores of solid matrices and effectively remove organic and inorganic species.

The following factors are important for effective extraction of metal species using ScCO_2 : the solubility of the chelating agent, the solubility and stability of the metal complex, the pressure, the temperature, and the chemical forms of metal species and

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sample matrix.¹³⁻¹⁵ Direct extraction of metal ions by ScCO_2 is highly inefficient because of the charge neutralization requirement that causes weak solvent-solute interactions. When metal ions are bound to organic ligands, however, they become quite soluble in ScCO_2 . In 1992, Laintz *et al.*¹³ first reported the extraction of Cu(II) from liquid and solid materials using ScCO_2 containing lithium bis(trifluoroethyl)dithiocarbamate (LiFDDC) as an extractant. Using 8-hydroquinoline as a chelating agent, Cr(III) has been successfully removed from solid samples in ScCO_2 .¹⁶ Foy and Pacey extracted Cr(VI) using two different dithiocarbamate derivatives LiFDDC and tetrabutylammonium dibutylidithiocarbamate to allow extraction of 1 ppm of Cr(VI) from a solid matrix with a recovery of 88.4%.¹⁷ Kersch and coworkers¹⁸ demonstrated SFE of heavy metals including Cr from fly ash in ScCO_2 using bis(2,4,4-trimethylpentyl)monothiophosphinic acid (trade name: Cyanex 302). Arancibia *et al.*¹⁹ successfully removed and quantified the amount of Cr in urine samples in a form of $\text{Cr}(\text{acac})_3$ (chromium acetylacetonate) complex using SFE and chromatography. Quantitative extraction was achieved at 20.2 MPa and 120°C with 2 mL methanol (as a modifier) and 30 min static extraction, followed by 5 min dynamic extraction. The paper presented here describes *in situ* chelation/SFE of direct extraction of Cr(III) and Cr(VI) from solid matrices using methanol-modified ScCO_2 -containing LiFDDC. Variables which influence the SFE extractions, such as extraction time, water, modifier, oxidation states of Cr, pressure, and temperature are discussed. Removal of Cr from environmentally real samples using ScCO_2 can reduce the leachable toxic heavy metals released into the environment. Extraction of Cr(III) and Cr(VI) is feasible using *in situ* chelation/SFE technique in ScCO_2 ; such extraction is kinetically difficult in traditional solvent extraction.

Experimental

Reagents and materials

Lithium bis(trifluoroethyl)dithiocarbamate was synthesized according to the procedure outlined in the literature.²⁰ The starting material, bis(trifluoroethyl)amine, was obtained from PCR Chemicals (Gainesville, FL). Other chemicals used in the synthesis including *n*-butyllithium (2.5 M in hexane), carbon disulfide, and isopentane were obtained from Aldrich Chemical Co. (Milwaukee, WI). All other reagents and solvents used in this study were of analytical grade and were obtained from Aldrich Chemical Company or Baxter Scientific (McGraw Park, IL). Deionized water from a Millipore Milli-Q system (Bedford, MA) was used for the preparation of all aqueous solutions. Cr(III) and Cr(VI) in atomic absorption spectroscopy (AAS) standards (1000 ppm) were purchased from EM Chemical. Wood samples (from a weathered telephone pole), containing chromated copper arsenate (CCA) from wood treatment processes, were obtained from a forest product laboratory, Department of Forestry, University of Idaho, USA. Each sample was dried, ground, and homogenized completely. The size of the pieces of CCA-treated wood sawdust was approximately 40 mesh.

Apparatus

All experiments were performed with a laboratory-built supercritical fluid extraction apparatus. SFC-grade CO_2 and 5% methanol modified CO_2 were obtained from Scott Speciality Gases (Plumsteadville, PA). The fluid was delivered to the SFE system using a microprocessor-controlled high-pressure pump

(Haskel Inc., Burbank, CA). The pressure of the system was monitored to ± 5 psi using a Setra Systems (Acton, MA) pressure transducer. The extractor consisted of an inlet valve (Supelco, Bellefonte, PA) and an outlet valve connected to a stainless-steel 3.47-mL commercial extraction cell (Dionex, Sunnyvale, CA). The extraction cell was placed in an oven whose temperature was controlled by a thermostat. Fused-silica tubing (Dionex, 50 μm i.d. and 20 cm in length) was used as the pressure restrictor for the exit gas. Static and dynamic extractions were performed and controlled by the outlet and inlet high-pressure valves.

Non-destructive instrumental neutron activation analysis (NAA) was used to identify and measure the quantities of Cr species. The samples and standards were irradiated in a 1 MW TRIGA nuclear reactor at a steady flux of $6 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for 1 h. After cooling for a couple of days, the activated samples and standards were counted on a large-volume ORTEC Ge(Li) detector with a resolution (FWHM) of 2.3 keV at the 1332 keV ^{60}Co peak. The detector has an efficiency of 15% relative to a 3×3 NaI crystal. The γ -rays of Cr were emitted at 320 keV, with a half live of 27.8 days. A Ge(Li) detector was used to count ^{51}Cr activities at 320 keV γ -peak. The detector output was fed to a Nuclear Data 4096-channel pulse-height analyzer and MCB software. The details of the NAA procedures are given elsewhere.²¹

Extraction procedures

For the extraction of Cr(III) and Cr(VI) species, two solid matrices were employed. (1) An aliquot containing 10 μg of Cr(III) or Cr(VI) ion solution prepared from AAS standard was spiked onto cellulose-based filter paper (Whatman 42, 0.7 cm $\times$ 2 cm in size). The piece of filter paper was then inserted into the open end of a glass tube (3 cm in length and 0.65 cm o.d.) where a small amount of glass fiber was mounted previously. (2) To a glass tube which contained 200 mg of sand grains held in place by a small amount of glass fiber, an aliquot containing 10 μg of Cr sample was spiked. For both cases, 10 μL of deionized water were then added directly afterwards. The head of the glass tube was also plugged with a piece of glass wool and then connected into a bulb-shaped glass tube (2 cm in length, 0.60 cm o.d.) in which 50 mg of LiFDDC ligand was loaded. Because the o.d. of the end of ligand tube is slightly smaller than the i.d. of the sample tube, the former can be partially inserted into the latter. These tubes were all mounted inside the extraction cell, which was then placed in the oven. The temperature and pressure were then increased to the desired values for extraction. Neat CO_2 or 5% methanol modified CO_2 was used in this study. The extracted Cr complexes were trapped by chloroform that was placed in two glass cylinders (1.2 cm i.d. and 10 cm in length) connected in series.

Initial retentions of Cr, Cu, and As in the wood sample are 18223 ± 250 , 9425 ± 180 , and 20054 ± 290 ppm, respectively, according to our elemental analyses from ICP-AES. For the real sample, wood from a weathered telephone pole containing CCA from wood treatment processes was used. A 50-mg amount of wood sample was tested with continuous dynamic extraction at a fixed temperature of 50°C at 10.1, 20.2, and 30.4 MPa.

The samples and the standard (10 μL of Cr (1000 ppm), AAS standard) were irradiated by the nuclear reactor under identical conditions. The extraction efficiencies were calculated based on the radioactivities of γ -rays of metal ions found in the sample residues after SFE relative to those of standards. Triplicate runs of all SFE samples were undertaken in this study. The RSD between the samples is around $\pm 3 - 7\%$.

Analytical procedures

The quantities of Cr species from residues and trapping solutions were tested by neutron activation analysis. The filter paper or sand grains after extraction was placed in a small polyethylene vial and heat sealed for neutron irradiation. The amount of Cr complexes in the trapping solution was determined by transferring a known volume of the solution into small polyethylene vials. The chloroform-containing Cr species was then evaporated to dryness. The residue was redissolved in 0.5 mL 50% HNO₃, and then heat sealed for neutron irradiation. The samples, along with 10 µg of standard in the same matrix, were irradiated simultaneously. After irradiation, the samples and standard were cooled down for 2 days before counting.

Results and Discussion

Extraction efficiencies of Cr species from sand and filter paper

Because of the reducing capability of dithiocarbamate ligands, the oxidation state of Cr(VI) species (Cr₂O₇²⁻, CrO₄²⁻) is reduced to trivalent state in the process of complex formation.^{4,5} To determine the concentrations of each Cr species in aqueous solutions, one first oxidizes Cr(III) by potassium permanganate (KMnO₄) followed by solvent extraction with dithiocarbamate ligands.⁶ The amount of Cr(III) is calculated from the difference in the concentrations between the aliquots, one with and one without oxidation.⁶ In an attempt to evaluate the feasibility of extracting Cr species from solid materials by ScCO₂, we performed a series of experiments by spiking known amounts of Cr(III) and Cr(VI) on sand and filter paper.

Cr(III) species can be extracted by neat CO₂ containing LiFDDC at 20.3 MPa atm and 60°C, with 10 min static extraction followed by 30 min of dynamic extraction. It was observed that extraction efficiencies of Cr(III) and Cr(VI) were higher in sand samples in comparison with those of filter paper samples. The extraction efficiencies of Cr(III) from sand and from filter paper were 46% and 35%, respectively. This implies that the interactions between substrate and analytes are smaller in a silica matrix than in a cellulose matrix. Addition of a small amount of water (10 µL) can increase extraction efficiencies of Cr(III) to 60% (sand) and 47% (filter paper), respectively. These results are very different from the known behavior of aqueous Cr(III) in conventional solvent extraction processes. The strong hydration of Cr(III) ion which prohibits the chelation of trivalent species with dithiocarbamate ligands in solvent extraction is no longer a problem in SFE.^{4,5} The extraction efficiencies of Cr(VI) by ScCO₂ containing LiFDDC are higher than those observed from Cr(III) under similar conditions. For Cr(VI), the result indicates that when the samples were in dry form, extraction efficiencies were 64% (sand) and 40% (filter paper), respectively. In the presence of water, the extraction efficiencies for Cr(VI) were raised to 72% and 67%, respectively, for sand and filter paper samples.

Further study indicated that, in the presence of a small amount of water, using 5% methanol modified CO₂ and LiFDDC as the extractant, the extraction efficiency tremendously increased to 92% (sand) and 90% (filter paper) for Cr(III), and 94% (sand) and 92% (filter paper) for Cr(VI), respectively. These results are summarized in Table 1.

Influence of water and methanol on extraction

As shown in Table 1, in the presence of water, Cr(III) species spiked onto the solid substrates can be extracted nearly quantitatively. The presence of water facilitates the chelation and transport of metal complexes from solid matrices to the CO₂

Table 1 Extraction efficiencies (*E*, %) of Cr(III) and Cr(VI) from solid matrices

Fluid phase		Cr(III)		Cr(VI)	
		(dry)	(wet)	(dry)	(wet)
Sand	CO ₂	46	60	64	72
Filter paper	CO ₂	35	47	40	67
Sand	5% MeOH + CO ₂	64	92	80	94
Filter paper	5% MeOH + CO ₂	50	90	74	92

Cr, 10 µg (1000 ppm); sand, 200 mg; filter paper, 0.7 × 2 cm²; 20.3 MPa and 60°C, 10 min static time plus 30 min dynamic time; ligand, LiFDDC; average data from triplicate runs; RSD, ±3–7%; (wet) means a small amount of water is added onto the sample.

fluid phase. The water may also function as a modifier for solute/matrix interactions by blocking the active sites of the matrix *via* hydration, thus reducing the adsorption of the solute by the active sites of polar matrix. This result may reverse when more water was added. For instance, addition of 35 µL water decreases the extraction efficiencies down to 5–10%. This result is consistent with the phenomenon observed by Foy and Pacey.¹⁷ In their research, on addition of 20 µL of H₂O, they found the extraction efficiency to be more than 80%. However, when the amount of water was increased to 60 µL, the extraction efficiency dropped down to 40%. Water at higher concentration is probably interfering with the ScCO₂ fluid, which in turn influences the solubilities of the chelates and the metal complex.¹⁸ When water comes into contact with CO₂, the pH value decreases due to the formation and dissociation of carbonic acid. For pressures between 7.1 and 20.3 MPa, and temperatures between 31.3 and 70°C, the pH of water dissolved with CO₂ was 2.9.²²

The efficiency of extracting Cr(III) and Cr(VI) improved significantly when methanol was added to the fluid phase, especially for Cr(III). The enhanced extraction efficiencies are most likely due to increased interactions between the solutes and the modified fluid phase. Methanol plays an important role for increasing the polarity of CO₂, thus facilitating the transportation of extracted solutes from solid matrices into the CO₂ fluid phase. The extraction efficiencies of Cr ions, after the modification of 5% methanol, can increase to more than 90%, as shown in Table 1. The change of solvent polarity by adding methanol with a small amount of water makes quantitative extraction of metal species into ScCO₂ feasible.

Optimization of the extraction

In order to obtain optimal extraction conditions, further studies were undertaken. Figure 1 shows the extraction efficiencies of Cr(III) from filter paper using 5% methanol modified CO₂, when dynamic extraction time was fixed at 10 min, while the static extraction time was varied from 5 to 60 min. The results indicate that extraction efficiencies reached 90%, and plateaued after 15 min of static extraction.

An investigation was also conducted at a fixed 10 min static extraction, by changing dynamic extraction times. The extraction efficiencies obtained were about 87% at 40 min and 90% at 60 min dynamic time, as shown in Fig. 2. Therefore, 20 min static extraction followed by 45 min dynamic extraction was chosen as standard extraction procedure in the consequent SFE experiments.

Both Cr(III) and Cr(VI) were extracted directly using ScCO₂. In order to acquire quantitative extraction efficiencies, some

Fig. 1 Different static extraction times with a fixed dynamic time (10 min). Matrix: filter paper, 5% methanol-modified CO_2 with 10 μL water. RSD: $\pm 3 - 6\%$.

Fig. 2 Different dynamic extraction times with a fixed static time (10 min). Matrix: filter paper, 5% methanol-modified CO_2 with 10 μL water. RSD: $\pm 3 - 6\%$.

modifications were undertaken. (1) Addition of methanol (5% mole) to CO_2 phase to change the polarity of the fluid phase and enhance the interactions between solute and solvent. (2) In the supercritical state, the solubilities of the chelating reagent and its complex are in proportion to the pressure (density) of the fluid (ScCO_2). When the density of CO_2 increases with pressure, the solubilities of the solutes increase accordingly. A pressure of 25.3 MPa atm was chosen for further study. (3) At a fixed pressure, increase of temperature will decrease the density of CO_2 , thus reducing the solvating strength of the solvent (ScCO_2). The proper temperature (50°C) was chosen based on this point of view. (4) Optimal extraction time, *i.e.*, 20 min static extraction and 45 min dynamic extraction as discussed in the previous section, was selected for consequent SFE experiments. By applying these conditions, we significantly enhanced SFE efficiencies of Cr(III) to more than 92% in both silica and cellulose matrices.

The extraction efficiencies of chromium ions from sand and filter paper with neat CO_2 in the absence of LiFDDC were insignificant ($< 2\%$), indicating there is no organometallic species in the matrix. The amounts of Cr(III) and Cr(VI) spiked were at least one order of magnitude less than the solubility limit of LiFDDC in the fluid phase.²³ Table 2 shows the extraction results for Cr(III) and Cr(VI) using these SFE conditions. *In situ* chelation/SFE provides a promising prosperity of extraction approach, in which Cr species including hydrated trivalent Cr ions can be quantitatively extracted into the ScCO_2 phase.

Application of *in-situ*/chelation SFE on environmental sample

In order to evaluate the feasibility of this *in situ* chelation/SFE method, we used wood samples to verify our methodology. The

Table 2 Extraction efficiencies (E , %) of Cr(III) and Cr(VI) from solid matrices under optimal conditions

Fluid phase	Ligand amount/mg	Matrix	E , % (Cr(III))	E , % (Cr(VI))
CO_2	—	Sand (wet)	< 1	< 2
CO_2	50	Sand (wet)	78	88
CO_2	50	Filter paper (wet)	59	79
$\text{CO}_2 + 5\%\text{MeOH}$	50	Sand (wet)	95	96
$\text{CO}_2 + 5\%\text{MeOH}$	50	Filter paper (wet)	92	94

Cr(III) or Cr(VI), 10 μg ; sand, 200 mg; filter paper, $0.7 \times 2 \text{ cm}^2$; 5% MeOH/ CO_2 ; 25.3 MPa and 50°C , 20 min static time plus 45 min dynamic time; ligand, LiFDDC; analyzed by NAA; triplicate runs; RSD, $\pm 4 - 6\%$.

Fig. 3 Extraction efficiencies of Cr from wood sample treated with CCA at different pressures using dynamic extraction by pumping 0.1 M LiFDDC/MeOH in CO_2 phase, at 20.3 MPa and 50°C . Wood sample 50 mg, extraction percentage is calculated from the final concentration of metal ions in accumulated trap solutions divided by the concentration of metals in wood before SFE.

concentration of metal ions in CCA-treated wood varies depending on the specific purpose of the lumber and manufacturer formulation of the CCA solution. Because dithiocarbamate ligand is less stable in the weak acidic medium, excess amounts of this ligand are usually used. LiFDDC (0.1 M) was prepared in methanol solution, and delivered into the high pressure SFE system *via* a HPLC pump. As can be seen in Fig. 3, when we used 0.1 M of LiFDDC/MeOH solution in ScCO_2 , about 2.5% Cr species was removed at 20.3 MPa and 50°C by cumulative dynamic extraction in 2 h, and finally 455 μg Cr/g wood waste was removed. The extraction efficiency for this sample was below our expectation. This is probably due to the following reasons. The chromium species in the wood sample can be in different chemical forms and oxidation states, and they are not readily extracted under the experimental conditions used. The chemistry in matrices of the real samples is different from that of spiked samples. In addition, dithiocarbamate derivatives are less stable in an acidic medium. The pH of ScCO_2 is around 2.9; which may accelerate the decomposition of dithiocarbamate derivatives in SFE processes.²²

In SFE of Cr in CCA-treated wood, both Cu and As species are also involved. The SFE profiles of copper and As species are shown in Fig. 3 as well. We understand that both Cr and As species could be in the different oxidation states. Divalent Cu cations probably compose the majority of the species of Cu existing in the matrix. The extractions of Cu are much higher than those of Cr and As. At 30.4 MPa, in the first 15 min, about 510 $\mu\text{g/g}$ of Cr was extracted from the wood sample, which was equivalent to about 26 μg of Cr in the 50 mg wood sample.

Within 2 h, the trap samples were collected cumulatively from the same wood sample and the amount of Cr can be removed up to 680, 455, and 175 $\mu\text{g/g}$ totally at 30.4, 20.3, and 10.1 MPa, respectively. Most leachable Cr ions can be removed from the wood matrix in the first 45 min. After that the extraction curve gradually approached a plateau (not shown). The efficiencies of SFE are pressure dependent. For example, at 30.4 MPa, about 4% of Cr could be extracted, while at 10.1 MPa, the extraction efficiency of Cr was 1% in 2 h extraction time, as shown in Fig. 3. The unextractable fraction of Cr species could be in different oxidation states and may strongly bind to the native ligands in matrices, thus making the SFE difficult.

Conclusions

Extractions of Cr(III) and Cr(VI) metal ions from solid matrices can be accomplished directly using ScCO_2 containing LiFDDC. Chromium ions spiked on the silica and cellulose matrices can be effectively extracted by *in situ* chelation/SFE in the presence of a small amount of water. Methanol can significantly improve the extraction efficiency of Cr. Trivalent Cr ions can be extracted completely under optimal SFE conditions, though they are not extractable by traditional solvent extraction methods. In real wood samples which contain CCA, Cr(III) and Cr(VI) species can be extracted by LiFDDC in ScCO_2 . The extracted Cr species in environmental samples represents the leachable portion in which their oxidation states and the matrix effect are different from the spiked samples. With the aid of a small amount of water in methanol modified CO_2 , *in situ* chelation/SFE technique provides a better approach and potential industrial applications for the removal of toxic Cr from environmental matrices in the field of decontamination of heavy metal containing wastes.

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