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Mobilization/Purging of Aqueous Metal Ions into Supercritical Carbon Dioxide

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April 1998

A thesis
submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements of the degree of M.Sc.

0-612-44112-1

ABSTRACT

The technology of supercritical fluid extraction (SFE) offers the opportunity to efficiently extract both relatively non-polar analytes as well as ionic materials (such as metal ions) that can be mobilized with the addition of complexing reagents. The nebulizer of a conventional flame atomic absorption spectrometer (FAAS) was modified to extend the range of metals amenable to *on-line* detection. The flow injection thermospray-FAAS (FI-TE-FAAS) interface provided efficient detection for a variety of less volatile elements (Co, Cr(III), Cr(VI), Fe, Ni, Mn and Al) present as ions in aqueous media or as complexes in the supercritical fluid (SC-CO_2) carrier phase. The range of possible metal analytes that can be monitored has been increased over the nine elements (Ag, As, Cd, Cu, Hg, Mn, Pb, Se and Zn) that could be detected with an all-silica interface. The acetylacetonate complexes offered considerable potential for metal detection in an SC-CO_2 carrier phase. Limits of detection (LODs) were used to compare the instrument responses to different metals. Metal ions from an undiluted, chromated copper arsenate (CCA) sample that was used for wood treatment was mobilized efficiently [Cu and Cr (100.0 ± 0.0% and 98.8 ± 0.0%) but less efficiently for As (81.9 ± 0.5%)]. A series of complexometric extractions were performed to optimize the mobilization/purging process for the CCA sample. For Cr(III), maximum derivatization efficiencies were achieved in an ammoniacal buffer (NH_4Cl/NH_3) at pH ≈8. Preliminary experiments have demonstrated great promise for the removal/trapping of metals from SC-CO_2. When coupled with supercritical fluid extraction, metals were removed from aqueous media then accumulated efficiently in a trap containing zero-valent iron (Fe^0) or an acid washed sea sand. Zero-valent iron particles were appreciably more efficient at trapping metal complexes than were the silica particles indicating an active involvement in the trapping process other than acting as a simple heat transfer medium. However, the Fe^0 released only small quantities of 2,4-pentanedione from the complexes. The sand trap was somewhat more efficient in this respect. Apparently, there is an optimum temperature for the release of the comlexing reagent from the complexes. It seems that a combination of the two trapping media would trap metals efficiently and would release at least some complexing reagent.

RÉSUMÉ

La technique d'extraction par fluide supercritique (EFS) offre la possibilité d'extraire des composés peu polaires de même que des ions métalliques avec l'ajout d'agent(s) complexant(s). Le nébulisateur d'un spectromètre par absorption atomique a été modifié dans le but d'augmenter le nombre de métaux pouvant être directement analysés. L'interface FI-TE-FAAS procure une méthode de détection efficace pour une variété d'éléments considérés moins volatiles tels que (Co, Cr(III), Cr(VI), Fe, Ni, Mn et Al) présents sous forme d'ions dissous en solution aqueuse ou fluide supercritique par dioxide de carbone (FS-CO_2). Une interface de quarzt conçue antérieurement se limitant a neuf éléments fut utilisée par comparaison. Des complexes d'acetylacetonate nous ont offert un potentiel de détection considérable en phase de fluide supercritique. Les résultats des limites de détection ont été utilisés pour comparer l'efficacité des modifications du système. Un condensé non-dilué de Chrome-Cuivre-Arsenique (CCA) normalement utilisé pour la préservation du bois, fût extrait avec succès [Cu et Cr (100 ± 0.0% et 98.8 ± 0.0%), cependant montrant une efficacité moindre pour l'arsenique (81.9 ± 0.5%)]. Une série d'extractions complexométriques a été évaluée afin d'optimiser la procédure d'extraction de notre échantillon (CCA). Au niveau du Cr(III), un tampon d'ammoniaque (NH_4Cl/NH_3), pH 8, a procuré une dérivatisation maximale. Des expériences préliminaires ont démontré le potentiel d'extraire et fixer des métaux par fluide supercritique. Jumelés avec l'extraction par fluide supercritique, les métaux extraits d'une solution aqueuse sont ensuite fixés sur les particules de fer (Fe^0) ou du sable de mer. Les particules de fer se sont avérées beaucoup plus efficaces pour accumuler les complexes métalliques que les particules de silice contenues dans le sable de mer, indiquant ainsi l'implication du milieu et non seulement l'effet de la température. Toutefois, le Fe^0 n'a libéré qu'une faible quantité de 2,4-pentadione provenant du complexe, par contre le sable de mer a été plus efficace. Apparemment, une température optimum serait nécessaire pour libérer l'agent complexant. Il semblerait qu'une combinaison de fer et sable serait un choix judicieux pour accumuler les métaux et libérer l'agent complexant.

ACKNOWLEDGEMENTS

I gratefully acknowledge Dr. William D. Marshall, for giving me the chance to join his research group, his valuable scientific guidance, constant encouragement and financial support throughout my studies. I would also like to thank the members of my committee, Dr. V. Yaylayan, Dr. I. Alli and Dr. W. Hendershot for their time and valuable final corrections of my thesis.

Thanks to my fellow graduate students and summer students, specially Dr. Yanxi Tan, for their encouragements and suggestions. A special thanks to Paul Pilon for our endless evening conversations. I also want to thank Lyse Marshall for reviewing my french abstract. Finally, to all my friends who helped and supported me throughout my studies.

My deepest gratitude goes to my mother, father and sisters, for their love, comprehension and understanding.

Merci.

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Chapter 1. Introduction

Supercritical fluid technologies represent a field in which several novel applications are under active exploration and development in industrial, academic and government laboratories. These applications are attractive in that they are energetically efficient yet innocuous for the environment. Despite continued new developments, supercritical fluids (SCFs) have attracted scientific curiosity for many years. The use of a supercritical fluid was first reported by the French scientist Baron Charles Cagniard de la Tour in 1821. Hannay and Hogarth in 1879, used supercritical ethanol to solubilize several inorganic salts including cobaltous chloride, potassium iodide, potassium bromide and ferric chloride.

Historically, the work performed by the Kerr-McGee Refining (USA) Company resulted in the Residual Oil Supercritical Extraction (ROSE) process that was developed in the 1950s for the removal of lighter products from the residues of the commercial distillation of crude oil. A significant development in supercritical fluid extraction was the Zosel patent. In 1970 he reported the decaffeination of green coffee with carbon dioxide (CO_2). This process was accomplished by soaking the beans in water and then immersing them in supercritical CO_2. The industrial food giant, Kraft General Foods (Maxwell House Coffee division), for example, has built an extraction vessel (7 ft in diameter and 70 ft) tall for supercritical CO_2 decaffeneination of coffee at their Houston, Texas, plant. This one application represents an annual market of $ 2-3 billion. Since 1980, there have been several developments in the field of supercritical fluid extraction (SFE), for the extraction of (1) the flavoring materials from hops, (2) cholesterol from butter, (3) perfumes and flavors from natural products, (4) residual solvents and monomers from polymers, and (5) unsaturated fatty acids from fish oils. More recently, SC-CO_2 has been explored as a medium for enzymatic reactions (Taylor, 1996). Supercritical fluid extraction with CO_2, has been investigated recently as a solvent for the extraction of taxol (a cancer treatment drug) from the bark of the yew tree, a species which is native to the Pacific northwest but which is widely distributed throughout regions with temperate climates.

The last ten years have seen the gradual shift in the number of SCF applications away from commodity chemicals and synthetic fuels toward more complex, highly specialized, and more valuable substances. In addition to applying the technology for isolation and purification, a considerable effort has been devoted to gaining a better fundamental understanding of (1) molecular structure, (2) phase behavior, (3) cosolvent effects, (4) solvation processes between solute and fluid phase, and (5) transport properties of supercritical fluids. Today, SCFs are being touted as a solvent medium for sample preparation prior to trace analysis and as mobile phases for the analytical and preparative scale SF chromatography.

1.1 Theoretical aspects of SCFs

A supercritical fluid is any fluid at a temperature and pressure above its critical values, Rizvi *et al.*, (1986). In fact, a supercritical fluid possesses a density that is similar to that of the liquid state and behaves like a liquid solvent. However, the fluid diffuses readily like a gas because its viscosity is low. Its relatively high density results in good solvating power, whereas its relatively low viscosity and diffusivity provide appreciable penetrating power into the sample matrix, Rizvi *et al.*, (1986). A pressure-temperature phase diagram (Figure 1) of a pure substance is characterized by a critical temperature (Tc) and pressure (Pc), where Tc of the substance is the temperature in excess of which the fluid no longer be liquefied. The fluid exists as a single phase, no matter how high the pressure. The region above both critical temperature and pressure is called the supercritical region. Thus, the compressed gas becomes a supercritical fluid and exhibits solvating properties between the liquid and gaseous states (Ellen *et al.*, 1992).

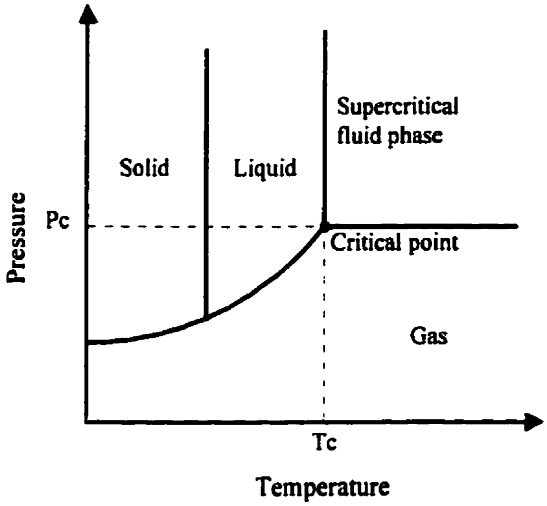

Figure 1: Pressure-temperature phase diagram of a pure substance.

Earlier research with SCFs has included the measurement and modeling of the phase equilibria between heavy organic solutes and the SCFs. Many of the early model compounds that were investigated were nonfunctional polycyclic aromatic compounds. The logical extension of the solute type was to polycyclic aromatic compounds containing oxygen, nitrogen or bromine functional groups. These were investigated in both non-polar and polar solvents to examine the effect of solvent size and polarity on the solubilities (Brennecke and Eckert, 1989). The general conclusions were that the solubility was dominated in most cases by dispersion forces, such that ethylene was a better solvent than CO_2. Only for nonpolar solutes, was the solubility in SC-CO_2 as high as in ethylene. A classical study seemed to indicate that the most efficient separations were to be achieved on the basis of volatility. It was fashionable to talk about the enhancement factor which is a dimensionless measure of solvent power, that has been defined as the measured solubility divided by the ideal gas solubility (Brennecke and Eckert, 1989). It was observed that the logarithm of the enhancement factor was generally a linear function of the solvent density. It was concluded that the enhancement was relatively insensitive to the solute structure but very dependent on the polarity and density of the solvent.

A later study extended the SCF database to three additional higher-temperature solvents: butane, ammonia and ethanol (Brennecke and Eckert, 1989). The researchers studied solutes with higher melting points that contained sulfur as well as oxygen and nitrogen. Whereas these studies expanded the solubility database greatly, the general conclusion was that differences in solubility were due principally to differences in vapor pressure. Another study of three hydroxybenzoic acid isomers and three dihydrobenzene isomers in supercritical CO_2 supported the same conclusions (Krukonis and Kurnik, 1985). The authors concluded that the solubility was correlated with the melting point (or vapor pressure) of the isomer and that any separation would be facilitated if there were appreciable differences in the melting points (or, alternatively, vapor pressures) of the isomers.

Several reasons have been identified for choosing one supercritical fluid over another liquid-phase solvent system (Ellen *et al.*, 1992), but generally the choice is governed by:

1) the unique solvating and favorable mass transport properties of the supercritical state
2) the ease with which the solvating character of the medium can be varied by adjusting the system pressure and/or temperature

Concerns about the hazardous nature of many common solvents, the costs and environmental dangers posed by waste solvent disposal, and the emission of hazardous solvent vapors into the atmosphere have generated appreciable interest in alternate methods that make use of benign solvating media including supercritical fluids.

Since, in general, the solubility of a solute is proportional to solvent density, the dissolution process can be made to be both efficient and selective (Bradley, 1989). Density generally increases with increasing pressure but tends to decrease with increasing temperature. Nevertheless, the temperature relationship is a rather complex one. As the temperature increases two things occur: (*i*) the vapor pressure of the solute increases that, in turn, increases the solubility of the solute but (*ii*) the density of the medium decreases that decreases the overall solubility. The solvent power of a SCF cannot be explained exclusively by density variations. Thus, a SCF has two facets, a “state effect” and a "chemical effect". The principal variable of a "state effect" is the density of the SCF, whereas the "chemical effect" is unique to each solute and dependent on its polarity (Vannort *et al.*, 1990). Another factor to be considered is the dielectric constant (ε), which is an indicator of the polarity of the supercritical fluid and which also increases with increasing pressure. The dielectric constant (ε) of a solvent provides a measure of how well that solvent can separate oppositely charged ions.

1.1.1 Types of supercritical fluids

Different substances with appreciably different critical temperatures and pressures can be used as supercritical fluids. Examples of common supercritical fluids are presented in Table 1.

Table 1: Characteristics of representative supercritical fluids.

Fluid	Critical temperature (°C)	Critical pressure (atm)	Solubility parameter (δ)[a]
carbon dioxide	31	73	10.7
nitrous oxide	36	72	10.6
ammonia	132	112	13.2
methanol	240	78	14.4
ethylene	32	48	6.6
ethane	10	51	6.6
water	374	227	–

[a]: Hildebrand solubility parameter in $(cal/cm^3)^{1/2}$

Carbon dioxide is the most desirable since it has a relatively low critical temperature (31°C) and a relatively low critical pressure (73 atm). Also carbon dioxide is: (1) inert and noncorrosive in a non ionizing environment, (2) nonflammable and nonexplosive, (3) abundant and inexpensive, (4) nontoxic, and (5) of low viscosity, low surface tension and high diffusivity (Bradley, 1989). Other supercritical fluids such as nitrous oxide (N_2O) (which is a potent oxidizing agent) have been used for different applications. For instance, Raynie (1993) recounted that nitrous oxide that had been used for the supercritical fluid extraction (SFE) of 1 g of ground coffee resulted in an explosion and destruction of the high pressure stainless steel extraction vessel. In consequence, N_2O should be used as an extractant in SFE only with extreme caution, especially when the samples contain high proportion of organic materials. Nitrous oxide should not be mixed with organic cosolvents in SFE applications. Hawthorne *et al.*, (1992a) compared SFE recoveries for different anthropogenic pollutants including polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) from a petroleum waste sludge and PAHs from railroad bed soil using different SCFs that included $CHClF_2$ (freon-22), N_2O and CO_2. Whereas SCF CO_2 yielded the lowest recoveries for each sample, $CHClF_2$ consistently provided the highest extraction efficiencies, most likely because of its higher dipole moment relative to the SCF CO_2. The study indicated that the ability of a supercritical extraction fluid to interact with sorptive sites on sample matrices (and possibly to modify the matrix, e.g., by the removal of water) may ultimately control SFE rates and recoveries from environmental solids. The drawbacks included the fact that $CHClF_2$ can contribute to ozone depletion and N_2O can present an explosion hazard.

1.1.2 Modified supercritical fluids

The principle limitation of supercritical carbon dioxide (SC-CO_2) is its limited ability to dissolve polar analytes even at very high densities. Consequently, it has been proposed that enhanced solubilities leading to better separations would be achieved best by using solvent mixtures, or "entrainer" mixtures that target specific interactions between the solute and the solvent or entrainer. The use of entrainers has improved selectivity while retaining the sensitivity of the solvating power of the medium to small changes in temperature and pressure. This has made SFE a very an attractive alternative to conventional separation techniques. Probably, the mostly widely used modifier is methanol, because of its solvent polarity and its ability to deactivate the active sites of the stationary support (Langenfeld *et al.*, 1994).

Janssen and Cramers (1990) described the role of the modifier in chromatography. Enhanced solubilities were explained by contributions to different mechanisms that might (1) increase the mobile phase polarity giving rise to the specific interactions between the solute and the mobile phase, (2) increase the mobile phase density and, (3) lead to the deactivation of active sites on the surface of the packing material. Modifiers in SFE are required to enhance extraction efficiencies, whereas in supercritical fluid chromatography (SFC) the modifiers aid in eluting the analyte out of column (Levy *et al.*, 1992). The influence of eight separate organic modifiers in combination with SC-CO_2 and ternary mixture (CO_2 + methanol/toluene) at two different concentrations (1 and 10% v/v) on the recovery of PCBs and PAHs from a variety of samples have been reported (Langenfeld *et al.*, 1994).

Modifiers can be introduced into either the fluid or the sample matrix. The use of premixed cylinders that can be obtained from commercial suppliers of fluids have been very popular. A second popular approach has been to add modifier by using two separate pumps. However, since high compressibility is a characteristic of SC-CO_2, a thermostated mixing tee must be used. This device mixes the fluids in a thermostated zone and then delivers the mixed fluid to the extraction vessel. Finally, the introduction of the modifier into the extraction vessel containing sample can be easily accomplished. This approach be useful for static extractions but not for dynamic extractions since the modifier is rapidly purged from the extraction vessel once the extraction begins (Taylor, 1995).

1.2 Sample preparation techniques

In recent decades, considerable time and effort has been devoted to improve the speed and selectivity of analytical procedures as well as developing and improving instrumentation, data handling and report-generating software. On the other hand, sample preparation has not received comparable levels of attention. Undoubtedly, sample preparation remains the most error prone, least glamorous and the most labor-intensive task in the analytical process. Any technique(s) that minimize (1) the use of toxic and carcinogenic organic solvents in the sample preparation process and (2) the problems of solvent waste disposal would be welcomed. If a procedure can be made faster or can be automated readily, the increased sample throughput would greatly enhance the desirability of the process (Taylor, 1996).

A frequently employed approach to sample preparation is the use of "solvent extraction". The term solvent extraction can refer to two different types of processes. One type, which is also known as *liquid-liquid extraction* (or *liquid ion exchange* for ionic species), refers to the separation of constituents from a liquid solution by contact with a second, immiscible liquid in which the constituents are more soluble. The other type, known more commonly as *leaching*, is the separation of constituents from solids by contact with a liquid in which the constituents dissolve (Freeman, 1989). Such transfers might be carried out for a variety of reasons, such as separation of a valuable constituent from impurities that were present in the original solution or the concentration of a constituent for ease of subsequent recovery or treatment. The choice of the time (1 to 72 hours) for Soxhlet extraction, the choice, the volume and the subsequent disposal of organic solvents must all be considered.

One of the major waste-treatment application of solvent extraction is the removal of phenols from wastewater effluents originating from refining industries. Related industrial applications include the treatment of wastes from coke oven and phenol-resin plant operations. The phenols that are transferred to the solvent phase can be recovered into an aqueous phase by a subsequent extraction with caustic. Removal efficiencies are typically in the range of 90% to 98%. Drummond *et al.*, (1985) investigated the efficiency of a treatment train for wastewaters originating in coal-liquefaction process. One step in the treatment process involved a solvent extraction with methyl ethyl ketone in a 36 stage, continuous countercurrent extraction column. At solvent feed rate of 0.4 L/min, and a solvent to wastewater ratio of 0.1, phenols were reduced from 9150 ppm in the incoming stream to 40 ppm in the raffinate. Reductions in total organic carbon (TOC) and chemical oxygen demand (COD) were 93% and 92%, respectively. The cleaned raffinate was suitable for biological treatment in an activated-sludge system.

Solid phase extraction (SPE) has become increasingly popular during the past few years. SPE is a convenient alternative for liquid-liquid extraction, the traditional method for cleaning and concentrating analytical samples (Taylor, 1996). In addition, SPE methods appreciably reduce the volume of chlorinated and non chlorinated organic solvents required for a typical sample preparation. Activation of the phase prior to sample introduction and selective rinsing of the phase to recover the extracted analyte (free of matrix components) for subsequent analysis are critical steps in this sample preparation procedure.

Many studies with SFE have identified definite advantages over conventional extraction methods. In general, extractions performed by SFE require less time and provide improved precision relative to separations obtained using conventional methods, such as Soxhlet extraction. A direct comparison of Soxhlet with low and high temperature supercritical CO_2 extraction for the recoveries of organics (PAHs, N- and S- heterocyclics, chlorinated phenols and pesticides) from environmental solids has been published. Generally, SFE at 200°C provided recoveries that were comparable with Soxhlet extractions (Hawthorne *et al.*, 1994). SFE of organophosphorous and organochlorine pesticides from soils was compared with classical sonication followed by Soxhlet extraction. It was reported that the mean recovery of the 12 pesticide compounds for the sonication, Soxhlet and SFE were 94.7%, 93.1% and 91.6% respectively. SFE demonstrated the best precision of the three techniques with a mean relative standard deviation of 2.94% (Snyder *et al.*, 1992).

David and Seiber (1996) reported efficiencies for three extraction techniques for the removal of nonpesticidal organophosphorous compounds (OPs) from soil. Conventional Soxhlet extraction was compared with supercritical fluid extraction (SFE) and with a low solvent volume flow through technique referred to as high-pressure solvent extraction

(HPSE). SFE, that had been optimized by varying temperature, pressure and the proportion of methanol modifier, was characterized by at least 90% recovery for the extraction of OPs from both spiked and native soils. HPSE experiments were characterized by consistent recoveries over a range of temperatures up to 200°C and pressures up to 170 atm. HPSE provided extraction efficiencies that were comparable to those obtained with Soxhlet extraction and SFE but with a substantial saving of both time and cost.

A comparison of liquid and supercritical carbon dioxide as an extraction solvent for plating bath treatment has been investigated by Laintz *et al.*, (1998). The use of liquid CO_2 rather than SC-CO_2 was used for economical reasons. Liquid CO_2 containing β-diketones (acetylacetone and its fluorinated analogs) as an extraction solvent for the removal of Ni^{2+} and Zn^{2+} from electroplating solution was investigated and compared to results obtained with SC-CO_2. Fluorinated acetylacetone showed a greater extraction efficiency, but over 70% of both Ni^{2+} and Zn^{2+} was extracted with acetylacetone with a 100-fold molar excess for both liquid and SC-CO_2. The addition of isopropyl alcohol as a modifier, increased the extraction efficiency to over 80% for both metals using both phases of CO_2 as carrier fluid. Recently, the technique of 'accelerated solvent extraction' (ASE) and supercritical fluid extraction (SFE) have been combined for the extraction of ecologically hazardous traces of organics (Friedrich and Kleiböhmer, 1997). The resulting 'supercritical CO_2-assisted liquid extraction' (SALE) technique incorporates the advantages of ASE (high extraction efficiency, variety of organic solvents available, rapid desorption of analyte molecules) with the advantage of SFE (gas-like diffusion properties, high transport ratios, low solvent consumption, easy trapping of extracted compounds, integration of clean-up steps). The SALE technique with TFA and toluene was demonstrated to be as efficient as the Soxhlet extraction for both PAHs and PCDDs/PCDFs.

1.3 Supercritical fluid extraction

Supercritical fluid extraction (SFE) is one of the more rapidly expanding of analytical techniques. Many laboratories are turning to SFE as a sample preparation method for the analysis of solutes in liquid or solid matrices. SFE provides an alternative technique for sample preparation that is rapid yet environmentally less hazardous. As a result of the U.S. Environment Protection Agency's voluntary organic reduction program and the total phaseout of chlorofluorocarbons (by Jan. 1, 1996), interest in methods that use benign solvating media such as supercritical fluids is increasing (Taylor, 1995).

To identify the optimal conditions for performing SFE, the analyst must define his analytical objectives, since for many applications, SFE is not a highly discriminating technique. Removing an analyte from a matrix requires knowledge of the solubility of the solute, the rate of transfer of the solute from the solid sample matrix to the solvent phase and interactions of the solvent phase with that matrix. In any extraction process, appreciable solubility of the target solute in the extraction solvent is a prerequisite.

King (1989) proposed four basic parameters that were necessary to understand solute/analyte behavior in a supercritical fluid extraction. The first is the miscibility pressure (or threshold pressure); the pressure at which the solute starts to dissolve in SCF. An approximate knowledge of this pressure (or corresponding density) is very useful, because it permits the analyst to choose a starting pressure for supercritical-fluid-based fractionation processes. The second parameter is the pressure at which maximum solubility of the analyte is achieved. This condition can be approximated by the Giddings' equation which relates the solubility parameter of the gas to its critical and reduced state properties (Giddings *et al.*, 1968). When the solubility parameter of the extracting fluid (gas) is equivalent to that of the solute, maximum solubility is attained. The third parameter is the pressure range for fractionation of the sample in which a solute's solubility will range between zero and its maximum value in the supercritical gas (or the pressure region between the miscibility and solubility maximum pressures). In this interval, it becomes possible to regulate the solubility of one solute relative to another in the SCF. However, it is extremely rare in SFE experiments that only one component from the other volatile materials without resorting to an auxiliary technique such as chromatography. Finally, the fourth parameter is the relevant physical parameters of the solute. The melting point is particularly important because solutes dissolve more readily in supercritical fluids if they are in the liquid state. SFE is more easily effected when the extraction is conducted at a temperature in excess the compound's melting point, since the solid state's cohensional energy is reduced appreciably (King and France, 1992). Collectively, these four parameters permit predictions of analyte solubility and serve as a basis for method development. The threshold or miscibility pressure, has been defined as the pressure at which the solute begins to dissolve in the supercritical fluid (McNally, 1995). The miscibility pressure for a given solute-solvent pair remains a somewhat ill-defined concept, since it depends on the technique that is used to measure the solute's solubility in the supercritical fluid. Unfortunately, for many compounds only small differences in their respective miscibility pressures exist, thereby complicating the regulation of pressure as a means of exploiting the small solubility differences that exist under these conditions.

1.3.1 Sample matrix effect

In SFE, as well as in most other extraction processes, it is the effect of the sample matrix that remain the least well understood. Variability among different matrix types can be wide, and the physical and chemical complexities of different matrices can render extractions inefficient (McNally, 1995).

The physical morphology of the substrate can also have an effect on the efficiency of SFE. With sufficient SF solvating power, the rate of the extraction process can be increased by increasing the surface area and/or the porosity of the matrix by grinding the sample. The chemical composition of the sample matrix can have either an enhancing or retarding effect on the extraction efficiencies that are obtained with SFE. The moisture content of the sample matrix can also influence SFE efficiency. For nonpolar analytes, the presence of water appears to be detrimental, whereas for polar analytes, the effect is beneficial. In several cases, drying agents such as anhydrous magnesium sulfate or florasil have been added to the sample and the resulting extractions were reported to be successful for a wide range of moisture levels (McNally, 1995). The removal of water can have a dramatic effect on the recovery of lipids from meat products (King *et al.*, 1989). The recovery of pigments from krill has been demonstrated to suffer from the same effects (Yamaguchi *et al.*, 1986). However, in certain specific cases, the presence of water may actually aid the recovery of the target analyte by acting as a "internal cosolvent" (King and France, 1992). Clearly, the role of water in SFE requires further study.

Water can influence the extraction efficiencies of heavy metals in several different ways, including satisfying the coordination requirements of the complexed metal, protonation of the metal binding sites and lowering the activation energy barriers for breaking the metal-binding site bonds, increasing the polarity of the supercritical fluid phase and establishing a low pH (approximately 3) within the system (Smart *et al.*, 1996). A direct measurement of the pH of water in contact with supercritical CO_2 was investigated by Toews *et al.*, (1995). The pH of the aqueous phase was determined for SC-CO_2 pressures of 70-200 atm and temperatures of 25-70°C. The measured pH varied from 2.80 and 2.95, and the RSD of <1.5% were achieved. Water in contact with CO_2 becomes acidic due to the formation of carbonic acid and its subsequent dissociation:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$$

If the complexing reagents are not ionized at the solution pH, complexation and transportation of metal ions into CO_2 will be inefficient. The pH of the solution can also influence the metal species present. Some metal species are extracted efficiently at a given pH, whereas other species can be extracted only inefficiently or not at all. An acidic medium can cause organic species to become charged, decreasing their solubility in the SC-CO_2 and altering the degree of matrix association. Knowledge of the pH of the system can be very useful for both predicting favorable extraction conditions and interpreting experimental results.

1.3.2 Temperature and pressure effects in SFE

Pressure and temperature represent the two most important physical parameters in SFE; they have both theoretical and practical implications for the extraction process.

Collectively, these two parameters define the density of the supercritical fluid. The common belief among analytical chemists is that the maximum solubility of a solute in the supercritical fluid is achieved at the maximum fluid density. The solubility of a substance in a supercritical fluid is affected by two factors, the volatility of the substance and the solvating effect (related to density) of the supercritical fluid. It was demonstrated by Miller and Hawthorne (1995) that the solubility of anthracene was increased by only a factor of 5 when the CO_2 pressure was increased from 150 to 400 bar (at a constant 50°C). In contrast, raising the temperature from 50 to 200°C at 150 bar increased anthrene solubility by a factor of 23, and at 400 bar, by a factor of 48. The large increase in solubility at higher temperature occurred despite the approximate 50% drop in CO_2 density when temperature was raised from 50 to 200°C.

Langenfeld *et al.*, (1993) studied the effects of temperature and pressure changes using pure CO_2 on the extractions of PCBs and PAHs from three certified reference materials. They observed that at 50°C, increases of the extraction pressure (355-659 bar) had no effect on extraction efficiencies from any of the samples. By contrast, efficient recoveries were obtained during 40 min of extraction from a highly contaminated soil regardless of temperature. PCBs were recovered efficiently from a sediment and PAHs from air particulates only if the temperature was raised to 200°C. At 200°C, PCBs were extracted efficiently at any pressure (152-659 bar), whereas both higher temperature and pressure increased the recovery of PAHs from air particulates. In the same study presented in section 1.2 (page 7), Hawthorne and Miller (1994) concluded that temperature was more important than pressure for achieving high extraction efficiencies when interactions between pollutant molecules and sample matrices were strong. It was argued that increased SFE temperature could be a useful alternative to adding an organic modifier for efficient recoveries from environmental samples.

Yang *et al.*, (1995) studied the combined effect of temperature and solvent modifier for the recovery, by SFE, of PAHs from different matrices. Raising the extraction temperature from 80 to 200°C increased PAHs recoveries from marine sediment, air particulates and diesel soot for either pure CO_2 or CO_2 modified with either methanol, toluene or diethylamine for all of the samples. The results demonstrated that the effect of temperature was independent of the sample matrix. In contrast, the effect of the modifiers was highly dependent on the matrix at both temperatures. The combination of modifier and 200°C yielded the highest recoveries, indicating that the effects of modifier and temperature were additive. Diethylamine at 200°C gave the highest PAH recoveries, and yielded good agreement with Soxhlet extractions.

It is not clear why increased extraction temperatures have often yielded such dramatic increases in extraction efficiencies, although at least two major effects might have been responsible (Bøwadt and Hawthorne, 1995). An increased temperature (1) would be expected to increase the kinetics of the desorption process and therefore, increase the overall extraction rate for those analytes that had been limited by their slow rate(s) of initial desorption. An increased temperature (2) can greatly increase the solubilities of analytes that have an appreciable vapor pressures (e.g., "GC-able" compounds), despite the predicted decrease in density that occurs with increasing temperature at constant pressure.

1.3.3 Flow-rate and sample size considerations in SFE

Once the operating parameters of the SFE have been selected (pressure and temperature conditions and if necessary, an entrainer) other parameters like flow-rate and sample size must be considered. The extraction can be performed in a static, a dynamic or coupled static/dynamic mode. A static extraction takes place when a fixed amount of SCF interacts with the analyte and the matrix. The high diffusivity of the fluid causes it to permeate the matrix and remove the analyte (Taylor, 1995). A dynamic extraction, on the other hand, uses fresh SCF that is continuously passed over or through the sample matrix.

The amount of sample needed for SFE is determined mainly by the detection limit of the analytical method, the size of extraction cells and the size requirement for a statistically representative sample of matrix. Samples ranging from 1 mg to hundreds of grams, SFE of samples <10 g has been most common simply because larger samples require larger amounts of supercritical fluid for quantitative extraction. Flow parameters often determine the success or failure of SFE. They can also be varied to provide information on the dynamics of the extraction process. If the flow of supercritical fluid is insufficient to sweep the cell void volume, the effectiveness of the extraction is reduced. Hawthorne *et al.*, (1995) reported that changing the extraction flow-rate was a simple way to determine whether the extraction was limited by chromatographic retention (e.g., the equilibrium process controlled by the adsorption of analytes to accessible active matrix sites and by analyte solubility) or limited by the kinetics of the initial desorption process. If changing the extraction flow-rate changed the extraction rate proportionally, then the extraction was limited primarily by chromatographic retention (including solubility). For these cases, an increased extraction flow-rate and/or a change of extraction conditions (to increase analyte solubility) is predicted to increase the extraction rate.

1.4 Derivatization and extraction of polar compounds

The derivatization of organic and inorganic compounds has been used to make polar, non-volatile or thermally labile target analytes amenable to GC analysis. Since derivatization procedures generally make analytes less polar, the same concept has been used to derivatize analytes *in situ* in order to make them easier to extract by SFE. Since most SFE fluids lack the ability to extract polar compounds, they remain relatively inert. The rapid diffusion characteristics of SCFs facilitate *in situ* derivatization. In the simplest approach, after the derivatizing reagent has been added directly to the sample, a static extraction is performed followed by a dynamic step (stage of the extraction process) in which the derivatized analytes are eluted from the extractor. Alternatively, reagents have been added to the CO_2 by passing the SC-CO_2 through a cell containing the reagent prior to entrainment into the sample cell. One approach for the extraction of ionic analytes is to first convert the analytes to less polar products, thus making them more soluble in the SC fluids.

Simultaneous supercritical fluid derivatization and extraction (SFED) was investigated as a rapid alternative to liquid solvent extraction followed by derivatization prior to gas chromatography. The addition of a silylation reagent, tri-sil concentrate, directly to the sample matrix, enabled the extraction of analytes from samples that had been extracted previously with conventional SFE (Hills and Hill, 1991). The combined derivatization extraction process was characterized by increased savings of time and improved recoveries of both derivatized and underivatized species. The derivatization reagent was considered to compete with the analyte for active sites of the matrix, thus displacing analyte compounds from the matrix. The conversion of analytes to less polar products under static SFE conditions with derivatization reagents including trimethylphenylammonium hydroxide (TMPA) and boron trifluoride in methanol has been studied by Hawthorne *et al.*, (1992b). The total time for derivatization and extraction can be less than 30 minutes, however some samples that contained high concentrations of reactive matrix components required multiple derivatization/extraction steps to achieve quantitative recoveries.

Lopez-Avila *et al.*, (1993) applied pentafluorobenzyl bromide (PFBBr) and triethylamine (TEA) for this derivatization using a 60 min static extraction followed by 30 min of dynamic extraction (400 atm and 100°C) to achieve variable recoveries of 13 chlorophenoxy acid herbicides. Lee *et al.*, (1993) have demonstrated that the *in situ* derivatization of eight chlorinated phenols from sediments using acetic anhydride in the presence of triethylamine was efficient. From sediments that had been spiked at 50-500 ng/g, the authors obtained 84-100% recovery of the different chlorinated phenols when extracted with CO_2 at 80°C and 370 bar during 10 min static and 5 min of dynamic extraction with flow-rate of 2 mL/min. The effect of temperature was also studied. It was concluded that 110°C gave the optimal overall recovery. Using sequential extractions it was discovered that these conditions yielded only ~80% recovery when applied to real sediments with field-aged residues. Nevertheless, SFE achieved recoveries that were as efficient as (or more efficient than) Soxhlet extraction or steam distillation with relative standard deviation of 5-10%.

Ion-pair reagents (also known as phase transfer catalysts) can be easily coupled with SFE because they are soluble in organic solvents and the reactions occur in non-aqueous media. Field *et al.*, (1992) used tetraalkylammonium salts as ion-pairing reagents to extract linear alkylbenzene sulfonates (LAS) and linear alkylsulfonates (SAS) from sewage sludge. The extracts were then analyzed without further treatment by injecting the crude extracts via a heated split/splitless injection port (where the ion pairs are converted to the alkylated LAS or SAS). With GC-MS analysis of the extracts, good quantitative agreement with conventional liquid solvent extractions was achieved using a 15-min static/15-min dynamic SFE procedure. Rochette *et al.*, (1993) investigated the extraction of 2,4-D from soils using a variety of pre-extraction soil treatments to enhance extraction recoveries. Initial experiments with silylation, ion-pairing, methyl esterification and ionic displacement were reported. Methyl esterification and ionic displacement during SFE proved to be more promising approaches for efficient extraction. A comparison between SFE and a standard Soxhlet extraction method demonstrated the potential for improving analytical measurement for highly polar pesticides in soil by modified SFE-CO_2 extraction reagents and ionic solutions.

1.5 SFE of metal ions and metal chelates

The majority of quantitative SFE studies have focused on the extraction of relatively non-polar analytes. Polar and ionic analytes are more difficult to extract because of their low solubility in carbon dioxide and their potential for strong interactions with active sites within the matrix. Novel reagents have been added to various SCFs to provide enhanced yet selective extraction of target analytes. One of the most common methodologies for the extraction of metal ions from aqueous and solid matrices is the reaction of the target metal ion with a 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 characteristically is toxic, and creates environmental concerns for both handling and safe disposal. The number of publications on SFE of metal ions, metal chelates and organometallic compounds is rather limited. The term chelate is derived from the Greek term meaning "clawlike", and describes the process in which the chelating agents literally wrap themselves around metal ions.

1.5.1 Solubility of metal complexes

A wide ranges of solubilities has been observed for metal complexes. The solubilities of these complexes are influenced by several parameters, including pressure and temperature of the supercritical fluid, the presence of a solvent modifier, the chemical characteristics of the ligand used, the identity of the metal, the oxidation state of metal and the complexant functional group(s), (Smart *et al.*, 1996). Perhaps because of the historical development of SFE in process engineering, the choice of analytical SFE conditions frequently has been based on the pressure and temperature conditions that result in maximal solubility of the target analytes in the supercritical fluid. In conventional liquid extractions, solvent polarity is typically increased to promote analyte solubility.

The experimental techniques for measuring the solubility of a compound (liquid or solid) in a supercritical fluid are either dynamic or static. In the dynamic case, excess solute is swept with SF. The solubility can be measured on the basis of the weight of the analyte dissolved in an exact volume of fluid. In this case solubility is expressed in moles of analytes per liter of SF at the given density. Solubility is also frequently reported as the mole fraction of analyte (moles of fluid can be obtained from volume and density). In this technique, solubility depends on the flow of fluid passing by the analyte (Asharaf-Khorassani *et al.*, 1997). In the static mode, the cell is loaded with a known quantity of solute and SF at a known density. Equilibration between the solute and SF is obtained using either re-circulation or diffusion to homogenize the fluid. Analysis with the re-circulation technique is usually accomplished by using a spectroscopic method such as ultraviolet spectroscopy. In the static diffusion approach, once the system has been pressurized, equilibrium between the solute and SF is attained by permitting the solubilized solute to diffuse into the SF for a certain period a time. After attainment of equilibrium, the cell is depressurized and the dissolved analyte is collected in an organic solvent. Analysis of the resulting solution is usually accomplished using a gravimetric method or spectroscopic method. A static system normally employs spectroscopic analysis while the dynamic mode relies on gravimetric analysis. The gravimetric method is the more frequently used procedure (Taylor, 1995). This involve the production of a saturated solution by passing the SF over the solute in an extraction cell, dropping the pressure to precipitate the solid (liquid) solute, and weighing it.

It is known that cationic metal ions are not soluble in pure CO_2 due to weak interactions between positively charged metal ion and non-polar CO_2 solvent extraction (M'Hamidi *et al.*, 1991). One might conclude that extraction and separation of metal ions via supercritical CO_2 is not feasible. However, metal ions can be solubilized, extracted and separated by reacting them with an organic ligand to form a neutral, stable metal complex. Rapid complexation kinetics between metal ions and ligand and a high stability constant for the resulting neutral complex will enhance the rate of the extraction process.

A key factor in supercritical CO_2 extraction of metal complexes from different matrices is a reasonable solubility for the metal chelate in supercritical CO_2. In this regard, different types of ligands have been used for complexation and extraction of trace metals into supercritical CO_2. The solubilities of 'free' complexing reagents in SC-CO_2 have been investigated by Smart *et al.*, (1997). These reagents included macrocyclic ligands, β-diketones, dithiocarbamates and organophosphorous compounds.

1.5.1.1 Macrocyclic ligands

Synthetic compounds such as crown ethers are capable of enveloping metal ions (especially alkali metal cations) within a pocket of oxygenated electron donor functional groups. The outside surface of the crown ether remains very hydrophobic and soluble in nonpolar solvents. The hydrophobicities of the resulting complexes is sufficiently large that the complexing reagents can extract a water soluble ionic reagent into a non-polar solvent (Harris, 1991). The only ligands from the macrocyclic class have been investigated systematically for the extraction of metals are the crown ethers. The first reported crown ether to have been synthesized was obtained in a modest 0.4% yield during an attempt to prepare a phenolic ligand from catechol and bis(2-chloroethyl)ether (Pedersen, 1988). Crowns ethers are a class of selective ligands that form stable complexes with metal ions based primarily on the ionic radius-cavity compatibility concept (Pedersen, 1988).

Modification to the structures of crown ether compounds by attaching negatively charged functional groups to the host can eliminate the need for the counter ions, that conventionally are required for the transfer of charged complexes into an organic phase. This approach has been described by Wai and Tang (1986) who have demonstrated that the extraction of metal ions by crown ether carboxylic acids was independent of the identity of the counter ion (anion) of the target analyte(s). A crown ether carboxylic acid (*sym*-dibenzo-16-crown-5-oxyacetic acid) was utilized to transfer lanthanides efficiently from aqueous solution into an organic solvent. A similar study has been conducted by Walkowiak *et al.*, (1990). The competitive solvent extraction of alkali-metal from aqueous solutions into chloroform with a series of lipophilic dibenzocrown ethers (sym-decyldibenzo-16-crown-5-oxyacetic acid) with pendant carboxylic acid groups was investigated by this group. Both extraction selectivity and efficiency were influenced by variations in the ring size of the crown ether and by the site of attachment of the lipophilic group. Preorganization of the binding site by proper positioning of the lipophilic group enhanced extraction selectivity.

The selective extraction of mercury with ionizable crown ethers into supercritical carbon dioxide was reported by Wang *et al.*, (1995). The solubility of a *tert*-butyl-substituted dibenzobistriazolo-crown ether in methanol (5 mol %) has been determined to be of the order of 1×10^{-3} M at 60°C and 200 atm, which is comparable to the solubility of the mercury-hexafluorodiethyldithiocarbamate complex (Hg-FDDC) under these conditions. Using this proton-ionizable crown ether as an extractant in methanol (5%) modified CO_2, quantitative extraction of Hg^{2+} were achieved from both sand and cellulose-based filter papers at 60°C and 200 atm if a small amount of water had been added in the solid matrix prior to the extraction. Extraction of Hg^{2+} from aqueous samples can also be achieved using methanol-modified CO_2 containing the macrocyclic ligands. The formation of non-polar extractable metal chelates with the ligand at the pH defined by the CO_2-H_2O system appears to be an important factor in determining the extraction efficiencies of the metal ions by this *in situ* chelation-supercritical fluid extraction technique.

The solubility of ferrocene and nickel complex in supercritical fluids has been investigated by Cowey *et al.*, (1995). The results indicated that the ferrocene complex was more soluble than the nickel complex at similar temperatures and pressures. The nickel complex was essentially insoluble in pure supercritical carbon dioxide and required the addition of 10 vol % methanol to achieve a measurable solubility. Ferrocene is a bis(*p*-cyclopentadienyl)iron complex, in which all the molecular bonding orbitals are filled and no free coordination sites on the iron are available (properties that are similar to aromatic compounds). The structure of the nickel complex was different since the metal ion was not as effectively "wrapped up" by the ligands. Presumably the increase in solubility of the nickel complex when the modifier was present was due to methanol solvating the two available trans sites, thereby reducing the polarity of the complex.

1.5.1.2 β-diketones

A β-diketone or 1,3 diketone are conventionally considered to consist of two ketone groups that are separated by a single carbon. Diketonate complexes with various metal cations are among the most frequently studied coordination compounds. Complexes of β-diketones with virtually every metal and metalloid in the periodic table appear to have been investigated. These reagents have been used in conventional solvent extraction for the preparation of analytical samples; their application has been extended to SFE as well. Most β-diketone-metal complexes are quite volatile; their applications to gas chromatography (GC) and to supercritical fluid chromatography (SFC) have been investigated extensively.

The most frequently studied β-diketone ligands are acetylacetone (AA), trifluoroacetylacetone (TAA), hexafluoroacetylacetone (HFA), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedone (FOD) and thenoyltrifluoroacetylacetone (TTA). Of these ligands, only thenoyltrifluoroacetylacetone (TTA) is a solid, the others being liquids at room temperature. Under conventional SFE conditions, all these ligands are characterized by appreciable miscibility with CO_2. The log of acid dissociation constant (pK_a) values β-diketones, AA, TAA, FOD, TTA and HFA have been reported to be 9.0, 6.7, 6.7, 6.2 and 4.4, respectively (Cheng *et al.*, 1982). This property enables HFA to extract metals from much more acidic media. The pK_as follow their ability to extract metals, suggesting an appreciable significant influence of the Lewis acidity of the chelating agent or the adduct formation process. Extensively fluorinated β-diketones are appreciably more efficient than their hydrogen analogs for the synergistic extraction of metal species. The additional electron-withdrawing effect of fluorine in the ligands coordinated with the metal ions are predicted to enhance the Lewis acidity of the metal chelates (Lin *et al.*, 1995a). The β-diketone ligands are used almost exclusively in protonated forms. The β-diketones are rendered acidic by the tautomeric equilibrium established between the enol and keto forms of these compounds (Figure 2).

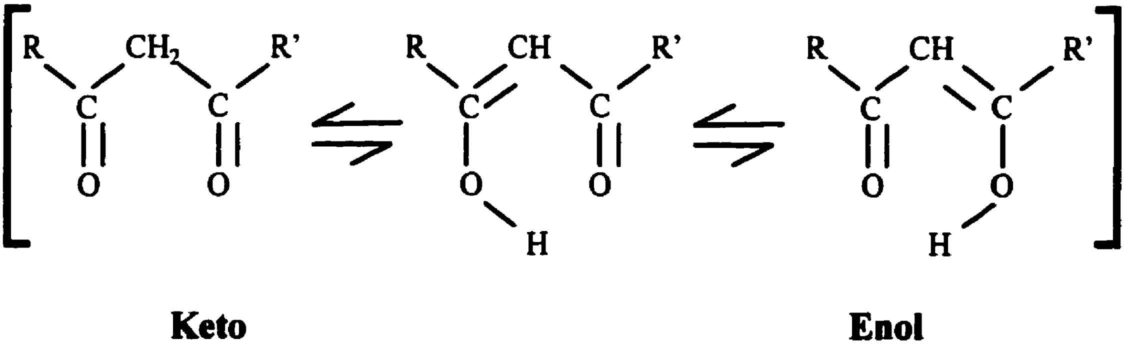

Figure 2: Struture of a β-diketone in its enol and keto forms.

The fluorinated ligands have been observed to exist almost exclusively in the enol form under the high pressures and temperatures of conventional SFE (Smart *et al.*, 1997). By contrast, the non-fluorinated ligand (AA) is found to be partly in each form in the SF phase.

The difference in the enhancement of the extraction of europium(III) with six β-diketones by addition of tetrabutylammonium into chloroform was investigated by Noro and Sekine (1993). The β-diketones were acetylacetone, benzoylacetone, benzoyltrifluoroacetone, trifluoroacetylacetone and hexafluoroacetylacetone. The extraction of the ternary complex of Eu(III) with β-diketones and tetrabutylammonium was very much different when using different β-diketones. The largest enhancement of extraction was observed with hexafluoroacetylacetone.

The FOD complexes are among the most volatile of the known lanthanide-β-diketone complexes. These properties make FOD a good candidate for *in situ* chelation-SFE of lanthanides and actinides (Lin *et al.*, 1993). The extraction of lanthanides and uranyl ions from cellulose-based matrices by pure supercritical CO_2 containing FOD was incomplete. However, a quantitative extraction was achieved if a small amount of water was used as a matrix modifier in combination with 5% methanol as a solvent modifier. A strong synergestic effect was observed in the SFE of actinides from solid samples when a mixture of tributyl phosphate (TBP) and fluorinated β-diketones was used (Lin *et al.*, 1994). The β-diketones included AA, TAA, FOD, TTA and HFA. TBP is considered to compete with the matrix for the unoccupied coordination sites on the complex by forming adducts and making them easier to transfer from the solid phase into the fluid phase. The extraction efficiency obtained from the synergistic extraction of actinides by mixtures of β-diketones and TBP increased in the order AA < TAA < FOD = TTA < HFA.

Saito *et al.*, (1990) have reported that the solubilities of acetylacetone complexes with different metals (60°C and 9.8-29.4 MPa) were strongly influenced by the extraction pressure, by the nature of the metal and the number of constituent acetylacetone ligands in the chelates. The highest solubility was observed for In and Ga, which can be correlated with their characteristic behavior being intermediate between metallic and non-metallic elements. For divalent or trivalent metal cations (Mn and Co), it was observed that the higher oxidation state complex was characterized with an enhanced solubility. This can be correlated with a more complete shielding of the 3+ metal ion center by the greater number of ligands so that the solvation of the resulting complex is enhanced owing to the increase in solute-solvent interactions between the SC-CO_2 and the complex.

The solubilities of copper(II) and chromium(III) β-diketonates in supercritical CO_2 have been investigated by Lagalante *et al.*, (1995). The mole fraction solubilities of ten copper(II) and five chromium(III) β-diketonates were measured in supercritical carbon dioxide with spectroscopic technique and found to vary over 4 orders of magnitude. The observed trends indicated that the solubility in supercritical carbon dioxide was dictated by the character of the hydrocarbon or fluorocarbon shell surrounding the central metal atom. The use of four dithiocarbamates and three fluorinated β-diketones as potential chelating agents for three transition metal ions (Cd^{2+}, Pb^{2+} and Hg^{2+}) extracted from spiked sand and filter samples by SFE have been reported by Wai *et al.*, (1996). At 250 atm and using CO_2 modified with 5% methanol, the recoveries of Cd^{2+}, Pb^{2+} and Hg^{2+} ions from spiked sand samples were $\geq$ 95% with lithium bis(trifluoroethyl)dithiocarbamate (LiFDDC) as the chelating agent; they ranged from 83-97% with diethylammonium diethyldithiocarbamate and from 87-97% sodium diethyldithiocarbamate as chelating agents, and from 68-96% with trifluoroacetylacetone, hexafluoroacetylacetone and thenoyfluoroacetone as chelating agents. The results suggest that the solubility of the metal chelate in the supercritical fluid plays a more important role than the solubility of the chelating agent in the supercritical fluid, as long as sufficient chelating agent is present in the fluid phase. Fluorination of the chelating agent, as in the case of LiFDDC, increase the solubility of the metal chelate and subsequently enhances the extraction efficiency for the metal ions.

Recently, Ashraf-Khorassani *et al.*, (1997) used an on-line SFE-HPLC to measure the solubilities of different metal β-diketonate complexes in SC-CO_2. For each measurement, the 0.5 mL extraction vessel was filled with metal chelate. Next the system was pressurized to 200 atm using pure CO_2. The HPLC flow of mobile phase then transported the chelate from the injection loop through the column to a variable-wavelength UV absorbance detector that was operated at 280 nm. The solubilities of metal hexafluroacetylacetonate complexes were observed to be two to three orders of magnitude greater than the solubilities of the corresponding metal acetylacetonates.

1.5.1.3 Dithiocarbamates

The complexing properties of dithiocarbamates are directly related to the presence of two donor sulphur atoms, that primarily determine the nature of the metals that can be bound and the strength of the complexes formed (Hulanicki, 1967). In the dithiocarbamate ion (see figure below), R and R' denote various alkyl substituents, that do not influence the metal-sulphur binding properties appreciably, but can influence some of the physical properties of the product complexes including solubility (Figure 3).

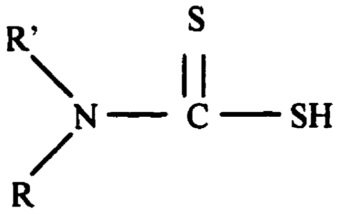

Figure 3: Structure of dithiocarbamate.

Laintz *et al.*, (1991) measured the solubilities of different metal diethyldithiocarbamate (DDC) and bis(trifluoroethyl)dithiocarbamate (FDDC) complexes in SC-CO_2 [the complexes included: $Ni(DDC)_2$, $Ni(FDDC)_2$, $Co(DDC)_3$, $Co(FDDC)_3$, $Cu(DDC)_2$, $Cu(FDDC)_2$, Na(DDC), Na(FDDC), $Bi(DDC)_3$, $Bi(FDDC)_3$]. Striking differences in the solubilities (several orders of magnitude) were observed between the fluorinated and non-fluorinated diethyldithiocarbamate-metal complexes. Subsequently, Laintz *et al.*, (1992a) have demonstrated that FDDC can form stable complexes with arsenic (As^{3+}) and other metal ions (Bi^{3+}, Co^{3+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Sb^{3+} and Zn^{2+}) the products of which can be separated by capillary SFC using CO_2 as a mobile phase. Again the solubilities of complexes composed of fluorinated ligands were enhanced relative to their hydrogenated analogs (DDC). The resulting metal-FDDC complexes exhibited appreciably increased solubilities in SC-CO_2 (of the order $\cong 10^{-3}$ mg/mL at 50°C and 100 atm) which was some 2-3 orders of magnitude greater than the corresponding nonfluorinated analogues. Using this FDDC extraction and SFC analysis, the detection of arsenic species in the presence of other metals were achieved with detection limit in the ppb level. In another investigation, Laintz *et al.*, (1992b) described an experimental approach for the extraction of Cu^{2+} from an aqueous solution and from a silica surface using supercritical carbon dioxide containing LiFDDC as the extractant. A quantitative extraction of the Cu^{2+} from the aqueous medium was readily achieved if the operating pressure was increased to 79.3 bar and 35°C, which corresponded to a CO_2 density of 0.37 g/cm^3.

As mentioned in section 1.5.1.2 (page 22), the use of four dithiocarbamates and three fluorinated β-diketones as potential chelating agents for three transition metal ions (Cd^{2+}, Pb^{2+} and Hg^{2+}) extracted from spiked sand and filter samples by SFE have been reported by Wai *et al.*, (1996). Virtually quantitative recoveries of Cd, Pb and Hg with bis(trifluoroethyl)dithiocarbamate, diethylammonium diethyldithiocarbamate or sodium diethyldithiocarbamate were reported. Again, perfluorination to produce (trifluoroethyl)dithiocarbamate increased the solubility of the product metal chelate.

Wai *et al.*, (1993) reported the extraction of mercuric ions from solid samples (cellulose matrix) using SC-CO_2 containing LiFDDC. The results demonstrated that a small amount of water added to the sample tended to facilitate the extraction of $Hg(FDDC)_2$. The efficiency of Hg^{2+} extraction was further enhanced by adding methanol to the fluid phase. The methanol, modifier enhanced the interactions between the solvent and the polar solute. Wang and Marshall (1994a) have reported that tetrabutylammonium dibutyldithiocarbamate (DBDTC) was effective in the extraction of Cd^{2+}, Pb^{2+} or Zn^{2+} from aqueous media by supercritical CO_2. Measurements of solubilities in SC-CO_2

corroborated the hypothesis that the nonpolar character of a series of tetraalkylammonium dialkyldithiocarbamate ion pairs was influenced (*i*) primarily by the chain length of the alkyl substituent on the carbamate nitrogen and (*ii*) to a lesser extent, by the chain length of the alkyl substituent(s) on the ammonium counterion. A silica flame-in-tube device was described by Wang and Marshall (1994b) for the sensitive detection, by AAS, of As, Cd, Cu, Mn, Pb, Se or Zn in supercritical extractor eluate. In operation, analyte metal in aqueous medium was derivatized by *in situ* complexation with tetrabutylammonium dibutyldithiocarbamate (TBADBDTC) and the product complex was mobilized into SC-CO_2, then purged from the extractor by replacing the headspace fluid with fresh mobile phase.

Wang and Marshall (1995) investigated supercritical CO_2 extraction as a method for characterizing the Cd, Zn and Cu bound to metallothionein (MT) that had been isolated from rabbit liver. In the presence of tetrabutylammonium dibutyldithiocarbamate (TBADBDTC) complexing agent, Cd was recovered quantitatively if the MT had been dissolved in water but none was recovered if the solid protein was extracted directly. That approach (with or without added complexing reagent) coupled with on-line detection by atomic absorption spectrometry showed great promise as a speciation technique for protein bound heavy metals.

The influence of selected natural complexants on the mobilization purging of copper from aqueous media into supercritical carbon dioxide has been reported by Wang and Marshall (1996a). The mobilization/purging of Cu(II) or Zn(II) from aqueous solution by *in situ* complexometric extraction into SC-CO_2 was described. The Cu solution was extracted virtually quantitatively with an half-life of 35 min but Zn was not mobilized efficiently due to the apparent formation of an insoluble zinc carbonate. Recoveries of Cu(II) from Cu-fulvic (FA) solutions of Cu-FA-sand suspensions were dependent on the concentrations of both Cu and FA in the sample. For a solution containing 1.2 μmol Cu^{II} + 1.05 μmol mL^{-1} FA, higher Cu(II) loading caused an apparent coagulation of the FA which was accompanied by the release of a portion of the bound Cu ($t½$ = 2.5 min) but the immobilization of the remainder. For lower concentrations of Cu-FA (0.48 μmol Cu(II) + 0.48 μmol FA per milliliter), no coagulation was evident and the Cu^{II} analyte was purged ($t_{½}$ = 16.7 min) virtually quantitatively. For extractions of Cu-FA-sand mixtures, recoveries were less than quantitative. Cu(II) was recovered quantitatively from 1% (m/m) oxalic acid but at a decreased rate of purging but this complexant increased Cu recovery from Cu-FA-sand suspensions only moderately.

1.5.1.4 Other extractive reagents

Organophosphorus reagents such as tributylphosphate (TBP) and phosphine oxides such as tributylphosphine oxide (TBPO), tri-n-octylphosphine oxide (TOPO) and triphenylphosphine oxide (TPPO) have been investigated by Lin *et al.*, (1995) for the SFE of uranium and thorium from nitric acid solutions. It was shown that TBPO, TOPO or TPPO when used as extractant provided higher efficiencies than TBP, especially at lower nitric acid concentration. The addition of another chelating agent such as thenoyltrifluoroacetone (TTA) enhanced the extraction of thorium. Similarly, Laintz and Tachikawa (1994) investigated the use of SC-CO_2 as a substitute extraction solvent in the processing of nuclear wastes. Their test system consisted of the extraction of lanthanide ions from acidic solution. Lanthanides were extracted from 6M HNO_3-3M $LiNO_3$ solutions using tributyl phosphate (TBP) modified CO_2. Synergistic effects were also investigated using a combination of thenoyltrifluoroacetone (TTA) and TBP modified CO_2. It was observed that near quantitative extraction efficiencies of Sm^{3+}, Eu^{3+}, $Gd^{3+}$and Dy^{3+} was achieved whereas the recoveries for La^{3+}, Ce^{3+}, Yb^{3+} and Lu^{3+} were much lower. When TBP was mixed with the fluorinatated β-diketone, extraction efficiencies were virtually quantitative (Lin *et al.*, 1993; Lin *et al.*, 1994).

Research to date on the SFE of metal ions has focused on the use of dithiocarbamate(s) and β-diketone(s) but recently, other fluorinated hydroxamic acid reagents for the extraction have been investigated by Glennon *et al.*, (1997). He reported, the synthesis of selected fluorinated mono-hydroxamic acids and their N-substituted derivatives. The novel ligands are perfluorooctanenohydroxamic acid (PFOHA), heptafluorobutylrichydroxamic acid (HFBHA) and their N-methylhydroxamic derivatives. Of these reagents, PFOHA was the most effective extractant of Fe(III) from spiked filter paper (97% extraction). The selectivity of this ligand for Fe(III) in the presence of Cu(II), Ni(II), Pb(II) and Zn(II) was appreciable.

1.6 SFE of metal anions

Anionic metals and metalloids are among the most toxic of inorganic pollutants. Conventionally, this group is considered to include arsenic (as arsenite or arsenate), hexavalent chromium (as chromate), cyanide, fluoride and selenium (as selenide, selenite or selenate). These anionic pollutants can result from direct industrial utilization in their anionic form(s) (e.g., chromate usage in metals plating), or as a consequence of natural but man-induced processes (acid mine drainage) or by-product of a manufacturing activity (metal ore smelting). To date, few papers have been published on the mobilization of metal anions with supercritical fluid extraction (SFE). Most reports have been concerned the mobilization of cationic species.

Hawthorne *et al.*, (1991) described the quantitative purging of linear alkylbenzesulfonates from soil, sediment and anaerobic digested sludge into methanol amended SC-CO_2 and Laintz *et al.*, (1992) have reported the complexometric extraction, with bis(trifluoroethyl)dithiocarbamate, of As^{III} and Sb^{III} (as well as As^{V} and Sb^{V} after pre-reduction) from natural waters. Reactive supercritical fluid extraction has been used for the speciation of moderately toxic dimethylarsenic acid (DMA), monomethylarsenic acid (MMA) and inorganic As^{III} and As^{V} in solid samples by Wenclawiak and Krah (1995). Derivatization with methylthioglycolate (TGM) was performed in SC-CO_2. Different extraction conditions have been tested. The arsenic derivatives were monitored by GC. A capillary-SFC method was evaluated for the analysis of TGM derivatizes and compared with GC.

Wang and Marshall (1996b) studied a FI system on-line detector to evaluate the feasibility of mobilizing/purging anions (chromate, selenate or selenite) from aqueous media by adding an alkylammonium halide directly to the SC-CO_2 mobile phase. At 30.6 MPa and 80°C, SC-CO_2 solubilized sufficient tetrahexylammonium bromide (THBA) to effect the efficient purging (93%) of selenate (60 µg) from aqueous solution during a 40 min extraction. At 24.1 MPa and 50°C, there was little difference in the recoveries (66 versus 62%) using THBA or tetrabutylammonium dibutylthiocarbamate (TBADABDTC) as pairing reagent. Selenite or chromate was also efficiently mobilized with either reagent. The Cr and Cu in an aqueous suspension containing chromated copper arsenate wood preservative were simultaneously mobilized using a mixture of THAB and TBADABDTC. Despite appreciable interactions with other components of the sample, 89 and 98%, respectively, of the Cr and Cu burdens were purged from the sample during 45 min extraction using a decompressed flow rate of 2.2 L/min.

1.7 Remediation treatments of metal pollutants

Conventional remediation technologies include precipitation, reduction, adsorption, incineration and stabilization/fixation. Classical precipitation is the most widely used technology for inorganic toxicant control. This approach has been especially popular for the control of metals. Hydroxide precipitation with lime is the most economical reagent for the precipitation of aqueous metal wastewaters (Ford, 1992). The principle disadvantages associated with hydroxide precipitation are the formation of a voluminous sludge that tends to increase the costs of disposal of the sludge and, limited metal removal from the aqueous phase due to solubility constraints. A further complication is the requirement to remove excess water from the sludge to decrease transportation costs. On the other hand, chemical reduction has been used primarily to reduce complexed metals such as hexavalent chromium, mercury, copper, soluble lead and silver. The overall reaction causes a decrease in oxidation states of the target ion(s), (Grosse, 1989). A widespread application of this technique is the reduction of hexavalent chromium, present initially as chromate (CrO_4^{-2}), or dichromate ($Cr_2O_7^{-2}$), to a more readily precipitated trivalent form (Cr^{+3}). Common reducing agents for chromate include soluble sulfur compounds such as metabisulfite, bisulfite, sulfur dioxide and ferrous sulfate. Although this approach has been successful in reducing the levels of chromate in waste streams, the addition of sulfides and/or sulfites to the effluent will necessitate other treatment(s). Other reduction processes can be more effective when treating aqueous waste streams to remove the excess of these reagents. Unfortunately, the surface contact reaction is diminished when treating slurries, tars or sludges.

Adsorption (or sorption) is a process that involves the contact of a free aqueous phase with a rigid particulate phase that has the propensity to selectivity remove or store one or more of the dissolved solutes (e.g., metal species) present in the solution (waste stream), (Grosse, 1989). A wide range of adsorbents and ion exchange resins have been used commercially in treating aqueous waste streams that are contaminated with metals. These processes include carbon adsorption, ion-exchange, adsorption onto hydrous solids and selective reactants. Usually, the sorbent has a limited uptake capacity, whereby one solute is exchanged for another (as in ion exchange processes). Once this capacity has been expended, backwashing or regeneration becomes necessary since desorption will occur, leaching potential pollutants back into solution.

Daley (1989) classified different clean-up processes based on their effectiveness. It seems that immobilization is effective for nonvolatile and volatile metals in soil, whereas solvent extraction is potentially effective (in certain situations) and finally thermal destruction is not expected to be effective for nonvolatile metals and not recommended for volatile metals in soil.

The primary objective in employing stabilization/fixation technique is to limit the mobility (or dissolution) of pollutants in a manner that inhibits the contamination of groundwater (Grosse, 1989). Materials are mixed with wastes to achieve physical immobilization and chemical alteration. Basically, stabilization is a process by which industrial wastes are treated to immobilize hazardous constituents and prevent dissolution of toxic materials into the environment. More specifically, stabilization is an encapsulation process that involves a reaction between the residual water present in the waste substrate and chemical additives or binders to reduce the solubility or chemical reactivity of the waste (Cheremisinoff and Hassinan, 1989). On the other hand, fixation processes actually convert the waste into a chemically fixed, easily transported solid with a greatly reduced propensity for leaching into the groundwater or surrounding soil matrix. Apparent disadvantages that are associated with this technique includes cost, applicability, leaching, chemical stability and land use. Other limitations that were enumerated by Daley (1989): include (*i*) metal complexing agents including cyanide, ammonia and EDTA render many stabilization processes ineffective, (*ii*) chromium(VI) can be leached from conventionally stabilized waste, (*iii*) conventional chemical stabilization tends to mobilize arsenic from biocides and pesticides. Finally, it is important to note that stabilization/fixation processes are generally applied to wastewater sludges that cannot be further treated by any other means prior to disposal.

The principal advantages and disadvantages of incineration have been enumerated by Cheremisinoff (1989). The advantages include: (1) solid waste is reduced in weight and volume, extending the life of the existing landfills, (2) if waste must be transported to greater distances to landfill sites, incineration may be economically advantageous when located locally and (3) incineration can provide resource recovery in the form of electricity generation and mineral reclamation from residues. On the other hand, the disadvantages are (1) the process requires large initial capital expenditures and relatively high operating costs, in the form of skilled labor, (2) improper operations can result in air, water and land pollution and (3) public opposition may result from residents having an incinerator built in their area.

The incineration of wastes produces pollutant emissions to the atmosphere, contaminated waste water and contaminated ash. Metals and metal compounds are present in the compounds of raw waste. For instance, municipal refuse may contain lead from lead-based paints, mercury and cadmium from batteries, aluminum foil, lead plumbing, zinc sheets, etc. These metals and salts are relatively volatile and have low boiling points, for example; Cd (b.p. 765°C), Hg (b.p. 357°C), As (b.p. 130°C), $PbCl_2$ (b.p. 950°C) and $HgCl_2$ (b.p. 302°C). The extent of evaporation of metals and metal compounds such as, cadmium, mercury, lead and arsenic are deemed of the most importance in relation to municipal waste incinerators. Although other metals may be present in the wastes, their toxicities or emission levels are much lower (Williams, 1994). Consequently, more sophisticated emissions control equipment is required to trap volatile heavy metals efficiently, particularly mercury. Water pollution from incinerators is not generally regarded as a major concern because of the limited amount of waste water generated. However, the waste water from municipal waste incinerator plants has been shown to be contaminated with appreciable quantities of heavy metals and inorganic salts. These levels usually are well below the permitted disposal levels. The neutralization of metals, in particular, nickel, zinc, cadmium, lead and mercury is necessary. $Ca(OH)_2$ is used to precipitate the major part of contaminants as hydroxide sludges. However, more than 60% of the mercury and other heavy metals remain in the waste water. Therefore, the addition of trimercapto-*s*-triazine (TMT 15) is required, which precipitates the metals below the permissible levels (Williams, 1994). Finally, contaminated ashes should not contain more than 1.5% of heavy metals but this is highly variable. The pollutants present in the ash residues from incineration become more significant when they are added in landfill sites where leaching of the pollutants may be a source of groundwater contamination. But, if the incinerator is operated properly, the residue or ash should be completely burnt out and biologically sterile. Solidification of ash prior to landfill can greatly reduce heavy metals in the leachate.

In summary, supercritical fluid extraction (SFE) with CO_2 is a promising technology for the extraction of both organic and heavy metals toxicants. The principle advantages of SFE with CO_2 are: (1) as with other extraction/concentration processes this approach provides the possibility for *on-site* decontamination, (2) the SCF state can be readily achieved at low temperature and pressure (conditions that are encountered in conventional high performance liquid chromatography), (3) the organic matter of natural matrices are not removed by the extraction process so that the decontaminated medium remains biologically productive, (4) the most troublesome metallic (inorganic) pollutants for stabilized wastes or for incineration processes (mercury, chromium and arsenic) are readily handled by the proposed process, (5) finally, this technique has already been used in industrial applications for the extraction of hops for the brewing industry, for the removal of caffeine from coffee beans and for the extraction of essential oils.

1.8 Objectives of the research

A series of objectives were identified that controlled the direction of the studies described in this thesis. If successful, the studies were anticipated to (*i.*) increase our understanding of the extraction process with supercritical fluids and (*ii.*) result in the development of more efficient methods for the mobilization of metal ions into SC-CO_2. The following objectives provided the rationale for the experiments.

1. An alternate procedure that minimized pressure surges during the pressurization sequence was anticipated to minimize both the bumping of the aqueous sample and the attendant undesired transfer of liquid-phase sample to the collecting medium.
2. The process of derivatization of metal ions [by forming non-polar metal-ligand complex(es)] was to be separated from the purging process. It was anticipated that this separation would permit more latitude in the choice of the reaction conditions for the derivatization process. Specifically, if the target metal ions were to be derivatized prior to pressurization with CO_2, the derivatization process itself would no longer be restricted to the constraint of reaction conditions that included an aqueous phase pH that was approximately three.
3. Other complexing agents were to be evaluated for their efficacy as reagents for the transfer of metal ions into SC-CO_2. Included among these transfer reagents were compounds that would release dialkyldithiocarbamate ($^-SC(S)NR_2$), alkylxanthate ($^-SC(S)OR$), β-diketones, alkylammonium ion (R_4N^+) or methylthioglycolate ($^-CH_2C(O)OCH_3$) ligand. Transfer reagents for the envisaged remediation process were to

be restricted to those derivatization reagents that were relatively inexpensive and readily available commercially.

4. The extraction process was to be modified further by adding a limited excess of derivatizing reagent directly to the aqueous sample rather than having the mobile phase dissolve then sweep the reagent through the extraction vessel thereby sequestering the target analyte(s) by *in situ* derivatization.

5. The process of simultaneously mobilizing analyte cation(s) and anion(s) with a combination of derivatizing reagents was to be extended to increase aqueous burdens of target analytes and to use of novel combinations of derivatizing reagents.

6. Different trapping agents were to be evaluated for their abilities to efficiently remove metal complexes from supercritical CO_2. It was envisaged that the trapping reagent could be interposed into the extractor eluate to immobilize the metal complexes as they exited from the extractor.

7. These same trapping agents were to be evaluated for their abilities to release complexing reagent back into the supercritical CO_2 while retaining the metal(s). If successful, the supercritical CO_2 containing the released complexing ligand could be recycled back to the extractor to create a continuous process. It was anticipated that this "recycle" mode of operation would also serve to recycle any uncomplexed derivatizing reagent.

8. Finally, the optimized mode of operation for extractions was to be applied to "real world" samples that contained appreciable burdens of metal ions.

Chapter 2

2. Introduction

One crucial step for the efficient detection of analyte metal(s) by optical atomic spectroscopy is the process of sample introduction which involves the conversion of analyte ion(s) dissolved in a suitable liquid carrier into isolated free atoms in the gaseous phase. This process is conventionally performed in two sequential steps. Firstly, an aerosol is generated from the liquid-phase sample in a process that is termed nebulization. Despite continued progress in the design of more efficient nebulizing devices, the size distribution of the resultant droplets remains rather heterogeneous. For flame atomic absorption spectroscopy (F-AAS) the second step of the process involves the atomization of the analyte ions and is carried out within an air-acetylene or a nitrous oxide-acetylene flame. To maintain a stationary flame front just above the optical path of the spectrometer requires a combined flow of fuel and oxidant gases amounting to several liters per minute. The net result is that the individual droplets of sample aerosol must be sequentially desolvated then the resulting solid crystals containing the analyte must be volatilized, dissociated and finally atomized all within a few milliseconds. In this time interval the droplet (and/or its transformation products) will have been swept from the level of the burner head up through the optical beam. During this millisecond interval only the smallest droplets (approximately 10 μm) will have had sufficient time to become atomized. It is more efficient to simply discard the larger droplets that cannot contribute to the detection process. In practice, the turbulent flow of the oxidant and support gases within the spray chamber assembly cause the larger droplets to impact on the inner surfaces of the chamber where they re-condense and are discarded to waste by gravity flow.

The maximum nebulizing efficiency of conventional flame-AAS has been estimated to be 10% and only 4-5% for inductively coupled plasma optical emission spectrometry (ICP-

OES). The limitations of the conventional nebulization process have been recognized for many years and have prompted the exploration of other sample introduction techniques.

Among alternative introduction techniques, the use of the 'thermospray' effect has met with some success. In this process a flowing liquid sample is pneumatically forced through a heated capillary transfer line. Within this transfer line the liquid becomes superheated but cannot be volatilize because of the physical constraints of the capillary tube. At the exit tip, the superheated liquid explodes as a fine mist that can be used in a subsequent atomization device. Bank *et al.*, (1988) indicated that three regions can be distinguished within the thermospray. Close to the inlet of the device a one-phase liquid flow is superheated and the temperature will increase. When sufficient heat has been absorbed, the liquid starts to vaporize and a two-phase flow of liquid and vapor develops. Bubbles and droplets are also formed in this region. The pressure drops towards the end of the capillary, whereas the temperature decreases only slowly. Once vaporization is complete, the temperature of one-phase vapor flow rises again sharply. This mode of the aerosol formation was first applied to liquid chromatography-mass spectrometry (LC-MS). The process of thermospray generation was first described by Blakley *et al.* in 1978 and subsequently the thermospray vaporizer has been developed as an interface between liquid chromatography and mass spectrometry. Improved versions of the thermospray coupled LC-MS have been reported by Blakley and Vestal (1983) and by Vestal and Fergusson (1985). The same thermospray technique has been used for sample introduction into ICP with improved mass transport efficiencies. Koropchak and Winn (1986); Gustavsson (1987) and de Loos-Vollebregt *et al.*, (1989) have reported the use of the thermospray effect as a sample introduction technique for inductively coupled plasma systems. The principal benefits of this interface design were enhanced analyte transport efficiencies, enhanced aerosol analyte concentrations, enhanced detection limits and controllable aerosols from liquid samples at relatively higher flow rates. Various attempts have also been made to introduce samples into an electrothermal atomization atomic absorption spectrometer (ETA-AAS) through aerosol deposition using conventional pneumatic nebulization. A drawback of this approach is that only a small fraction of the sample is actually deposited within the furnace, and precise timing of the deposition period is required. The flow injection (FI) thermospray approach has been reported to overcome these shortcomings (Bank *et al.*, 1988).

In the first application of the thermospray effect to AAS, the liquid analyte solution was pumped through a stainless steel capillary transfer line maintained at a high temperature with a heating block. The resulting thermospray emerged inside the mixing chamber directly below the burner head. The total conversion of liquid to aerosol and the resulting 4-10 fold increase in analytical signal have been reported by Robinson and Choi (1987). The same system was also used to study the effect of heavy metals (Al, Cd, Cu, Hg and Zn) on the chemical speciation of chlorophylls in duckweed. The flame-AAS instrument was used as a metal-specific detector for HPLC. This study quantified the detrimental effects of heavy metals on the magnesium-chlorophyll complexes (Robinson and Choi, 1989). A publication on the coupling of FI-thermospray-AAS have been authored by Larsen and Blais (1993). Their system used a modular thermospray interface that did involve minor modifications of the spray chamber. The thermospray unit consisted of two separate thermoelectric elements that heated a 50 μm silica capillary carrying the mobile phase and the nebulizer gas (air). The front end of the capillary was then inserted into the aspiration needle of a Perkin-Elmer nebulizer system. The FI-thermospray-AAS system provided 6.3-6.9 fold increases in signal-to-noise levels (on a peak height basis) when compared to a pneumatic nebulization FI-AAS system.

Flow injection analysis (FIA) which was first developed some 20 years ago, has proved to be an efficient sample introduction technique for AAS. Fang (1995) defined FIA as "a flow analysis technique performed by reproducibly manipulating sample and reagent zones in a flow streaming under thermodynamically non-equilibrated conditions". The advantages of such a technique are improved: (1) sensitivity, (2) selectivity, (3) low sample, solvent and reagent consumption, and (4) reliably. Problems that are associated with conventional FAAS systems have been listed earlier as the low atomization efficiency and strong dependence of the nebulization assembly on a multitude of experimental conditions. Therefore, the combination of FIA and FAAS techniques have been demonstrated to offer several advantages over conventional operation. Burguera *et al.*, (1988) reported that a microwave oven/flow injection/atomic spectrometric system permitted the determination of zinc, cadmium or calcium in small samples of human kidney and liver tissues (ca. 1 g). Good precision (ca. 2-6 % relative standard deviation) were achieved and good accuracy was corroborated with standard additions and standard reference materials. Welz *et al.*, (1991) have investigated a FI on-line co-precipitation dissolution system in combination with FAAS that has been applied successfully to the determination of cadmium, cobalt and nickel in a variety of biological materials. No interferences were observed from high concentrations of copper and iron in these samples.

The objectives of the current study were to: (*i.*) optimize the performance of and (*ii.*) evaluate the nebulization-atomization characteristics of an AAS spray chamber burner head assembly that had been modified to nebulize a continuous stream of liquid carrier by thermospray effect. Aliquots of sample were then to be added to the carrier stream using a flow injection technique. Atomization efficiencies were to be compared for different analyte metal ions and for different interface operating conditions. Once the thermospray operating parameters had been optimized for an analyte element, the relative atomization efficiencies for different elements were then to be compared by calculating the corresponding limit of detection (LOD) for that element. This latter parameter attempted to determine the smallest quantity of analyte element that could be reliably distinguished from the background signal of the instrument.

2.1 Materials and methods

2.1.1 Flow injection-thermospray-flame atomic absorption assembly

The modified nebulizer/spray chamber assembly of a Philips model PU 9100 is presented in Figure 4. The Philips model PU 9100 spectrometer was virtually analogous in operation to the Zeiss FMD-3 spectrometer that was utilized by Wang (1995). The nebulizer spray

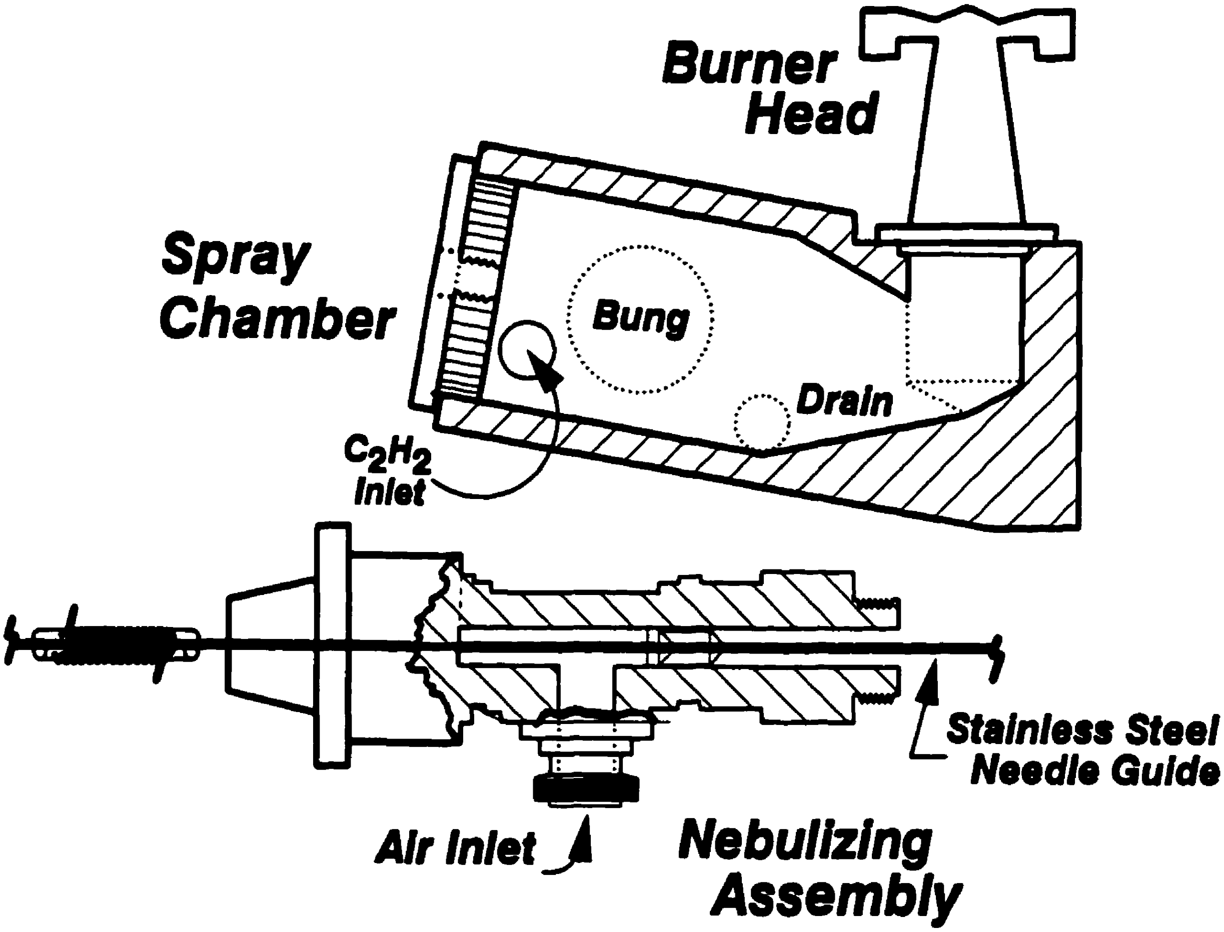

Figure 4: Cross-sectioned view of the modified AAS nebulizing assembly in which a 21 cm x 0.9 mm i.d. served to position the silica capillary restrictor within the spray chamber. An insulated heating coil superheated the mobile phase within the restrictor causing efficient volatilization, by thermospray effect, into the spray chamber. Air flow to the nebulizing nozzle and directly to the spray chamber was heated to 200°C.

chamber – assembly was modified to accept the 50 μm i.d. silica capillary restrictor. The demountable glass impact bead of the nebulizer chamber was removed and the nebulizing jet of the spray nozzle was replaced with a 21 cm length of hollow needle (1.10 mm o.d. x 0.90 mm i.d., see Figure 4), which extended some 2.5 cm into the interior of the spray chamber. The stainless steel needle served as a guide tube to position the exit tip of silica restrictor within the spray chamber. The stainless steel needle guide tube was heated by positioning the exposed portion of the silica restrictor tube – guide tube assembly inside a 40 turn heating coil (20-gauge Kantal-A high resistance heating wire coiled around a 8.5 cm x 0.8 cm o.d. silica tube). The flow of air, controlled by a Matheson flow meter (model J1-1A101) were conducted to the nebulizing jet assembly (Figure 4) and to the spray chamber via 6.4 mm o.d x 3.2 mm i.d. high temperature flexible silicone tubing (rated to 250°C, Cole Parmer Instrument Co., Niles, IL, USA). Oxidant gas was preheated by passing the line of silicone tubing through a radiant heater (CRFC-7512/120 vacuum formed ceramic fiber radiant heater 30.48 cm x 7.62 cm o.d. x 0.64 i.d., OMEGA Technologies Company, Qué., Canada). The heaters were separately energized by a direct current from variable transformer (Variac model 3PN116C) that was connected to the high resistance circuit of the heater. The AAS responses to analyte metal in the mobile phase was recorded with a personal computer and a chromatographic capture and data reduction program (Turbochrome 3, Perkin Elmer Corp., Wilton, CT).

2.1.2 Reagents and standards

All chemicals used were ACS reagent grade or better. Working solutions were prepared from stock standard solutions (1000 μg/mL) from BDH® (Montréal, Québec, Canada) or Sigma-Aldrich® (Milwaukee, WI, USA). All glassware was successively washed in a soap solution, soaked in nitric acid (20% v/v), rinsed with copious quantities of distilled deionized water and dried in the oven. Acetylacetonate complexes were purchased from Sigma-Aldrich® and were used without further purification. Double deionized water from a Millipore Milli-Q-Plus system (Faer Lawn, NJ) was used for the preparation of all aqueous working solutions and methanol (Fisher Scientific, Montréal, Canada) was used to prepare solutions of the acetylacetonate complexes.

2.1.3 Interfacing for the FI-TE-FAAS

A schematic diagram and description of the modified nebulizer/spray chamber has been presented in section 2.1.1 (page 40). Two different types of burner heads that were comparable with both nitrous/acetylene and air/acetylene flames, was used for all measurements. In the case of the acetylacetonate complexes, SC-CO_2 was used as the mobile phase whereas double deionized water served as the transfer solvent and was delivered at 0.6-0.7 mL/min from an HPLC pump (Varian Star Model 9010, Varian Associates, Palto Alto, CA). Aliquots, of sample, 10 µL, were added to the loop of a Valco 6-port rotary injection valve then interposed into the stream of flowing solvent. Quantification was performed using the method of external standards.

2.2 Results and discussion

The FI-TE-FAAS was evaluated in terms of limits of detection (LODs) which is generally defined as the smallest concentration or amount of analyte that can be detected with reasonable certainty for a given analytical procedure. SC-CO_2 or water were nebulized by thermospray effect into a mixture of fuel (acetylene) and oxidant gases (air or nitrous oxide) within the spray chamber. Previous experiments (Wang, 1995) have demonstrated that heating of the oxidant gas inlets increased the AAS response appreciably. The same observations had also been made by Larsen and Blais (1993) who reported an additional contribution to signal enhancement by heating the nebulizer and oxidant gases, an effect that was attributed to increase desolvation of the thermospray aerosol within the mixing chamber. The flow rates of both gases were readily controlled with individual flow meters and an outlet temperature of approximately 200°C for the oxidant gas, was achieved with a ceramic heater. Decompressed SC-CO_2 at 800 mL/min or 0.6 mL/min for water were used as the carrier solvent and were connected directly to the 6-port injection valve. Optimized flow rates of fuel and oxidant gases were determined for each element. The thermospray temperature was separately optimized depending on whether SC-CO_2 or water was used. The LODs of analyte element (Cr, Ni, Co, Fe, Al, Cd and Mn) are presented in Table 2.

Mobile phase thermospray operating temperature (measured as the skin temperature of the quartz tube heating coil assembly) for the SC-CO_2 was appreciably lower (300-350°C) than for water (925-1000°C). Typical responses for the FI of analyte metal, entrained in SC-CO_2 or water are presented in Figure 5. Previous experiments with an analogous system had indicated approximately a 10-fold improvement in response over a conventional pneumatic nebulization (Wang, 1995). By comparison to previous reported LODs (Wang, 1995) a further 3 to 94-fold improvement was achieved by optimizing the instrument operating parameters. An interesting feature of the FI-TE-FAAS system is that it works equally well for aqueous and SC-CO_2 phase. The acetylacetonate complexes offer considerable potential for metal detection in an SC-CO_2 phase, the lipophilic nature of these complexes in SC-CO_2 mobile phase make them volatile and sufficiently soluble to be transported and atomized efficiently within the optical beam. When using the SC-CO_2 mobile phase, it was necessary to use soluble pre-formed complexes since the free ions present in aqueous samples are too polar to be transported into the optical beam. Even though acetylacetonate complexes offer considerable potential for metal detection in SC-CO_2 phase, a lower thermospray temperature was necessary for these complexes since they tended to decompose rather readily at higher temperatures. An interesting series of silica T-tube devices have been reported previously (Blais *et al.*, 1990; Momplaisir *et al.*, 1994; Tan *et al.*, 1994 and Wang, 1995) that consisted of: (a) an upper optical tube within the optical beam of the AA spectrometer, (b) individual oxygen and hydrogen inlets, (c) a sample introduction tube, (d) a spray chamber, each of which was heated with Variac heaters. These novel T-tube silica interfaces provided excellent LODs but were limited to nine of the more volatile elements (Ag, Pb, Cd, Cu, Zn, Hg, Mn, Se and As) and to lower flow rates of mobile phase, especially *on-line* SC-CO_2. Even though the operating principles are similar to the FI-TE-FAAS, the latest interface device has advantages over

Table 2: Limits of detection (LODs) of various metal ions in aqueous or SC-CO_2 phase.

Element	Wavelength (nm)	Carrier	FAAS/FES (ng)[b]	Type of flame
Fe[a]	248.1	SC-CO_2	2.8 / 18.0	air / acetylene
Fe[a]	248.1	SC-CO_2	1.9 / 89.8	N_2O / acetylene
Ni[a]	232.0	SC-CO_2	0.9 / 7.7	air / acetylene
Ni	232.0	H_2O	0.6 /32.0	air / acetylene
Cd	228.8	H_2O	0.5 / 3.0	air / acetylene
Co	240.7	H_2O	0.8 / 5.7	air / acetylene
Co[a]	240.7	SC-CO_2	1.1 / 12.6	air / acetylene
Mn	279.5	H_2O	0.3 / 7.2	air / acetylene
Al[a]	309.3	SC-CO_2	49.1 / 150.6	N_2O / acetylene
Cr(VI)	357.9	H_2O	0.6 / 39.4	air / acetylene
Cr(III)[a]	357.9	SC-CO_2	1.7 / 21.4	air / acetylene
Cr(III)[a]	425.4	SC-CO_2	1.7 / 21.4 (**FES**)	N_2O / acetylene

[a]: metal–acetylacetonate complex.

[b]: flame atomic absorption spectrometry (FAAS) and flame emission spectrometry (FES).

LOD = $3\, s_b / S$ and LOD = $3[s_b^2 + s_i^2 + (i/S)^2\, s_s^2]^{1/2}/S$ where S, i, s_s *and* s_i are the slope, intercept and respective standard deviations of the calibrations plot (obtained from linear regression) s_b is the standard deviation of the peak-to-peak baseline noise / 5.

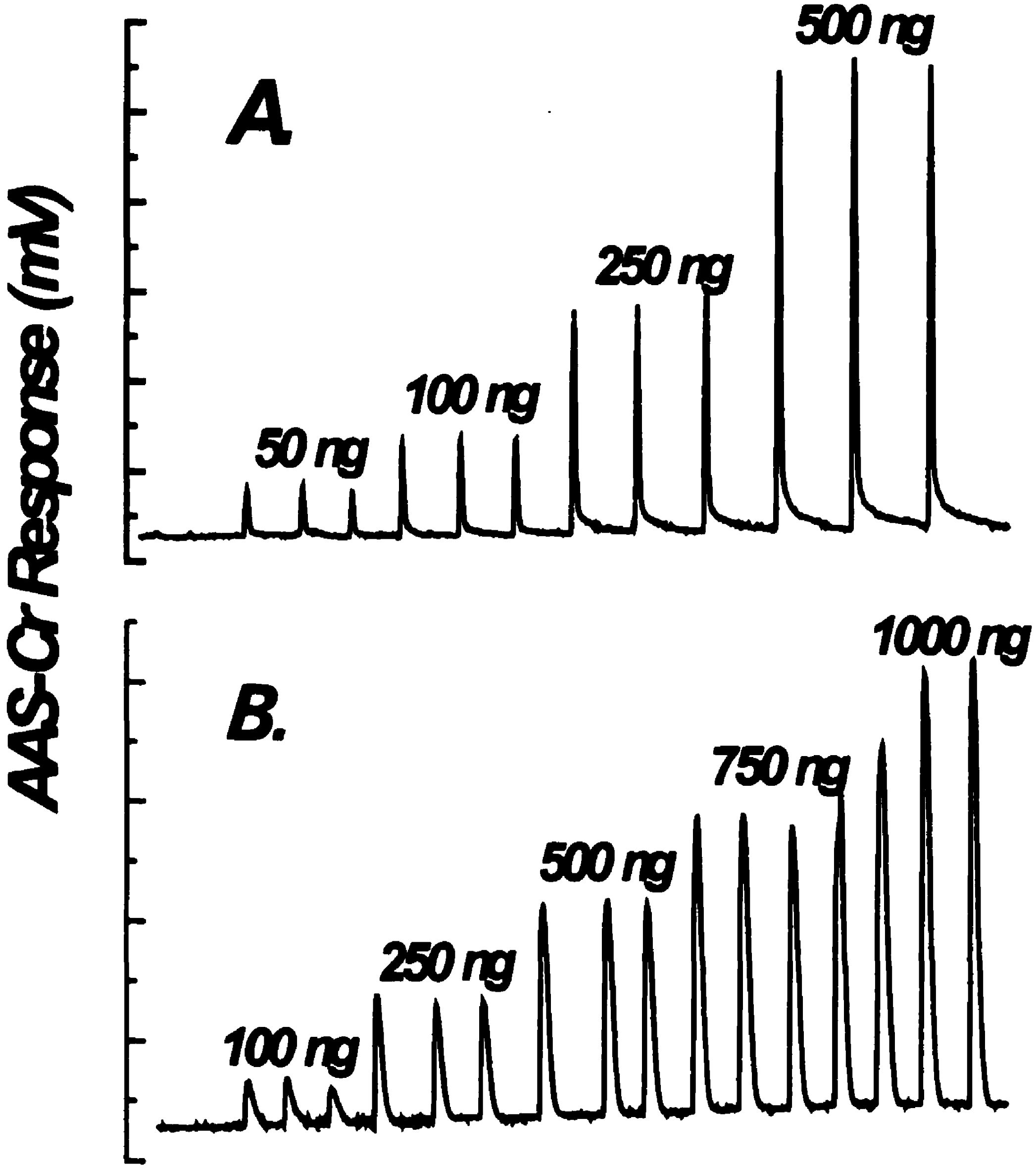

Figure 5: Typical flame-AAS responses to (A) chromium acetylacetonate in supercritical carbon dioxide or (B) chromate in aqueous mobile phase.

silica T-tubes since: (*i.*) the limited number of detectable elements is overcome by the current device which provided sensitive limits of detection for a broad range of analyte elements (Table 2). A major disadvantage of T-tube devices is that they are energy limited in that higher surface temperatures will cause the silica skin to flow and melt whereas the FI-TE-FAAS can easily resist these high temperature. Thus less volatile elements such as Cr, Co, Fe and Ni can readily be detected. To overcome the energy limitation of the all silica devices, one could change the mobile phase. By doing so, the thermospray temperature can be reduce dramatically thus preventing the melting of the T-tube interface. Alternatively, metal ions can be derivatization into a more volatile complex.

In Table 2, the elements determined with the FI-TE-FAAS technique were characterized by low to sub-ng limits of detection. Surprisingly, each element (with the notable exception of aluminum) resulted in very similar LODs. This might be due to a limitation of the FI-TE-FAAS system. Flame emission spectrometry (FES) or flame photometry has been used for the detection of Cr(III) with a nitrous oxide-acetylene flame (Table 2). FES is a simple method of analysis that is used extensively in clinical analysis of body fluids and in agriculture for the analysis of soils, plants and fertilizers. Posta *et al.*, (1996) reported the on-line preconcentration of Cr(III) and Cr(VI) on a reverse phase C18 silica based column followed by determination with high performance flow flame emission spectrometry. Good limits of detection (LODs) were reported for both chromium species. In our hands, the same operating parameters provided no significant improvement over the conventional F-AAS. Even though, FES provided an interesting comparison with F-AAS, this type of detection was abandoned when it became evident that no appreciable enhancement sensitivity of lipophilic complexes was available with this approach. Their solubilities in this medium provide an effective way to monitor the course of an SC-CO_2 extraction.

2.3 Conclusion

The FI-TE-FAAS interface has been demonstrated to provide efficient detection for a variety of less volatile elements (Co, Cr(III), Cr(VI), Fe, Ni, Mn and Al) present as ions in an aqueous carrier or as lipophilic complexes in a SC-CO_2 carrier phase. The range of possible metal analytes that can be monitored has been increased over the nine elements (Ag, As, Cd, Cu, Hg, Mn, Pb, Se and Zn) that can be monitored with the all-silica interface. The reported LODs would be improved somewhat if a 10-cm single slot rather than the 5-cm burner head had been used for these studies. The latter burner head was chosen to provide a direct comparison (same head) between the sensitivities achieved with the air-acetylene and the nitrous oxide-acetylene flames. The principle advantages of flow injection remains the small quantities of sample that are necessary for successful quantitation and the ability to deal with higher levels of dissolved solids that would block the burner head during continuous sample introduction.

Several advantages also accrue from the capacity to monitor the metal content of CO_2 eluate from a supercritical fluid extractor. The concentration of metal analyte in the eluate can be used to optimize the operating parameters of the extractor during the course of the extraction, to model the performance of the extractor and to determine when a pre-selected efficiency of metal mobilization into a supercritical carbon dioxide has been achieved. The technique of metal mobilization will be presented in greater detail in the next chapter.

Chapter 3

3. Introduction

There are relatively few remediation strategies which can be optimized for natural matrices (soils, sediments or waste waters) that have been contaminated with both organic and heavy metal toxicants. Conventional remediation strategies have been directed to either organic or heavy metal oxidants. For organic pollutants, a number of strategies can be considered for the remediation of a particular site including thermal treatment, stream and air stripping, bioremediation, chemical treatment and various other extraction-concentration processes. In contrast, fewer treatment techniques are available for environmental media that have been contaminated with heavy metals. Particularly troublesome are those metallic species that can be volatilized during conventional processes involving heat treatment. Efficient scrubbing of the stack gases is necessary to limit the spread of these contaminants. In addition, conventional chemical stabilization (solidification/neutralization) tends to convert As(V) species into the more soluble As(III) species yet oxidative incineration-thermal destruction processes can produce Cr(VI) which can be leached from conventional stabilized waste. One promising technology that can be made efficient for mobilizing heavy metals is the use of supercritical fluid extraction (SFE). In principle, non-polar contaminants can be added to the supercritical fluid mobile phase to sequester/mobilize heavy metal contaminants.

Since metallic ions are only sparingly soluble in this non-polar medium, appreciable solubility of the metal can be achieved only with a suitable derivatization of the target ion(s). Complexation with fluorinated and non-fluorinated isologs of dialkyldithiocarbamates and β-diketonates, organophosphates and ionisable crown ethers have been exploited to mobilize metallic cations (Chapter 1). Alternatively, selected metal anions have been mobilized into SC-CO_2 by ion associate extraction with tetraalkylammonium ion (Wang and Marshall, 1996b). A popular approach to mobilization has been to introduce the complexing/ion pairing reagent into the extraction vessel in a continuous fashion and cause it to react with the target metal(s) as it swept through the sample medium. With this mode of operation, the reaction conditions of the derivatization are limited to the conditions of the extraction process. Appreciably more latitude is achieved if the derivatization step is performed *off-line*. With this modified approach, the derivation sequence and the mobilization of the resulting derivatives can be optimized separately. The attractive features of SC-CO_2 are the cost (estimated to be approximately one-tenth of the cost of an organic solvent), the toxicological inocuity of the decompressed gas, its environmental friendliness and its ready/safe disposal simply by venting to the atmosphere.

The most widely used formulations of CCA wood preservative contain ~48% Cr as CrO_3, ~18% Cu as CuO and ~34% As as As_2O_5 and are applied to different species of wood by heat/pressure methods following recommended procedures that typically involve the recycling of metal-containing condensates (American Wood Preservers Association, 1978; Canadian Standards Association, 1989). The Cr and Cu in CCA condensate have been mobilized using excess tetrabutylammonium dibutyldithiocarbamate ($NBu_4^+\ {}^-SC(S)NBu_2$) that had been added to the SC-CO_2 mobile phase prior to contacting the aqueous sample. Preliminary trials (Wang and Marshall, 1996b) had indicated that the Cu was purged rapidly as the $Cu(DBDTC)_2$ complex (mean half life of 3.5 min) but that the NBu_4HCrO_4 was mobilized only more slowly (mean life ~19 min). It has also been reported by Wenclawiak and Krah (1995) that As(V) can be mobilized efficiently from aqueous media into SC-CO_2 after derivatization with methylthioglycolate.

The objectives of the current studies were to mobilize/purge the chromium, copper and arsenic ions from CCA condensate using a minimum of readily available commercial reagents. Whereas previous trials had employed an excess of the complexing/ion pairing reagent that had been added continuously to the SC-CO_2 mobile phase, the current study attempted to limit both the quantity of reagent and mobile phase required to effect the purging operation. In addition, alternate separation strategies were to be explored.

3.1 Experimental

3.1.1 Supercritical fluid extractor

The supercritical fluid extractor (Figure 6) a CCS Instrument Systems Model 3100, Avondale, PA, USA consisted of 50 mL capacity, temperature and pressure equilibration vessel (TPEV) connected in series with a 10 mL capacity extraction vessel (EV). Each vessel was mounted vertically within a separate compartment of the extractor and enclosed within a thermostatted heating jacket that permitted isothermal operation between ambient and 150°C over the course of the extraction. In operation, the aqueous sample was initially pressurized to the desired operating pressure by opening pneumatically controlled needle valves 4, 2, 7, 6 and 1 while closing valves 3 and 5. Once the operating pressure had been achieved, the flow of fluid to the extraction vessel was reversed by opening valve 5 while closing valve 6. The TPEV acted as a supplementary dampener to smooth the pressure pulses generated by the air driven pump. Frequently, the TPEV was permitted to remain filled between extractions. Liquid mobile phase modifier was added by means of a high performance liquid chromatography (HPLC) pump located between the TPEV and the EV. In operation, the derivatization sequence was completed prior to purging the reaction product(s) from the extractor. Typical programmed runs consisted of dynamic extraction for 14 min at 17.24 MPa during which mobile phase modifier was added at 0.25 mL/min, followed by a polishing sequence in which the addition of modifier was interrupted. After 22 min, the operating pressure was increased to 24.13 MPa for the duration of the extraction.

3.1.2 Supercritical fluid extractor – F-AAS interface

Eluate from the extractor was directed via a 50 µm inner diameter silica capillary restrictor to the nebulizing chamber of a Philips Model PU 9100 flame AAS instrument. Within the nebulizer, a 21 cm x 0.9 mm (inner diameter) hollow needle served to position the silica

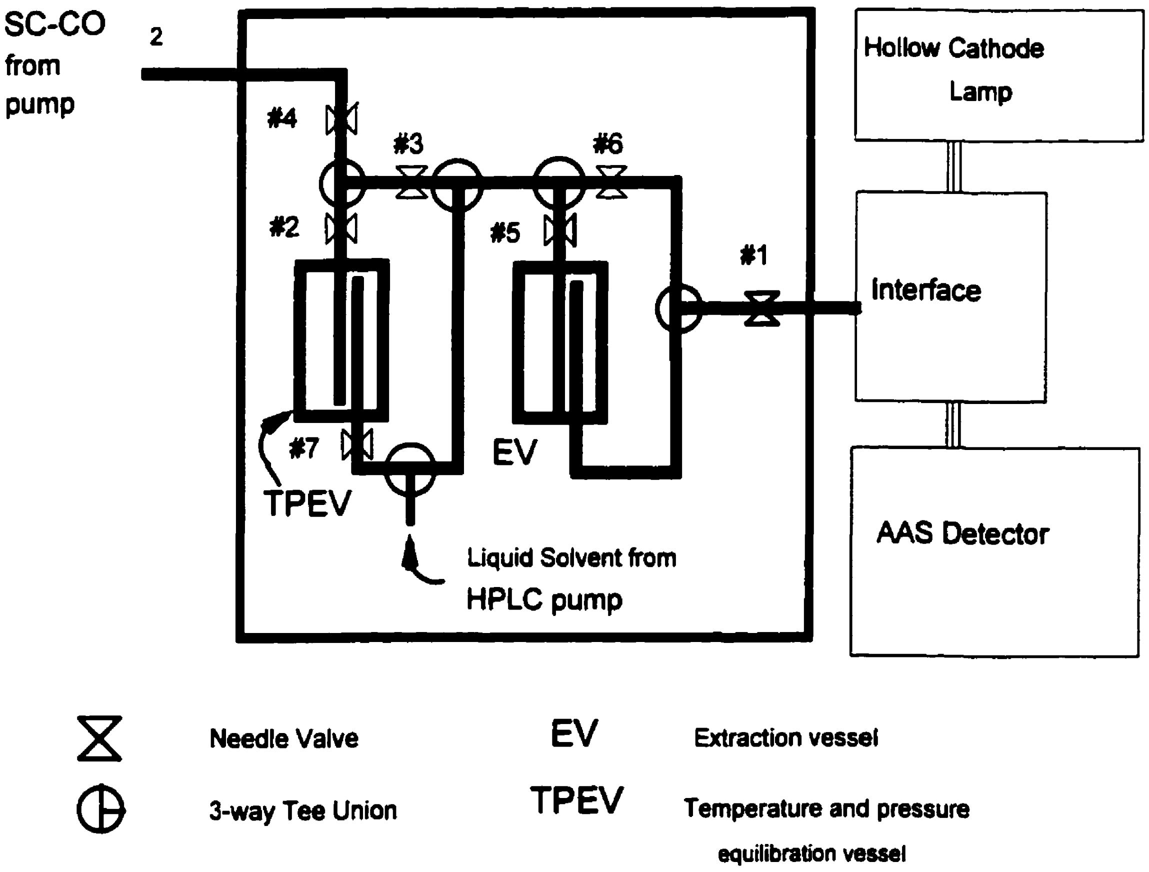

Figure 6: A supercritical fluid extractor incorporating a temperature and pressure equilibration vessel (TPEV) connected in series with an extraction vessel (EV) that has been directly interfaced with a modified flame atomic absorption spectrometer.

capillary restrictor within the spray chamber. An insulated heating coil (positioned immediately prior to the entry to the nebulizer) superheated the SC-CO_2/liquid modifier within the restrictor causing efficient analyte volatilization (by thermospray effect) directly into the spray chamber. Analytes were atomized within an air-acetylene flame. The air flow to the spray chamber was preheated to 200°C with a ceramic heater.

3.1.3 Open focused microwave reactor

Prior to SC extraction, for certain trials 25-30 mL aqueous Cr(III) was reacted with excess 2,4-pentanedione or 8-hydroxyquinoline contained in a 300 mL capacity quartz reactor vessel fitted with an efficient condenser. The reaction was conducted in an open focused microwave reactor (Synthewave 402, Prolabo, Fontenay-sous-Bois, France) at 42 or 55% total power (corresponding to 95 or 120°C) for 5-45 min. Alternatively, a pulse mode at 42% total power (1 min on 1 min off) was also evaluated.

3.1.4 Reagents

Aqueous Cr(VI), Cr(III), Cu(II), As(V) and As(III) standards. 25 μg/mL in double distilled deionized water, served as substrates for the complexometric extractions. Aqueous standards, complexing reagents, 2,4-pentanedione, ammonium pyrollidinedithiocarbamate, 8-hydroxyquinoline or the sodium salts of diethyldithiocarbamic, ethyl-, butyl-, hexyl- or octylxanthic acid as the acetylacetonate complexes of Cr and Cu were purchased commercially (Aldrich Chemical Co., Milwaukee, WI, USA) or were synthesized following standard procedures.

3.1.5 Modeling studies

Curve fitting was performed with a commercial software package (Microcal Origin V 3.5, Microcal Software Inc., Nothhampton, MA, USA) using an unweighted least-squares iterative routine. Predicted equilibrium concentrations of CO_3^{2-}, HCO_3^- and pH as a function of temperature and pressure were performed using the data base contained in MINEQL+ (version 3.0), Environmental Research Software, Hallowell, ME, USA.

3.1.6 Extractions of CCA condensate

The sample of CCA condensate was obtained from a commercial wood treatment facility. Prior to extraction with solvent amended SC-CO_2, the crude suspension was treated with excess sodium diethyldithiocarbamate, filtered through a thin layer of Celite (contained in a fine porosity sintered glass filter) to remove precipitated metal chelates then treated with excess methylthioglycolate and refiltered through fresh Celite. A 7 mL filtrate was added in a 10 mL capacity EV and subjected to SC-CO_2 extraction.

3.2 Results and discussion

Chromium(VI) ion in an aqueous carrier and chromium 2,4-pentanedione complex [$Cr(AcAc)_3$] in supercritical carbon dioxide (SC-CO_2) were detected efficiently, (Table 2 and Figure 5) with the modified flame-AAS spectrometer. As reported previously (Wang and Marshall, 1996) the SC-CO_2 eluate from the extractor was volatilized, by thermospray effect, into a conventional air-acetylene flame. The limits of detection (LODs) were generated in the absence of the extraction vessel. Rather, a quantity of analyte was interposed into the mobile phase then transported directly to the detector using a flow injection technique. Cr(III) in aqueous medium proved to be more resistant to the nebulization/atomization process in the energy-limited modified interface. The limits of detection for Cu(II) were as reported previously and the detection of arsenic in the SC-CO_2 eluate was inefficient with these operating conditions (Wang and Marshall, 1996b). A conventional flame-AAS unit was used to determine the residual content of Cr, Cu and/or As in the aqueous samples after the complexation/mobilization treatments.

For the mobilization studies, the extraction vessel of the supercritical extractor was pressurized using a back fill technique that minimized pressure surges and the resulting bumping that could have resulted in liquid sample loss by entrainment with the supercritical mobile phase. Post 50 min of extraction of a 7 mL sample, the volume of remaining liquid was ≥ 6.4 mL which indicated that losses of liquid phase sample were minimal. Provision to add liquid phase solvent to the supercritical mobile phase was provided with HPLC pump set to deliver low constant flow rates of either ethyl acetate or isobutylmethyl ketone. These solvents were chosen for their combination of desirable characteristics including their moderate polarities, their relative insolubilities in water, their lack of appreciable mammalian toxicity and their ease of olfactory detection. The limits of olfactory detection in aqueous media have been reported to be 3.9 and 0.68 mg/L for ethyl acetate and isobutyl ketone respectively.

Preliminary trials indicated that the mobilization of Cr(VI) could be made efficient by adding the complexing reagent directly to the sample (Table 3) and that a polar co-solvent was not necessary to effect the efficient purging. Although the mobilization of the 175 μg of Cr(VI)/7 mL, was not quantitative, approximately 95% of the target anion was mobilized rapidly with a 19-fold excess of diethyldithiocarbamate added directly to the aqueous sample prior to extraction. A typical flame-AAS response to Cr(VI) in the extractor eluate (Figure 7) indicated that the mobile fraction of this ion was purged rapidly from the aqueous phase (175 μg/7 mL). Curve fitting trials indicated an excellent fit to a single Gaussian distribution model once the signal corresponding to an identical extraction in the absence of any analyte Cr had been subtracted. It was also possible to model the trailing edge of the Gaussian distribution as an exponential decay. With the exponential decay model, the result of simple first-order kinetics, the goodness of fit (chi square) to the sum of two exponential decays was not improved significantly relative to goodness of fit to a single exponential decay. The time constant for the single exponential decay corresponded to half-life ($t_{½}$) of 0.63 min, which indicated that some 95% of the mobile fraction of the total analyte burden would be purged from the extractor in less than three minutes. Since mobilization times are dependent on the relative volumes of headspace and aqueous sample as well as the pressure of the extraction and the mobile phase flow rate, the situation can be simplified somewhat if one considers the number of exchange volumes of

Table 3. Mobilization efficiencies of metal ions from aqueous media into SC-CO_2.

Target Ion	**Complexing / derivatizing reagent**	**Extraction conditions**	**Percent extraction (%)**[a]
Cr(VI),175 µg/7 mL	100 mg NaDEDTC[b]	SC-CO_2 + 0.25 mL/min IBMK	97.4 ± 0.0
Cr(VI), 175 µg/7 mL	50 mg NaDEDTC	SC-CO_2 + 0.25 mL/min IBMK	93.0 ± 0.1
Cr(VI), 175 µg/7 mL	50 mg NaDEDTC	SC-CO_2	95.0 ± 0.1
As(III), 175 µg/7 mL, pH 2.0	50 mg NaDEDTC	liquid-liquid ext'n (3 x 5 mL IBMK)	93.3 ± 0.3
As(V), 175 µg/7 mL, pH 2.0	150 µL $HSCH_2C(O)OCH_3$	liquid-liquid ext'n (3 x 5 mL IBMK)	89.5 ± 1.0
As(V) + Cr(VI) each 87.5 µg/7 mL	50 mg NaDEDTC + 150 µL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	66.7 ± 1.4 As 94.7 ± 0.1 Cr
As(III) + Cr(VI) each 87.5 µg/7 mL	100 mg NaDEDTC + 150 µL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	58.9 ± 2.0 As 95.0 ± 0.1 Cr
As(V) + Cr(VI) each 87.5 µg/7 mL, pH 2.0	40 mg NaDEDTC + 150 µL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	81.4 ± 1.6 As 93.1 ± 3.8 Cr

[a] One standard error of the mean reflects three replicate determinations of the residual content of analyte in one extracted sample.

[b] NaDEDTC ≡ sodium diethyldithiocarbamate

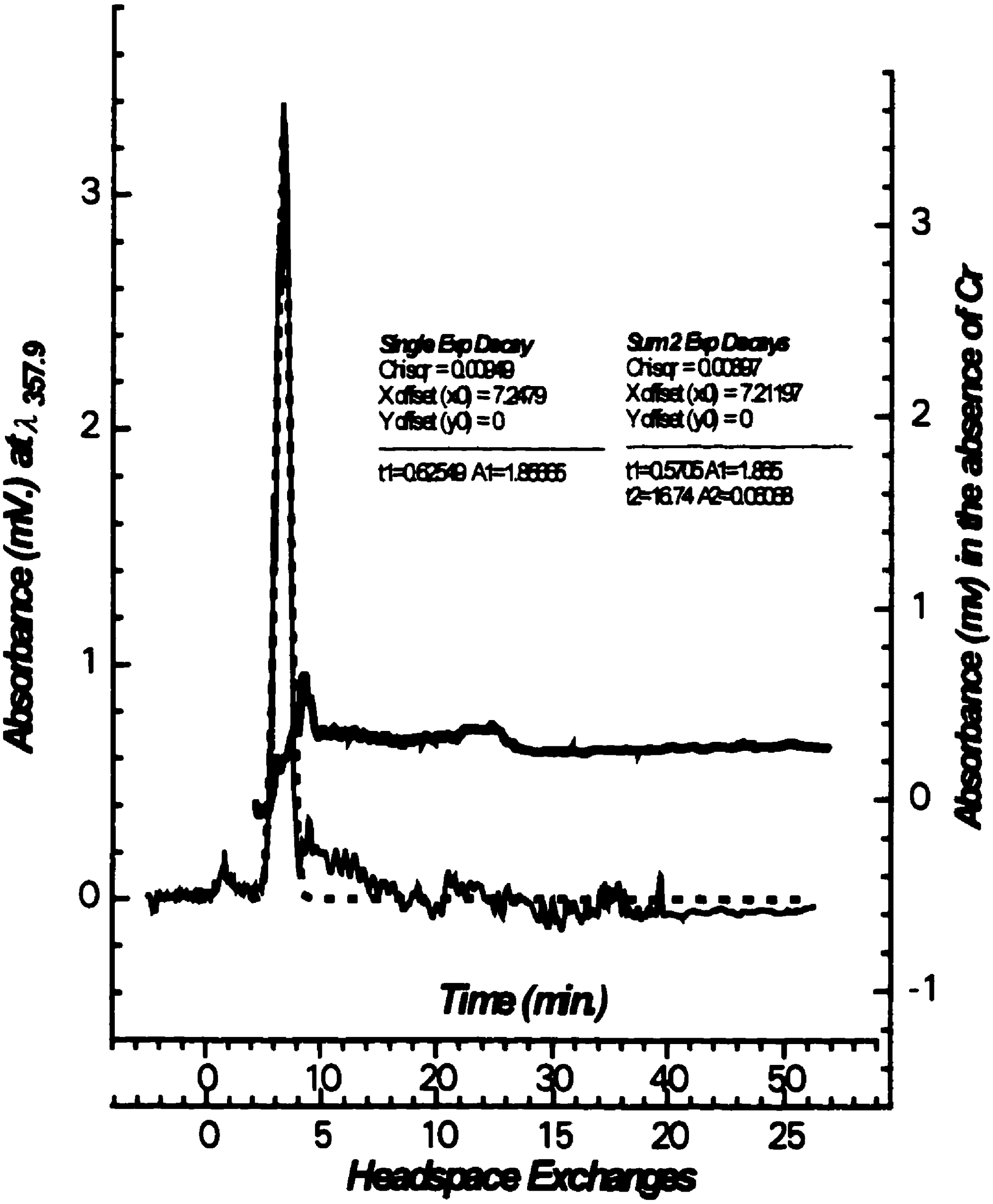

Figure 7: The flame AAS response to Cr(VI), 175 µg/7 mL, that had been mobilized with 50 mg sodium diethyldithiocarbamate into a mixed mobile phase consisting of 0.8 mL/min SC-CO_2 (17.24 MPa/50°C) and isobutylmethyl ketone (0.25 mL/min).

headspace required to effect the purging operation. Virtually all of the dislodgable fraction of the total Cr burden was purged from the extractor within five exchange volumes of the headspace. When combined with the residue data in the sample after extraction, the mobilization of the Cr(VI) species was both rapid and efficient. This rate of purging was shortened appreciable relative to the rate ($t_{½}$ of 19.6 min) that had been observed for the mobilization of aqueous Cr(VI) as the tetrabutylammonium ion pair (Wang and Marshall, 1996b).

The Cr(III) species proved to be more resistant to mobilization/purging in our hands. The trivalent form of chromium is considered to exist in association with six firmly bound water molecules (Sekine and Hasegawa, 1977). In contrast with other hydrated transition metals, these complexed water molecules are not readily exchanged (rate of exchange is characterized by a half-life of 40 hours). At more alkaline pHs, the water molecules can be replaced by OH^- (hydrolysis). In sea water it is suggested that the predominant form of Cr(III) is $Cr(H_2O)_4(OH)_2^+$. Complexation with other inorganic species is not considered to be important in natural waters. However, it had been demonstrated by Gardner and Ravenscroft (1996) that Cr(III) could be extracted, virtually quantitatively, from an ammoniacal buffer into an organic solvent with 8-hydroxyquinoline (oxine). The complexation reaction was accelerated with a microwave induced source of heat. A systematic investigation of this process (Table 4) corroborated the observations that (*i.*) a virtually quantitative transfer from an ammoniacal buffer containing 25 μg Cr(III)/mL into an organic solvent could be achieved with three successive 5-mL extractions with either ethyl acetate or isobutylmethyl ketone and (*ii.*) that the presence of ammonia was beneficial to the transfer efficiency. In the presence of ammoniacal buffer, a small (10 to 100-fold) excess of a variety of univalent bidentate chelating reagents (8-hydroxyquinoline, 2,4-pentanedione, or the sodium salts of ethyl-, butyl-, hexyl- or octylxanthate and diethyldithiocarbamate) resulted in a virtually quantitative transfer of Cr(III) to the organic phase. Moreover, in the presence of an ammoniacal buffer (NH_4Cl/NH_3) the microwave treatment was not necessary; a virtually quantitative transfer to the organic phase was achieved with three successive extractions with 5 mL ethyl

Table 4. Recovery efficiencies in organic medium of various Cr(III) complexes that had been prepared under different reaction conditions.

Microwave duration (min)	**Complexing reagent**	**Extraction parameters**	**Percent recovery (%)**
15	oxine[a], 7-fold excess / pH 10.0	ammoniacal buffer/ IBMK[b]	99.6
15	oxine, 70-fold excess / pH 8.7	ammoniacal buffer/ IBMK	99.6 ± 0.03
15	oxine, 7-fold excess / pH 8.0	ammoniacal buffer/ IBMK	99.6 ± 0.03
15	oxine, 7-fold excess / pH 6.0	ammoniacal buffer/ IBMK	83.3 ± 0.2
15	oxine, 7-fold excess	HCO_3^- / IBMK	7.0 ± 45.1
5	oxine, 10-fold excess /pH 8.4	ammoniacal buffer/ IBMK	99.5 ± 0.02
5	NaDEDTC[c], 90 mg /pH 8.6	ammoniacal buffer/ IBMK	83.2 ± 0.2
5	AcAc[d],100-fold excess / pH 8.5	ammoniacal buffer/ IBMK	99.0
	NaHexXan[e] /	HCO_3^- / IBMK	60.4 + 0.9
	NaHexXan	CO_3^{2-} / IBMK	70.8 ± 0.2
	oxine, 70-fold excess / pH 8.0	ammoniacal buffer/ IBMK	95.2 ± 0.04
	NaOctXan[f] 50 mg / pH 8.5	ammoniacal buffer/ IBMK	70.5 ± 0.5
	NaHexXan, 90 mg / pH 8.5	ammoniacal buffer/ IBMK	96.2 ± 0.09
	NaHexXan, 15-fold excess/ pH 8.5	ammoniacal buffer/ IBMK	80.5 ± 1.0
	AcAc, 0.71 mL / pH 8.5	ammoniacal buffer/ IBMK	63.6 ± 0.7

NaOctXan / pH 8.0	ammoniacal buffer/ IBMK	95.5 ± 0.06
NaHexXan, 39 mg / pH 8.0	ammoniacal buffer/ IBMK	96.8 ± 0.05
NaEtXan[g] / pH 8.0	ammoniacal buffer/ IBMK	96.2 ± 0.02
NaDEDTC / pH 8.0	ammoniacal buffer/ IBMK	96.9 ± 0.4
NaHexXan / pH 5.4	IBMK	57.4 ± 0.8
NaDEDTC / pH 5.4	IBMK	53.6 ± 0.4
NaHexXan, 39 mg / pH 3.4	NH_4Cl / IBMK	32.9 ± 0.7
NaEtXan, 38 mg / pH 3.4	NH_4Cl / IBMK	27.2 ± 2.8
NaDEDTC, 25 mg / pH 3.4	NH_4Cl / IBMK	29.3 ± 0.7
NaEtXan / pH 1.4	IBMK	9.9 ± 2.1
NaHexXan / pH 1.4	IBMK	8.2 ± 5.4
NaDEDTC / pH 1.4	IBMK	11.2 ± 3.6

[a] oxine ≡ 8-hydroxyquinoline, [b] IBMK ≡ isobutylmethyl ketone, [c] NaDEDTC ≡ sodium diethyldithiocarbamate, [d] AcAc = 2,4-pentanedione, [e] NaHexXan ≡ sodium hexylxanthate, [f] NaOctXan ≡ sodium octylxanthate, [g] NaEtXan ≡ sodium ethylxanthate.

acetate or isobutylmethyl ketone. One disconcerting aspect of this study was the observation that the presence of CO_3^{2-} / HCO_3^- apparently was deleterious to the efficiency of the Cr(III) recovery.

The transfer of the process to the supercritical fluid phase was somewhat more complicated (Table 5). The efficiency of the formation/mobilization of the $Cr(chelate)_3$ complex proved to be very pH dependent. The possibility of forming this complex *in situ* was not promising in that the predicted pH of CO_2 saturated aqueous media is distinctly acidic. The pH of aqueous solutions in contact with SC-CO_2 can be approximated using Henry's Law and the acid dissociation constants of carbonic acid to determine the degree of dissociation based on ideal gas behavior. As suggested by Figure 8, the predicted pH of CO_2-saturated aqueous 0.3500 M $NaHCO_3$ at 50°C, ranged from 5.4-4.8 for CO_2 pressures between 10.34 and 41.37 MPa. Similarly, for aqueous media that has been pressurized with CO_2 to 24.14 MPa at 50°C, the predicted pH is raised from 2.8 to 5.2 as the $NaHCO_3$ content is increased from 0 to 0.5 M (Figure 9). For temperatures between 25-70°C, accurate spectrophotometric measurements of the dissociation of bromophenol blue in water in contact with SC-CO_2 that had been pressurized to 7.092-20.265 MPa (70-200 atm) indicated pHs between 2.80 and 2.95 in close agreement with the predicted value by Toews *et al.*, (1995). The addition of carbonate/bicarbonate is predicted to increase the pH of the aqueous phase (Figure 9). However, the net effect on the efficiency of the extraction is more difficult to predict. Dialkyldithiocarbamate $[SC(S)NR_2]$ and alkylxanthate [SC(S)OR] are susceptible to an inactivating acid catalyzed hydrolysis. Whereas the acid decomposition rates for these two classes are approximately equal at pH 3, alkylxanthates are decomposed approximately 100-times more slowly at pH 5 (Hayashi *et al.*, 1986 and Hayashi *et al.*, 1984). In the presence of a limited excess of chelating reagent, their relative stability in acidic media can become an important factor for the success of the extraction. On the other hand, the increased concentration of CO_3^{2-} / HCO_3^- can cause the target Zn(II) ion, and presumably other cations as well to precipitate under kinetically controlled non-equilibrium conditions (Wang and Marshall, 1996b). It was decided to perform the complexation step separately from the supercritical extraction.

Table 5. Extraction efficiencies of Cr(chelate)$_3$ into supercritical carbon dioxide in the presence/absence of microwave accelerated derivatization.

Microwave duration (min)	Chelating reagent	Extractor operating conditions	Percent extraction [a]
15 min	oxine[a]	HCO_3^- / EtOAc	18.3 ± 27.8
15 min	oxine	HCO_3^- / IBMK	26.0 ± 19.0
5 min	oxine, 10-fold excess	NH_4Cl/NH_3, pH 8.4 / IBMK, 0.25 mL/min	80.0 ± 0.16
5 min	oxine, 10-fold excess	NH_4Cl/NH_3, pH 8.5 / IBMK, 0.25 mL/min	91.8 ± 0.05
5 min	oxine, 10-fold excess	NH_4Cl/NH_3, pH 8.5 / 2 mL IBMK	91.5 ± 0.05
5 min	AcAc[b], 100-fold excess	NH_4Cl/NH_3, pH 8.5 0.25 mL/min IBMK	91.8 ± 0.05
5 min	AcAc, 100-fold excess	NH_4Cl/NH_3, pH 8.5 0.25 mL/min IBMK	91.5 ± 0.09
5 min	NaHexXan[c], 130-fold excess	NH_4Cl/NH_3, pH 8.5 0.25 mL/min IBMK	96.2 ± 0.09
5 min	NaBuXan[d], 150-fold excess	NH_4Cl/NH_3, pH 8.6 0.25 mL/min IBMK	87.4 ± 0.2
5 min	NaDEDTC[e], 150-fold excess	NH_4Cl/NH_3, pH 8.6 0.25 mL/min IBMK	73.1 ± 0.2
	NaHexXan, 45-fold eccess	NH_4Cl/NH_3, pH 8.5 0.25 mL/min IBMK	83.8 ± 0.1

NaHexXan, 58-fold excess	NH_4Cl/NH_3, pH 8.4 0.25 mL/min IBMK	76.4 ± 0.1
NaHexXan, 58-fold excess	NH_4Cl/NH_3, pH 8.0 0.25 mL/min IBMK	77.0 ± 0.1
NaHexXan, 45-fold excess	NH_4Cl/NH_3, pH 8.5 0.25 mL/min IBMK	77.7 ± 0.2
NaHexXan, 58-fold excess	Na_2CO_3, 0.25 mL/min IBMK	70.8 ± 0.2
NaHexXan, 58-fold excess	NH_4HCO_3, 0.25 mL/min EtOAc	51.8 ± 7.1

[a] based on three replicate determinations, [b] oxine ≡ 8-hydroxyquinoline, [c] AcAc ≡ 2,4-pentanedione, [d] NaHexXan ≡ sodium hexylxanthate, [e] NaBuXan ≡ sodium butylxanthate, [f] NaDEDTC ≡ sodium diethyldithiocarbamate.

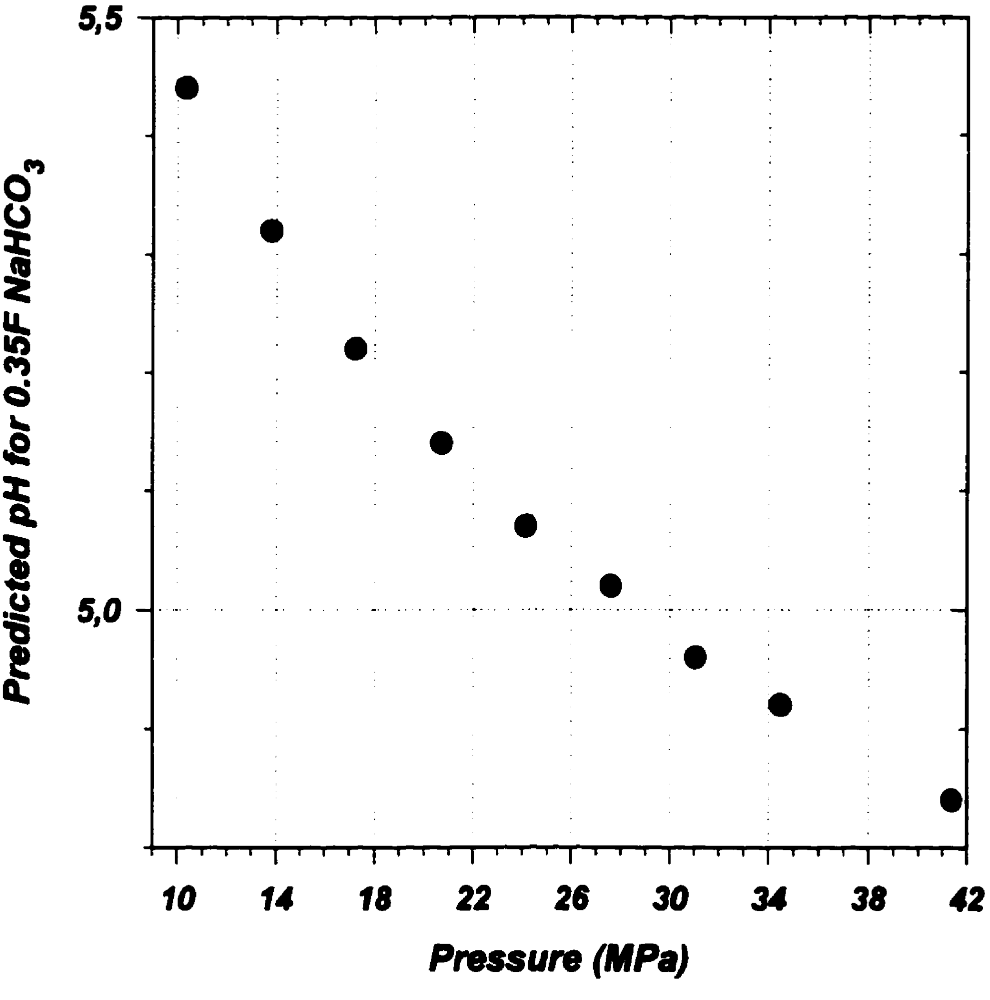

Figure 8: Predicted decrease in pH with increasing pressure of SC-CO_2 above an aqueous 0.35M sodium bicarbonate at 50°C.

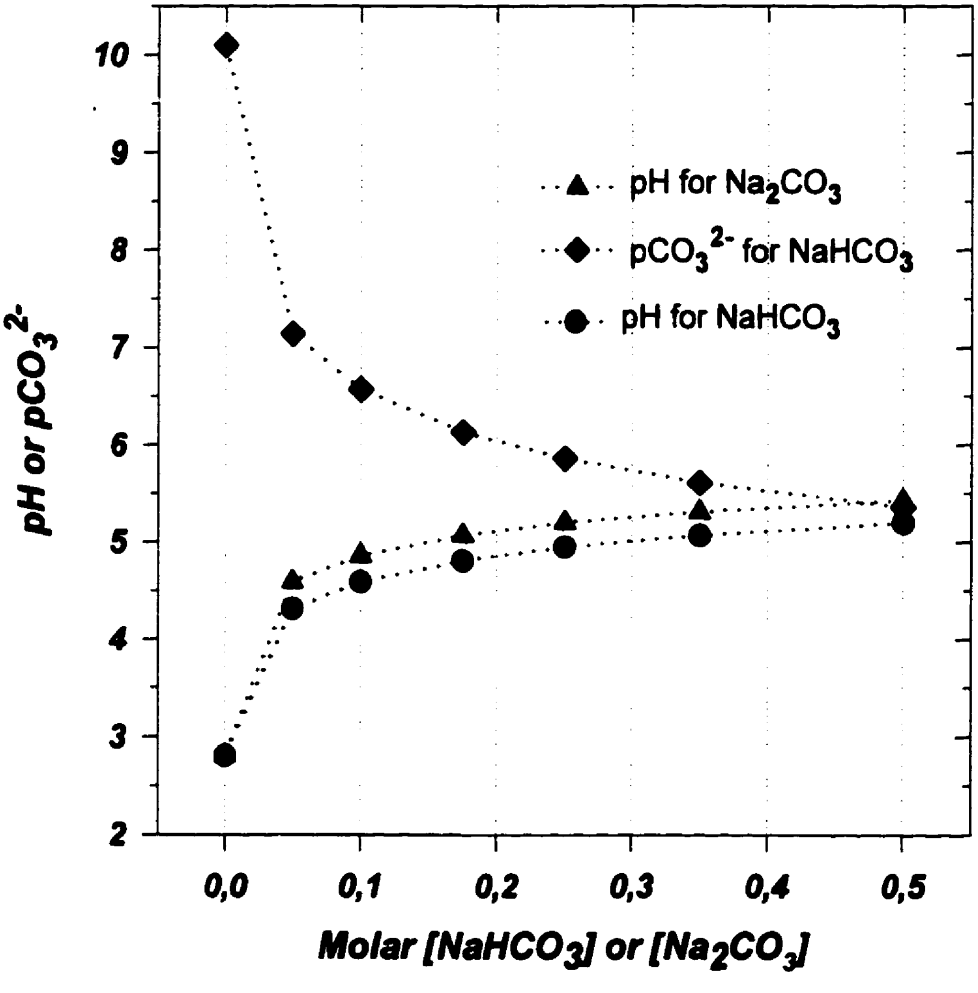

Figure 9: Predicted variations in pH or pCO_3^{2-} with increasing concentrations of bicarbonate or carbonate for an aqueous solution that has been saturated with SC-CO_2 at 50°C.

The results of selected Cr(III) mobilization trials are presented in Table 5. Recoveries were ~80% for the hexylxanthate mediated complexation/extraction into modified SC-CO_2. A procedural modification involved an initial pressurization of the aqueous sample, 175 μg Cr(III)/7 mL contained in 0.3 M $NaHCO_3$, in the TPEV. Once pressurized, the aqueous sample was filtered through a 3 cm column of 10 μm silica and transferred to the EV that contained 50 mg solid NaDEDTC. The aqueous phase was then extracted following the usual procedure. Although the recoveries in these trials were somewhat variable, some 50% of the initial Cr(III) burden was trapped on the silica gel column and a further 38% was removed by the complexometric extraction. For higher concentrations of target Cr(III) in aqueous media, it would be a more rapid process to combine a filtration stage with subsequent complexometric extraction.

Whereas the mobilization of Cu from CCA condensate into a constant flow of dibutyldithiocarbamate had been virtually quantitative (Wang and Marshall, 1996b) the mobilization of As(V) in the absence of prior conversion to As(III) was anticipated to be difficult. As(III) has been successfully mobilized into SC-CO_2 with bistrifluoroethyldithiocarbamate (Laintz *et al.*, 1992a) and As(V)/As(III) has been purged from spiked sand and soils with methylthioglycolate (Wenclawiak and Krah, 1995). However, it was not clear whether Cr(VI) or preformed Cr(chelate)$_3$ would survive the reduction/complexation of As(V) with the methylthioglycolate. As a strategy, it might have been possible to reduce the As(V) and Cr(VI) to As(III) and Cr(III) respectively and to evaluate the mobilization/purging of the reduced species from the aqueous CCA suspension. Given the less than quantitative recoveries of Cr(III) in the feasibility trials, it was decided to perform the extractions without pre-reduction of the target analytes.

On the basis of the residual As remaining in the aqueous phase (Table 3), As(III) apparently was partitioned into the MIBK reasonably efficiently (~93%) from a 125-fold excess of the same diethyldithiocarbamate reagent and As(V) was extractable (~90%) after derivatization with methylthioglycolate. Whereas the As(III) complexation reaction was very rapid, the As(V) derivatization with methylthioglycolate apparently required several minutes of reaction prior to purging. However, the efficiency of the corresponding mobilization of As(III) and As(V) into SC-CO_2 was further reduced to ~59 and ~67% in the presence of Cr(VI) although purging of the latter ion remained efficient (~95% extraction). Acidifying the crude reaction mixture to pH 2.0 prior to SC extraction increased the purging efficiency to ~81%.

The procedure was then applied to a sample of condensate from a chromated copper arsenate (CCA) treatment facility. Based on three replicate determinations, the mean concentrations of copper, chromium and arsenic in this suspension were determined to be 445.5 ± 0.0%, 771.0 ± 1.1% and 556.7 µg/mL ± 6.4% respectively. Initial feasibility trials consisted of CCA solutions that had been diluted ten-fold with water prior to extraction. As summarized in Table 6, the residual concentrations in the treated CCA solutions were reduced to low µg/mL concentrations when the extraction was performed in the presence of 50 mg of sodium diethyldithiocarbamate and 150 µL of methylthioglycolate. The efficiency was improved somewhat when solid precipitate was filtered from the crude suspension prior to extraction and further improved when the filtrate was acidified to pH 2.0. It was suspected that the rates of mobilization/purging of the metal chelates was limited by the decreased rate of solubilization directly from the solid phase. It remains unclear why the mobilization efficiency of metal chelates was improved when the aqueous phase was acidified (pH 2.0), but previous trials with Cu-, Pb- and Zn-dithiocarbamate complexes had been characterized by increased rates of mobilization/purging at lower pHs of the aqueous phase (Wang and Marshall, 1994a). Although virtually quantitative for Cu (99.9% removal) and efficient for Cr (97.0% removal), the arsenic proved to be somewhat more resistant to purging (86.9% removal). The final studies were performed directly on undiluted suspension of CCA condensate. With optimized derivatization/filtration and extraction conditions, the purging of As remained less than quantitative (~81% removal). The residual concentrations of Cr, Cu and As in the aqueous medium were 9.8 ± 2.4%, 0.01 ± 0.0% and 107.0 µg/mL ± 2.2% respectively.

Table 6. Removal efficiencies of metal ions from chromated copper arsenate (CCA) condensate with various extraction procedures.

Target Ions	Complexing / derivatizing reagent	Extraction conditions	Mean % removal [a]	Mean residual metal [a] (μg/mL)
As, Cr and Cu in 7 mL CCA condensate (dil'n x 10), pH 3.7	50 mg NaDEDTC + 150 μL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	Cu = 99.7 ± 0 Cr = 90.0 ± 0.1 As = 74.3 ± 0	Cu = 0.1 ± 0.0 Cr = 8.2 ± 0.7 As = 15.1 ± 0.0
As, Cr and Cu in 7 mL CCA condensate (dil'n x 10), pH 3.7, filtration	50 mg NaDEDTC + 150 μL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	Cu = 99.8 ± 0 Cr = 97.2 ± 0.01 As = 78.1 ± 0.3	Cu = 0.08 ± 0 Cr = 2.4 ± 0.2 As = 13.3 ± 0.08
As, Cr and Cu in 7 mL CCA condensate (dil'n x 10), pH 2.0, filtration	50 mg NaDEDTC + 150 μL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	Cu = 99.9 ± 0 Cr = 97.0 ± 0.02 As = 86.9 ± 0.8	Cu = 0.03 ± 0 Cr = 2.5 ± 0.2 As = 7.8 ± 5.1
As, Cr and Cu in 7 mL CCA condensate (undiluted), pH 2.0, filtration	150 mg NaDEDTC + 450 μL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	Cu = 99.9 ± 0 Cr = 93.2 ± 0.7 As = 75.9 ± 4.5	Cu = 0.25 ±0 Cr = 58.0 ± 0.8 As = 148.3 ± 5.1
As, Cr and Cu in 7 mL CCA condensate (undiluted), pH 2.0, filtration	300 mg NaDEDTC + 450 μL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	Cu = 100 ± 0 Cr = 97.6 ± 0.7 As = 59.3 ± 4.5	Cu = 0.085 ± 0 Cr = 19.9 ± 0 As = 248.0 ± 1.6
As, Cr and Cu in 7 mL CCA condensate (undiluted), pH 1.85, 2 filtrations	300 mg NaDEDTC + 0.82 mL $HSCH_2C(O)OCH_3$	SC-CO_2 + 0.25 mL/min IBMK	Cu = 100 ± 0 Cr = 98.8 ± 0.03 As = 81.9 ± 0.5	Cu = 0.01 ± 0 Cr = 9.8 ± 2.4 As = 107.0 ± 2.2

[a] based on three replicate determinations.

It is considered that a complexometric extraction into SC-CO_2 might serve as a preliminary decontamination process but that the aqueous medium would require subsequent treatment to meet wastewater quality criteria. Nonetheless, a single equilibration with only a three-fold molar excess of dithiocarbamate reagent reagent followed by filtration and purging of the filtrate with SC-CO_2 amended organic solvent (0.25 mL/min for 14 min) efficiently removed both the Cu and Cr from the aqueous substrate. While this work was in progress, the report of a technique involving supercritical CO_2 assisted liquid extraction (SALE) of polychlorinated dibenzo-*p*-dioxins, their furan analogs and polycyclic aromatic hydrocarbons from sediment and fly ash was published by Friedrich and Kleiböhmer (1997). The similarities of approach are striking.

3.3 Conclusion

The mobilization/purging of metal ions (Cr, Cu and As) from aqueous condensate of chromated copper arsenate (CCA) provided a quantitative extraction of the Cu, near quantitative extraction for Cr and less efficient extraction of the As. A series of complexometric extractions were performed to optimize the mobilization/purging of metal ions from the CCA sample. The SC-CO_2 was modified with isobutylmethyl ketone (MIBK) and used to increase the solubility of the added complexing agents and the pre-formed complex. It seemed that the organic solvent helped to preserve the complex intact for *on-line* detection. Cr(III) was much less reactive under the same conditions, so that, derivatization at a higher pH in an ammoniacal buffer with/without the help of a open-focused microwave was necessary. Even though Cr(III) was not present in the CCA sample, experiments were carried out to define the influence that the oxidation state of a metal ion has on the extraction efficiency. Finally, both a ten-fold dilution and undiluted CCA aliquots were SC-CO_2 extracted; Cr and Cu gave similar results but the mobilization efficiency of As was reduced modestly. The less than quantitative mobilization of As would necessitate further treatment(s) to further reduce the levels of this ion.

Chapter 4

4. Introduction

One aspect of the overall process of mobilization/purging of heavy metals from aqueous media into supercritical carbon dioxide (SC-CO_2) that has received less attention remains the re-isolation (by trapping) of the purged analytes. Researchers, for the most part, have preferred to base their calculation of mobilization efficiencies on the decrease of analyte concentration(s) that remain in the sample. However, appreciable portions of analyte complex can remain sorbed/deposited on either the walls of the extractor or within the transfer lines of the instrument. This problem of "incomplete" recovery can be exacerbated if a limited excess of the complexing reagent is used to perform the mobilization. The conventional approach to metal mobilization has been to continuously add excess complexing reagent to the mobile phase and cause both the complexation reaction with target metal(s) and mobilization of the lipophilic products as the mobile phase percolates through the aqueous sample. Product metal complex accumulates above the aqueous sample and is purged from the extractor by replacing the headspace fluid with fresh mobile phase.

Several techniques to trap analyte(s) from the SC-CO_2 extractor eluate have been described. The techniques have included the use of an empty collection flask, sorption/adsorption of the product metal complex onto the surface of a porous (inert or active) solid support and trapping within a limited volume of liquid solvent. The phenomenon of adiabatic cooling (as the mobile phase SC-CO_2 is vented to atmospheric pressure at the exit of the extractor) can cause specific problems that are not encountered when liquid phase is eluted from a separatory device. The cooling can cause aqueous media or other less volatile solutes to freeze at the tip of the capillary restrictor. If sufficient solute is present the tip can actually become blocked. Elemental sulfur from certain environmental samples has been reported to be problematic in this respect (Pyle and

Setty, 1991). One generally negative aspect of the application of supercritical fluid extractions to remediation remains the fact that soluble toxic substrates are transferred from one medium to another but they are not detoxified *per se*. It would be advantageous to combine the extraction process with a separate immobilization proces or a detoxification process so that products mobilized during the extraction would become less toxic to biological systems (either less available or less acutely poisonous).

One approach that could be applied to the detoxification of metal ions would be to effect a change of oxidation state of the target ion(s). The product ions would become less biologically available and/or less acutely toxic. The use of zero-valent metals as a sacrificial medium to mediate a corrosion process has become the object of intense study in recent years. In this process, the metal is oxidized in anoxic medium while target ions/compounds are reduced. A variety of organochlorine compounds have been dechlorinated efficiently by zero-valent iron or iron/palladium mixtures (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994). The products hydrocarbon and chroride are virtually innocuous relative to the toxicities of the starting materials. The process is promising because of the efficiency of the transformation, the low cost and the applicability to a wide concentration range of substrate(s). Other reductive transformations have involved brominated and iodinated organics, nitro-organics, nitrate and certain anions as substrates. The reduction process has been applied to the *in situ* remediation of sub-surface aquifers and has been reported to be less expensive than "pump and treat" technologies (Appleton, 1996).

Pyle and Setty (1991) reported a technique using granular copper to remove elemental sulfur (S_8) from supercritical carbon dioxide (SC-CO_2) extracts of soils. SFE of sulphur-containing soils and sediments was hindered by deposition of elemental sulphur in the restrictor, stopping the flow of CO_2. It was found that a copper scavenger column placed after the sample cell removed the elemental sulphur, making SF extraction and quantification possible. Quantification was performed by GC-MS and results were compared with certified standard reference materials (SRMs).

Powell *et al.*, (1995) have reported the reduction of chromium(VI) to the chromium(III) oxidation state with elemental or zero-valent iron. The process, effected in aqueous media containing natural aquifer materials with varying geochemistries, served as a model for the sub-surface chromate reduction process. This process is very promising for two reasons: (*i.*) the acute toxicity of Cr(III) is appreciably less than the toxicity of the Cr(VI) starting material and (*ii.*) the product was strongly sorbed to the iron particles. The authors postulated that the product Cr(III) ions had actually become intercalated within the surface iron atoms. Different forms of iron metals were tested. Impure or partially oxidized iron was most effective, with iron quantity being the most important rate factor, followed by aquifer material type and solid:solution ratio. Evidence for chromium–iron hydroxide solid solution $(Cr_x,Fe_{1-x})(OH)_3(ss)$ formation was obtained by electron probe microanalysis.

Another possible trapping system, alumina, was suggested by the work of Sperling *et al.*, (1992) who reported a rapid and sensitive method for the species-selective determination of chromium(III) and chromium(VI) in water samples by flame atomic absorption spectrometry using on-line preconcentration on a microcolumn packed with activated alumina (acidic form).

Kundu and Roy (1993) reported an elegant complexometric titration procedure for the determination of calcium and magnesium in an admixture. This procedure was interesting for our purposes because it documented the thermal stability of magnesium acetylacetonate complex at ambient temperatures and the instability of this complex at 90°C. It suggested the possibility that the Mg-complex could be generated in an aqueous medium, mobilized into SC-CO_2 then decomposed at higher temperature to liberate the free metal cation. It seemed possible that free acetylacetone would also be liberated (by the acidic environment of the SC-CO_2) and could then be recycled back to the extractor and become available to complex fresh metal cation. A cyclical process was envisaged in which a limited quantity of complexing reagent could be made to mobilize/purge a stoichiometric excess of metal cation from an aqueous solution. On the other hand, it was recognized that not all metal acetylacetonate complexes are equally susceptible to thermally induced decomposition. Cr(acetylacetonate)$_3$ is sufficiently stable to be determined by gas chromatography.

The objectives of this work were to perform preliminary experiments to identify conditions that would permit: (*i.*) the efficient trapping of metal ion from metal complex (in a SC-CO_2 carrier phase) onto a porous support while (*ii.*) releasing the ligand into the carrier phase so that it could be recycled back to the extraction vessel. The net result would be to create a cyclical extraction process in which a limited quantity of complexing reagent could be used to mobilize then trap target metal(s) from an aqueous medium.

4.1 Materials and methods

4.1.1. Supercritical fluid extractor and trapping column

The supercritical fluid extractor was essentially as described in section 3.1.1. (page 51) of this thesis. Minor modifications to the system included the addition of a post-extraction reactor unit that was followed by a second trapping vessel. The reactor consisted of a 15 cm x 0.46 cm stainless steel (ss) HPLC column that had been filled with test trapping material (either 50-mesh electrolytic grade iron particles, Fisher Scientific, or acid washed sea sand, ACP Chemicals Ltd., Montréal, Canada). The HPLC column was jacketed with a 60-turn heating coil (20-guage KantalA high resistance heating wire) that was energized with a direct current from a variable transformer (Variac model 3PN116C) that was connected to the high resistance circuit of the heater (Figure 10). The liquid phase-trap consisted of a 25 cm length of a 0.050 mm inner diameter silica capillary tubing that acted as the capillary restrictor for the extractor. The exit tip of the extractor dipped into chloroform contained in a 25-mL test tube.

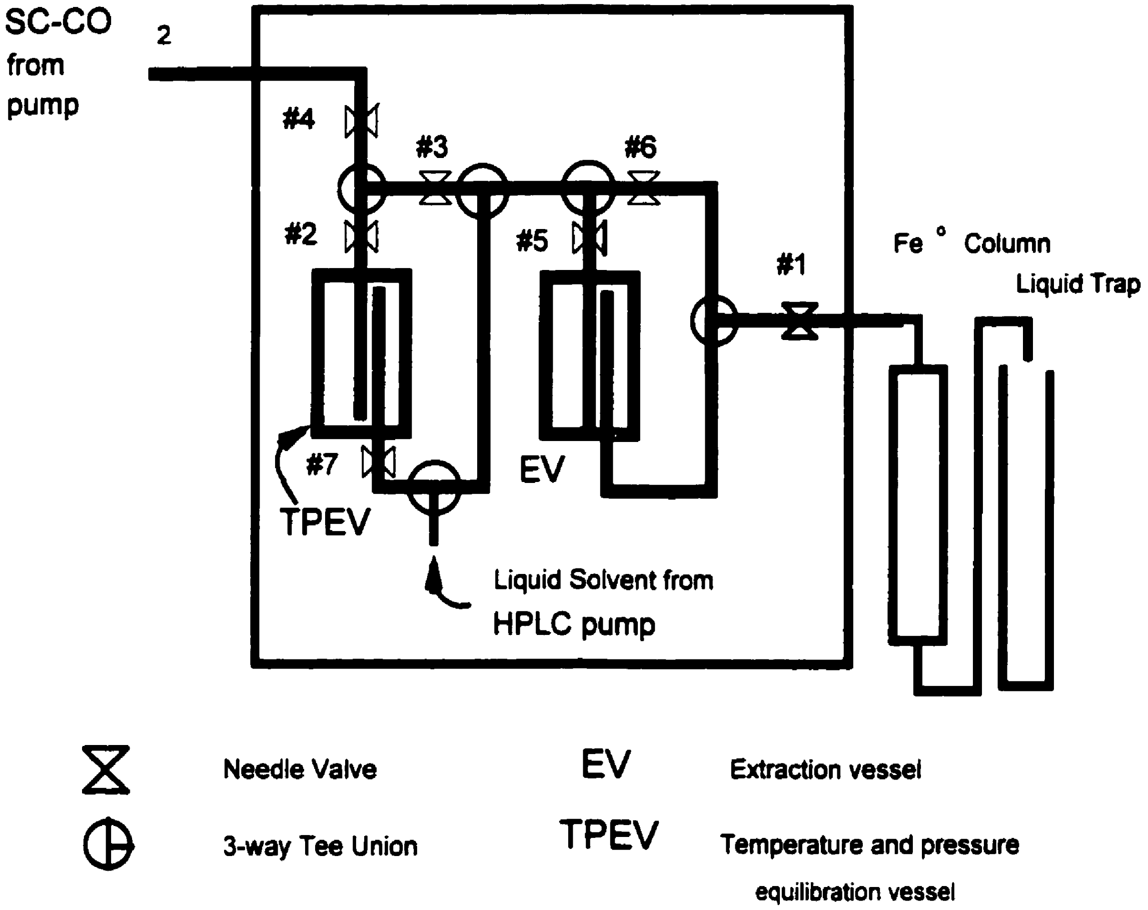

Figure 10: Supercritical fluid extractor with post-extraction column (Fe^0).

4.1.2 Reagents and standards

All chemicals, ACS reagent grade or better, were purchased from Sigma-Aldrich® (Milwaukee, WI, USA), Fisher Scientific (Montréal, Canada) or ACP Chemicals Ltd. (Montréal, Canada). Whereas the acetylacetonate complexes of cobalt and manganese (used without further purification) were dissolved in ethyl acetate, the arsenic and chromium salts were dissolved in double deionized water (Millipore Milli-Q-Plus system, Faer Lawn, NJ). Cupric acetate dissolved in Tris buffer (pH of 8.5) was used to quantify the released acetylacetone. The electrolytic grade iron particles, 50-mesh, and the acid washed sea sand were used as solid trapping materials. All glassware was successively washed in a soap solution, soaked in nitric acid (20% v/v), rinsed with copious quantities of distilled deionized water and dried in the oven.

4.1.3 Methods

A 7 mL volume of aqueous solution, containing 87.5 µg/mL each of As(V) and Cr(III) was maintained at 50°C within the extraction vessel of the extractor. The extraction was then carried out with a mixed mobile phase consisting of 0.25 mL/min IBMK or ethyl acetate and 0.75 mL/min SC-CO_2 as described in section 3.1.1 (page 51). Alternatively, 0.5 mL of acetylacetonate mixture (250 µg of each analyte metal) was added to 6.5 mL distilled deionized water; the mixture was heated to 50°C then extracted with IBMK or ethyl acetate-amended mobile phase as above. The temperature of the solid-phase trapping column was maintained at a pre-selected temperature (150-400°C) for the duration of the extraction. The effluent from the solid-phase trap was decompressed to atmospheric pressure then percolated through a 20 cm height (25 mL) of 1:1 (v/v) chloroform-water.

To quantify the acetylacetone released from the solid trap, companion liquid-phase extractions were performed by adding either an equivalent amount or excess acetylacetone to a cupric acetate Tris buffer solution (pH 8.5) that had been overlayered with chloroform.

The quantity of product Cu-complex that had been transferred to the chloroform phase was determined by AAS.

4.2 Results and discussion

The SFE system that was used in these preliminary trials, represented a slight modification of the original design (section 3.1.1, page 51) in that it incorporated a separately heated iron or sand trap mounted in series directly after the extraction vessel. As represented schematically in Figure 10, this scavenger column was similar in concept to the design reported by Pyle and Setty (1991). These authors described a stainless steel HPLC column, filled with granules of copper metal, that removed elemental sulfur efficiently from SC-CO_2 extracts of environmental matrices. Plugging of the restrictor tip with precipitated sulfur was avoided by using this copper trap. It was anticipitated that the iron metal trapping material in the current system would efficiently remove metal complex from the SC-CO_2 extractor eluate. At the same time, the heated metal trap might accelerate the thermal decomposition of metal acetylacetonate complex with the liberation of 2,4-pentanedione (acetylacetone). To test this hypothesis, the eluate from the trapping column was decompressed directly into an aqueous copper solution that had been overlayered with chloroform. In operation, any liberated 2,4-pentanedione would react with the aqueous Cu^{2+} and the product complex would be transferred to the chloroform phase. At the same time any metal acetylacetonate complex that was not trapped on the iron column would also be accumlated in the chloroform phase of the liquid trap. Whereas the formation of $Cu(AcAc)_2$ complex by reaction of aqueous Cu^{2+} (pH 7-10) with excess 2,4-pentanedione is considered to be instantaneous and virtually quantitative, it was not clear whether the same reaction would be equally efficient if a limited quantity of 2,4-pentanedione was reacted with excess Cu^{2+}. Table 7 presents the recovery of preliminary liquid phase extractions in which a limited quantity of 2,4-pentanedione was reacted with excess aqueous Cu^{2+} contained in a pH 8.5 Tris buffer (de Anik *et al.*, 1970). Three successive extractions with chloroform recovered a total of 92% of 2,4-pentanedione as the copper(acetylacetonate)$_2$ bidentate ligand, electronically neutral lipophilic complexes (that

Table 7: Zero-valent iron (Fe^0) column.

Column temp. (°C)	Iron column				
	Target analytes	**Extraction vessel (% removal ± RSD)**	**Mobile phase**	**2,4-pentadione recovered in the 2nd trap (% ± RSD)**	**Metal residues in the 2nd trap (% ± RSD)**
200	As(V) + Cr(VI) each 87.5 μg/mL [a]	As (66.7 ± 1.4) Cr (88.7 ± 0.1)	$SC\text{-}CO_2$ + 0.25 mL/min IBMK for 14 min	Not determined	N.D. [b]
200	Pure 2,4-pentanedione		$SC\text{-}CO_2$ + 0.25 mL/min IBMK for 14 min	74.8	0.5 [as Fe(AcAc)x]
200	$Cr(AcAc)_3$ $Co(AcAc)_3$ $Mn(AcAc)_3$	Cr (98.12 ± 0.03) Co (95.13 ± 0.11) Mn (44.50 ± 0.61)	$SC\text{-}CO_2$ + 0.25 mL/min IBMK for 14 min		Cr (0.13 ± 0.01) Co (N.D.) Mn (N.D.)
200	$Cr(AcAc)_3$ $Co(AcAc)_3$ $Mn(AcAc)_3$	Cr (97.27 ± 0.02) Co (87.84 ± 0.32) Mn (77.64 ± 0.45)	$SC\text{-}CO_2$ + 0.25 mL/min IBMK for 14 min		Cr (0.11 ± 0.08) Co (N.D.) Mn (N.D.)
400	$Cr(AcAc)_3$ $Co(AcAc)_3$	Cr (98.12 ± 0.03) Co (95.13 ± 0.11)	$SC\text{-}CO_2$ + 0.25 mL/min IBMK for 14 min	0.27 ± 0.05	Cr (0.04 ± 0.00) Co (0.02 ± 0.00)
Liquid-liquid extraction				91.89 ± 0.43	

[a]: Derivatizing reagents (50 mg of NaDEDTC + 150 μL of $HSCH_2C(O)OCH_3$)

[b]: None Detected

are soluble in SC-CO_2) can yield a maximum of two or three equivalents of 2,4-pentanedione depending on the formal oxidation state of the metal that was present in the original complex. It was anticipated that the acidity of the water saturated SC-CO_2 in the Fe^0 environment would promote the liberation of 2,4-pentanedione. At the same time, Fe^{3+} ion generated by the corrosion of the elemental iron trapping material might also be volatilized by forming $Fe(AcAc)_3$.

The granular iron (Fe^0) trapping material that was assayed for metal binding capacity was characterized by a high affinity for metal complexes (Table 7) but this material did not mediate the release of free 2,4-pentanedione from the complexes to any appreciable extent. When a separate aliquot of free 2,4-pentanedione was added directly to the head of the iron column while SC-CO_2 was used to entrain any volatile products into the second (liquid) trap approximately 75% was recovered as $Cu(AcAc)_2$ in the liquid trap. Moreover, only traces of iron (accounting for approximately 0.5% of the mobilized 2,4-pentanedione) were liberated by the process. These observations indicated that the 2,4-pentanedione in the metal acetylacetonate complex remained bound to the surface of the iron particles. The reason for the binding remains unclear at present. In a preliminary trial a mixture of sodium diethyldithiocarbamate (50 mg) and methylthioglycolate (150 μL) was used to mobilize arsenate and chromate (each 87.5 μg) from the extraction vessel. Although the mobilization was not quantitative, no residue of either chromium or arsenic could be detected in either the aqueous or the chloroform phase of the liquid trap. The Fe^0 trap efficiently removed both the $As(SCH_2CO_2H)_3$ and the $Cr[SC(S)\ NEt_2]_3$ complexes from the SC-CO_2 mobile phase.

Two different temperatures (200 and 400°C) were evaluated with a mixture of pre-formed $Co(AcAc)_3$, $Cr(AcAc)_3$ and $Mn(AcAc)_2$ complexes. Apparently, the increased temperature did not influence the capacity of the iron column to sorb metal analytes efficiently. In each of the two replicate trials at 200°C, traces of chromium (corresponding to $0.13 \pm 0.1\%$ or $0.11 \pm 0.08\%$ of the quantity initially added to the aqueous solution in the extractor) were accumulated in the chloroform trap, neither cobalt nor manganese residues could be detected in this solvent in either trial. Whereas $Cr(AcAc)_3$ and $Co(AcAc)_3$ complexes were purged efficiently from the extraction vessel into the SC-CO_2 (98.1, 97.3 and 95.1, 87.8% extraction respectively), the $Mn(AcAc)_2$ was mobilized less efficiently (44.5 and 77.6% extraction). A precipitate was visible in the aqueous solution contained in the extraction vessel at the determination of both trials. Despite the inefficient liberation of 2,4-pentanedione, the Fe^0 column remains an efficient technique for removing metal-acetylacetonate complexes from flowing supercritical carbon dioxide.

Separate experiments were also performed using a trap composed of acid washed sea sand (Table 8). The silica particles in the sand column were anticipated to be less reactive than the Fe^0 particles. In these trials, a mixture of $Cr(AcAc)_3$ and $Co(AcAc)_3$ were added to the extraction vessel, a mixture of ethyl acetate and SC-CO_2 was used as the mobile phase and three temperatures of the sand trap were evaluated. The mobilization, at 50°C, of both acetylacetone complexes was very efficient (96 and 95% mobilization respectively), however the sand column was less efficient than the Fe^0 column at trapping the volatilized metals. For the sand column, the trapping efficiency improved with increasing temperature however the release of 2,4-pentanedione from the complexes was inefficient in all cases. Whereas, some 24% of the total acetylacetonate was liberated from the mixture of complexes at 200°C, both higher and lower sand column operating temperatures reduced the recovery of 2,4-pentanedione even further. A more efficient release of 2,4-pentanedione can be anticipated for those complexes that are thermally labile. It also seems likely that a combination of a sand trap followed by a Fe^0 scavenger column would serve to remove metal complexes efficiently from the mobile phase while liberating some of 2,4-pentanedione that could be recycled.

Table 8: Acid washed sea sand column.

Column temp. (°C)	**Sand column**				
	Target analytes	**Extraction vessel (% removal ± RSD)**	**Mobile phase**	**2,4-pentadione recovered in the 2nd trap (% ± RSD)**	**Metal residues in the 2nd trap (% ± RSD)**
150	$Cr(AcAc)_3$ $Co(AcAc)_3$	Cr (97.30 ± 0.02) Co (94.63 ± 0.00)	SC-CO_2 + 0.25 mL/min EtOAc for 14 min	10.16 ± 4.57	Cr (25.86 ± 1.98) Co (10.20 ± 0.90)
200	$Cr(AcAc)_3$ $Co(AcAc)_3$	Cr (97.39 ± 0.01) Co (96.08 ± 0.08)	SC-CO_2 + 0.25 mL/min EtOAc for 14 min	23.70 ± 0.41	Cr (23.44 ± 0.80) Co (0.20 ± 0.00)
400	$Cr(AcAc)_3$ $Co(AcAc)_3$	Cr (97.17 ± 0.01) Co (94.87 ± 0.11)	SC-CO_2 + 0.25 mL/min EtOAc for 14 min	3.55 ± 0.86	Cr (1.48 ± 5.01) Co (0.31 ± 0.00)

4.3 Conclusion

These preliminary experiments have demonstrated great promises for the removal/trapping of metals from supercritical carbon dioxide. When coupled with supercritical fluid extraction, metals can be removed from aqueous media then accumulated efficiently on the Fe^0 trapping material. Zero-valent iron particles were appreciably more efficient at trapping metal complexes than were the silica particles indicating an active involvement in the trapping process other than acting as a simple heat transfer medium. The avidity of the binding for the metal complexes was sufficient to remove them virtually quantitatively from the supercritical mobile phase. However, the Fe^0 released only small quantities of 2,4-pentanedione from the complexes. The sand trap was somewhat more efficient in this respect. Apparently, there is an optimum temperature for the release of the complexing reagent from the complexes. It seems that a combination of the two trapping media would trap metals efficiently but would release at least some complexing reagent.

References

American Wood Preservers Association, **1978**. American wood preservers' association standards. Standard P5-78, Washington, DC.

Appleton, E.L. **1996**. A Nickel-Iron Wall Against Contaminated Groundwater. Environmental Science and Technology, 30, pp. 536A-539A.

Ashraf-Khorassani, M., Combs, M. and Taylor, L.T. **1997**. Supercritical Fluid Extraction of Metal Ions and Metal Chelates from Different Environments. Journal of Chromatography A, 774, pp. 37-49.

Bank, P.C., de Loos-Vollebregt, M.T.C. and de Galan, L. **1988**. Flow Injection Thermospray Sample Deposition for Electrothermal Atomization-Atomic Absorption Spectrometry. Spectrochimica Acta, 43B, pp. 983-987.

Blais, J.-S., Momplaisir, G.-M. and Marshall, W.D. **1990**. Determination of Arsenobetaine, Arsenocholine, and Tetramethylarsonium Cations by Liquid Chromatography-Thermochemical Hydride Generation-Atomic Absorption Spectrometry. Analytical Chemistry, 62, pp. 1161-1166.

Blakley, C.R., McAdams, M.J. and Vestal, M.L. **1978**. Crossed-Beam Liquid Chromatography-Mass Spectrometer Combination. Journal of Chromatography, 158, pp. 261-276.

Blakley, C.R. and Vestal, M.L. **1983**. Thermospray Interface for Liquid Chromatography/Mass Spectrometry. Analytical Chemistry, 55, pp. 750-754.

Bøwadt, S. and Hawthorne, S.B. **1995**. Supercritical Fluid Extraction in Environmental Analysis. Journal of Chromatography A, 703, pp. 549-571.

Bradley Jr, R.L. **1989**. Removal of Cholesterol from Milk Fat Using Supercritical Carbon Dioxide. Journal of Dairy Science, 72(10), pp. 2834-2840.

Brennecke, J.F. and Eckert, C.A. **1989**. Phase Equilibria for Supercritical Fluid Process Design. AICHE Journal, 35(9), pp. 1409-1427.

Burguera, M., Burguera, J.L. and Alarcón, O.M. **1988**. Determination of Zinc and Cadmium in Small amounts of Biological Tissues by Microwave-Assisted Digestion and Flow Injection Atomic Absorption Spectrometry. Analytica Chimica Acta, 214, pp. 421-427.

Canadian Standards Association. **1989**. Wood preservation: forest products. CSA Publication CAN/CSA-080-M1989, Toronto, ON1989, p.81.

Cheng, K.L., Ueno, K. and Imamura, T. **1982**. Handbook of Organic Analytical Reagents, CRC Press, Boca Raton, FL, pp. 85-108.

Cheremisinoff, P.N. **1989**. Encyclopedia of Environmental Control Technology: Pollution Reduction and Contaminant Control, vol. 6, chap. 20, pp. 529-541.

Cheremisinoff, P.N. and Hassinan, W.T. **1989**. Encyclopedia of Environmental Control Technology: Waste Minimization and Recycling, vol. 3, chap. 16, pp. 313-339.

Cowey, C.M., Bartle, K.D., Burford, M.D., Clifford, A.A., Zhu, S., Smart, N.G. and Tinker, N.G. **1995**. Solubility of Ferrocene and a Nickel Complex in Supercritical Fluids. Journal of Chemical Engineering Data, 40, pp. 1217-1221.

Daley, P.S. **1989**. Cleaning Up Sites with On-Site Process Plants. Environmental Science and Technology, 23, pp. 912-916.

David, M.D. and Seiber, J.N. **1996**. Comparison of Extraction Techniques, Including Supercritical Fluid, High-Pressure Solvent, and Soxhlet, for Organophosporus Hydraulic Fluids from Soil. Analytical Chemistry, 68, pp. 3038-3044.

de Anik, K., Khopkar, S.M. and Chalmers, R.A. **1970**. Solvent Extraction of Metals. London, New York, Van Nostrand Reinhold Co.

de Loos-Vollebregt, M.T.C., Tiggelman, J.J., Bank, P.C. and Degraeuwe, C. **1989**. Thermospray Sample Introduction into a Horizontal Low-flow Inductively Coupled Plasma with End-on Observation. Journal of Analytical Atomic Spectrometry, 4, pp. 213-217.

Drummond, C.J., Noceti, R.P., Miller, R.D., Feeley III, T.J. and Cook, J.A. **1985**. Details of a Treatment Train Capable of Significantly Improving the Quality of H-Coal Process Wastewaters, Reducing Contaminant Concentration to Low Levels. Environmental Progress, 4, pp. 26-33.

Ellen, M.E., McNally, P. and Bright, F.V. **1992**. Fundamentals Studies and Applications of Supercritical Fluids. ACS Symposium Series 488, pp. 1-15.

Fang, Y. **1995**. Flow Injection Atomic Absorption Spectrometry. New York, John Wiley & Sons.

Field, J.A., Miller, D.J., Field, T.M., Hawthorne, S.B. and Giger, W. **1992**. Quantitative Determination of Sulfonated Aliphatic and Aromatic Surfactants in Sewage Sludge by Ion-Pair/Supercritical Fluid Extraction and Derivatization Gas Chromatography/Mass Spectrometry. Analytical Chemistry, 64, pp. 3161-3167.

Ford, D.L. **1992**. Toxicity Reduction Evaluation and Control. Lancaster, PA.: Technomic publishing, chap. 5, vol. 3, pp. 109-181.

Freeman, H.M. **1989**. Standard Handbook of Hazardous Waste Treatment and Disposal. Section 6.6., New York: McGraw-Hill Book Company.

Friedrich, C. and Kleiböhmer, W. **1997**. Supercritical CO_2-Assisted Liquid Extaction of Polycyclic Aromatic Hydrocarbons and Polychlorinated Dibenzo-p-Dioxins and -Furans from Solid Matrices. Journal of Chromatography A, 777, pp. 289-294.

Gardner, M.J. and Ravenscroft, J.E. **1996**. Determination of Chromium(III) and Total Chromium in Marine Waters. Fresenius Journal of Analytical Chemistry, 354, pp. 602-605.

Giddings, J.C., Myers, M.N., McLaren, L. and Keller, R.A. **1968**. High Pressure Gas Chromatography of Nonvolatile Species. Science, 162, pp. 67-73.

Gillham, R.W. and O'Hannesin, S.F. **1994**. Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron. Ground Water, 32, pp. 958-967.

Glennon, J.D., Hutchinson, S., Walker, A., Harris, S.J. and McSweeney, C.C. **1997**. New Fluorinated Acid Reagents for the Extraction of Metal Ions with Supercritical CO_2. Journal of Chromatography A, 770, pp. 85-91.

Grosse, D.W. **1989**. Encyclopedia of Environmental Control Technology: Hazardous Waste Containment and Treatment, vol. 4, chap. 21, pp. 541-611.

Gustavsson, A. **1987**. Characterization of an Interface for Sample Introduction into an Inductively Coupled Plasma. Spectrochimica Acta, 42B, pp. 111-118.

Harris, D.C. **1991**. Quantitative Chemical Analysis. W.H. Freeman and Company, third edition.

Hawthorne, S.B., Miller, D.J., Walker, D.D., Whittington, D.E. and Moore, B.L. **1991**. Quantitative Extraction of Linear Alkylbenzenesulfonates using Supercritical Carbon Dioxide and Simple Device for adding Modifiers. Journal of Chromatography, 642, pp. 301-317.

Hawthorne, S.B., Langenfeld, J.J., Miller, D.J. and Burford, M.D. **1992a**. Comparison of Supercritical $CHClF_2$, N_2O and CO_2 for the Extraction of Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons. Analytical Chemistry, 64, pp. 1614-1622.

Hawthorne, S.B., Miller, D.J., Nivens, D.E. and White, D.C. **1992b**. Supercritical Fluid Extraction of Polar Analytes using in situ Chemical Derivatization. Analytical Chemistry, 64, pp. 405-412.

Hawthorne, S.B. and Miller, D.J. **1994**. Direct Comparison of Soxhlet and low-and high-Temperature Supercritical CO_2 Extraction Efficiencies of Organics from Environmental Solids. Analytical Chemistry, 66, pp. 4005-4012.

Hawthorne, S.B., Galy, A.B., Schmitt, V.O. and Miller, D.J. **1995**. Effect of SFE Flow Rate on Extraction Rates: Classifying Sample Extraction Behavior. Analytical Chemistry, 67, pp. 2723-2732.

Hayashi, K., Sasaki, Y., Inomata, S. and Yanagidani, T. **1984**. Acid Dissociation Constants of Alkylxanthic Acids and Formation of Cadmium(II) and Zinc(II) Xanthate Complexes in 1:1 Water DMF. Bull. Chem. Soc. Jpn., 57, pp. 3074-3076.

Hayashi, K., Sasaki, Y., Tagashira, S. and Yanagidani, T. **1986**. Acid Dissociation Constants of Dialkyldithiocarbamic Acids and O,O'-dialkyl S-hydrogen Dithiophosphates and Formation Constants of their Complexes with Cadmium(II), Zinc(II) and Lead(II) in 1:1 Water DMF Medium. Bull. Chem. Soc. Jpn., 59, pp. 1255-1256.

Hills, J.W. and Hill Jr., H.H. **1991**. Simultaneous Supercritical Fluid Derivatization and Extraction. Analytical Chemistry, 63, pp. 2152-2155.

Hulanicki, A. **1967**. Complexation Reactions of Dithiocarbamates. Talanta, 14, pp. 1371-1392.

Janssen, H.G. and Cramers, C.A. **1990**. Some Aspects of Capillary Supercritical Fluid Chromatography. Journal of Chromatography, 505, pp. 19-35.

King, J.W., Johnson, J.H. and Friedrich, J.P. **1989**. Extraction of Fat Tissue from Meat Products with Supercritical Carbon Dioxide. Journal of Agricultural and Food Chemistry, 37, pp. 951-954.

King, J.W. **1989**. Fundamentals and Applications of Supercritical Fluid Extraction in Chromatographic Science. Journal of Chromatography Science, 27, pp. 355-364.

King, J.W. and France, J.E. **1992**. Basic Principles of Analytical Supercritical Fluid Extraction. *Book title*: Analysis with Supercritical Fluids: Extraction and Chromatography, pp. 32-60.

Koropchak, J.A. and Winn, D.H. **1986**. Thermospray Interfacing for Flow Injection Analysis with Inductively Coupled Plasma Atomic Emission Spectrometry. Analytical Chemistry, 58, pp. 2558-2561.

Krukonis, V.J. and Kurnik, R.T. **1985**. Solubility of Solid Aromatic Isomers in Carbon Dioxide. Journal of Chemical and Engineering Data, 30, pp. 247-249.

Kundu, D. and Roy, S.K. **1993**. De-masking of Magnesium-Acetylacetone Complex for Direct Ethylenediaminetetraacetic Acid Titration of Calcium and Magnesium in the Same Solution and at the Same pH. Analyst, 118, pp. 905-907.

Lagalante, A.F., Hansen, B.N., Bruno, T.J. and Sievers, R.E. **1995**. Solubilities of Copper(II) and Chromium(III) β-Diketonates in Supercritical Carbon Dioxide. Inorganic Chemistry, 34, pp. 5781-5785.

Laintz, K.E., Wai, C.M., Yonker, C.R. and Smith, R.D. **1991**. Solubility of Fluorinated Metal Diethyldithiocarbamates in Supercritical Carbon Dioxide. The Journal of Supercritical Fluids, 4, pp. 194-198.

Laintz, K.E., Shieh, G.M. and Wai, C.M. **1992a**. Simultaneous Determination of Arsenic and Antimony Species in Environmental-Sample using bis(trifluoroethyl)dithiocarbamate Chelation and Supercritical Fluid Chromatography. Journal of Chromatographic Science, 30, pp. 120-123.

Laintz, K.E., Yu, J.-J. and Wai, C.M. **1992b**. Separation of Metal Ions with Sodium bis(trifluoroethyl)dithiocarbamate Chelation and Supercritical Fluid Chromatography. Analytical Chemistry, 64, pp. 311-314.

Laintz, K.E., Wai, C.M., Yonker, C.R. and Smith, R.D. **1992c**. Extraction of Metal Ions from Liquids and Solid Materials by Supercritical Carbon Dioxide. Analytical Chemistry, 64, pp. 2875-2878.

Laintz, K.E., Hale, C.D., Stark, P., Rouquette, C.L. and Wilkinson, J. **1998**. A Comparison of Liquid and Supercritical Carbon Dioxide as an Extractant Solvent for Plating Bath Treatment. Analytical Chemistry, 70, pp. 400-404.

Langenfeld, J.J., Hawthorne, S.B., Miller, D.J. and Pawliszyn, J. **1993**. Effects of Temperature and Pressure on Supercritical Fluid Extraction Efficiencies of Polyclyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls. Analytical Chemistry, 65, pp. 338-344.

Langenfeld, J.J., Hawthorne, S.B., Miller, D.J. and Pawliszyn, J. **1994**. Role of Modifiers for Analytical-Scale Supercritical Fluid Extraction of Environmental Samples. Analytical Chemistry, 66, pp. 909-916.

Larsen, E.H. and Blais, J.-S. **1993**. Performance of a Modular Thermospray Interface for Signal Enhancement in Flame Atomic Absorption Spectrometry Coupled On-line to Flow Injection or Liquid Chromatography. Journal of Analytical Atomic Spectrometry, 8, pp. 659-664.

Lee, H.B., Peart, T.E. and Hog-You, R.L. **1993**. Determination of Phenolics from Sediments of Pulp Mill Origin by in situ Supercritical Carbon Dioxide Extraction and Derivatization. Journal of Chromatography, 636, pp. 263-270.

Levy, J.M., Storozynsky, E. and Ashraf-Khorassani, M. **1992**. Use of Mofifiers in Supercritical Fluid Extraction. ACS Symposium Series 488, pp. 336-361.

Lin, Y., Brauer, R.D., Laintz, K.E. and Wai, C.M. **1993**. Supercritical Fluid Extraction of Lanthanides and Actinides from Solid and Liquid Materials with a Fluorinated β-diketone. Analytical Chemistry, 65, pp. 2549-2551.

Lin, Y., Wai, C.M., Jean, F.M. and Brauer, R.D. **1994**. Supercritical Fluid Extraction of Thorium and Uranium Ions from Solid and Liquid Materials with Fluorinated β-diketones and Tributyl Phosphate. Environmental Science and Technology, 28, pp. 1190-1193.

Lin, Y., Smart, N.G. and Wai, C.M. **1995a**. Supercritical Fluid Extraction and Chromatography of Metal Chelates and Organometallic Compounds. Trends in Analytical Chemistry, 14, pp. 123-133.

Lopez-Avila, V., Dodhiwala, N.S. and Beckert, W.F. **1993**. Developments in the Supercritical Fluid Extraction of Chlorophenoxy Acid Herbicides from Soil Samples. Journal of Agricultural and Food Chemistry, 41, pp. 2038-2044.

Matheson, L.J. and Tratnyek, P.G. **1994**. Reductive Dehalogenation of Chlorinated Methanes by Iron Metal. Environmental Science and Technology, 28, pp. 2045-2053.

McNally, M.E.P. **1995**. Advances in Environmental SFE. Analytical Chemistry, 67, pp. 308A-315A.

M'Hamidi, R., Bocquet, J.F., Chhor, K. and Pommier, J. **1991**. Journal of Supercritical Fluids, 4, pp. 55-59.

Miller, D.J. and Hawthorne, S.B. **1995**. Determination of Solubilities of Organic Solutes in Supercritical CO_2 by On-Line Flame Ionization Detection. Analytical Chemistry, 67, pp. 273-279.

Momplaisir, G.-M., Lei, T. and Marshall, W.D. **1994**. Performance of Novel Silica T-Tube Interface for the AAS Detection of Arsenic and Selenium Compounds in HPLC Column Eluate. Analytical Chemistry, 66, pp. 3533-3539.

Noro, J. and Sekine, T. **1993**. Solvent Extraction of Europium(III) Anionic Complexes with Several β-Diketones as Ion-Pairs with Tetrabutylammonium into Chloroform. Bull. Chem. Soc. Jpn., 66, pp. 1647-1651.

Pedersen, C.J. **1988**. The Discovery of Crown Ethers. Science, 241, pp. 536-540.

Posta, J., Gáspár, A., Tóth, R. and Ombódi, L. **1996**. Cr(III) and Cr(VI) On-Line Preconcentration and Determination with High Performance Flow Flame Emission Spectrometry in Natural Samples. Fresenius Journal of Analytical Chemistry, 355, pp. 719-720.

Powell, R.M., Puls, R.W., Hightower, S.K. and Sabatini, D.A. **1995**. Coupled Iron Corrosion and Chromate Reduction: Mechanisms for Subsurface Remediation. Environmental Science and Technology, 29, pp. 1913-1922.

Pyle, S.M. and Setty, M.M. **1991**. Supercritical Fluid Extraction of High Sulfur Soils with Use of Copper Scavenger. Talanta, 38, pp. 1125-1128.

Raynie, D.E. **1993**. Warning Concerning the Use of Nitrous Oxide in Supercritical Fluid Extractions. Analytical Chemistry, 65, pp. 3127-3128.

Rizvi, S.S.H., Daniels, J.A., Benado, A.L. and Zollweg, J.A. **1986**. Supercritical Fluid Extraction: Operating Principles and Food Applications. Food Technology, July, pp. 57-64.

Robinson, J.W. and Choi, D.S. **1987**. The Development of a Thermospray Flame Atomizer for AA Improved Sensitivity, Interfacing with HPLC. Spectroscopy Letters, 20, pp. 375-390.

Robinson, J.W. and Choi, D.S. **1989**. Application of HPLC-Thermospray Flame AAS: Interaction Between Heavy Metals and Duckweed Chlorophyll. Spectroscopy Letters, 22, pp. 779-794.

Rochette, E.A., Harsh, J.B. and Hill Jr., H.H. **1993**. Supercritical Fluid Extraction of 2,4-D from Soils using Derivatization and Ionic Modifiers. Talanta, 40, pp. 147-155.

Saito, N., Ikushima, Y. and Goto, T. **1990**. Liquid/Solid Extraction of Acetylacetone Chelates with Supercritical Carbon Dioxide. Bull. Chem. Soc. Jpn. 63, pp. 1532-1534.

Sekine, S. and Hasegawa, Y. **1977**. Solvent Extraction Chemistry - Fundamentals and Applications, Marcal Dekker, Inc., New York, NY, pp. 570-573.

Smart, N., Lin, Y. and Wai, C.M. **1996**. Supercritical Fluid Extraction of Metal Ions from Solids Samples. American Environmental Laboratory, February, pp. 38-42.

Smart, N.G., Carleson, T., Kast, T., Clifford, A.A., Burford, M.D. and Wai, C.M. **1997**. Solubility of Chelating Agents and Metal-Containing Compounds in Supercritical Fluid Carbon Dioxide. Talanta, 44, pp. 137-150.

Snyder, J.L., Grob, R.L., McNally, M.E. and Oostdyk, T.S. **1992**. Comparison of Supercritical Fluid Extraction with Classical Sonication and Soxhlet Extractions for Selected Pesticides. Analytical Chemistry, 64, pp. 1940-1946.

Sperling, M., Xu, S. and Welz, B. **1992**. Determination of Chromium(III) and Chromium(VI) in Water Using Flow Injection On-Line Preconcentration with Selective Adsorption on Activated Alumina and Flame Atomic Absorption Spectrometric Detection. Analytical Chemistry, 64, pp. 3101-3108.

Tan, Y., Momplaisir, G.-M., Wang, J. and Marshall, W.D. **1994**. Performance of Silica T-Tube Interface for the Determination of Cadmium, Copper, Lead, Zinc and Mercury in Flowing Liquid Streams by Atomic Absorption Spectrometry. Journal of Analytical Atomic Spectrometry, 9, pp. 1153-1159.

Taylor, L.T. **1995**. Strategies for Analytical SFE. Analytical Chemistry, 67, pp. 364A-370A.

Taylor, L.T. **1996**. Supercritical Fluid Extraction. New York: John Wiley & Sons.

Toews, K.L., Shroll, R.M., Wai, C.M. and Smart, N.G. **1995**. pH-Defining Equilibrium between Water and Supercritical CO_2. Influence on SFE of Organics and Metal Chelates. Analytical Chemistry, 67, pp. 4040-4043.

Vannort, R.W., Chervet, J.P., Lingeman, H., Dejong, G.J. and Brinkman, A.T. **1990**. Coupling of Supercritical Fluid Extraction with Chromatography Techniques. Journal of Chromatography, 505, pp. 45-77.

Vestal, M.L. and Fergusson, G.J. **1985**. Thermospray Liquid for Chromatography/Mass Spectrometer Interface with Direct Electrical Heating of the Capillary. Analytical Chemistry, 57, pp. 2373-2378.

Wai, C.M. and Tang, J. **1986**. Solvent Extraction of Lanthanides with a Crown Ether Carboxylic Acid. Analytical Chemistry, 58, pp. 3233-3235.

Wai, C.M., Lin, Y., Brauer, R. and Wang, S. **1993**. Supercritical Fluid Extraction of Organic and Inorganic Mercury from Solid Materials. Talanta, 40, pp. 1325-1330.

Wai, C.M., Wang, S., Liu, Y., Lopez-Avila, V. and Beckert, W.F. **1996**. Evaluation of Dithiocarbamates and β-diketones as Chelating Agents in Supercritical Fluid Extraction of Cd, Pb, and Hg from Solid Samples. Talanta, 43, pp. 2083-2091.

Walkowiak, W., Charewicz, W.A., Kang, S.I., Yang, I.-W., Pugia, M.J. and Bartsch, R.A. **1990**. Effect of Structural Variations within Lipophilic Dibenzocrown Ether Carboxylic Acids on the Selectivity and Efficiency of Competitive Alkali-Metal Cation Solvent Extraction into Chloroform. Analytical Chemistry, 62, pp. 2018-2021.

Wang, J. and Marshall, W.D. **1994a**. Recovery of Metals from Aqueous Media by Extraction with Supercritical Carbon Dioxide. Analytical Chemistry, 66, pp. 1658-1663.

Wang, J. and Marshall, W.D. **1994b**. Metal Speciation by Supercritical Fluid Extraction with On-Line Detection by Atomic Absorption Spectrometry. Analytical Chemistry, 66, pp. 3900-3907.

Wang, S., Elshani, S. and Wai, C.M. **1995**. Selective Extraction of Mercury with Ionizable Crown Ethers in Supercritical Carbon Dioxide. Analytical Chemistry, 67, pp. 919-923.

Wang, J. **1995**. Extraction of Heavy Metals with Supercritical Carbon Dioxide. Ph.D. Thesis, McGill University.

Wang, J. and Marshall, W.D. **1995**. Supercritical Fluid Extraction with Carbon Dioxide for the Characterization of Cadmium, Copper and Zinc Bound to Metallothioneins. Analyst, 120, pp. 623-628.

Wang, J. and Marshall, W.D. **1996a**. Influence of Selected Natural Complexants on the Mobilization and Purging of Copper from Aqueous Media into Supercritical Carbon Dioxide. Analyst, 121, pp. 289-295.

Wang, J. and Marshall, W.D. **1996b**. Anion Mobilization from Aqueous Media by Ion Associate Extraction into Supercritical Carbon Dioxide with On-Line Detection by Flame Atomic Absorption Spectrometry. Analyst, 121, pp. 817-823.

Welz, B., Xu, S. and Sperling, M. **1991**. Flame Atomic Absorption Spectrometric Determination of Cadmium, Cobalt, and Nickel in Biological Samples Using a Flow Injection System with On-Line Preconcentration by Co-precipitation without Filtration. Applied Spectroscopy, 45, pp. 1433-1443.

Wenclawiak, B.W. and Krah, M. **1995**. Reactive Supercritical Fluid Extraction and Chromatography of Arsenic Species. Fresenius Journal of Analytical Chemistry, 351, pp. 134-138.

Williams, P.T. **1994**. Waste Incineration and the Environment; Pollutants from Incineration: An Overview, pp. 27-52.

Yamaguchi, K., Murakami, M., Nakano, H., Konosu, S., Kokura, T., Yamamoto, H., Kosaka, M. and Hata, K. **1986**. Supercritical Carbon Dioxide Extraction of Oils from Antarctic Krill. Journal of Agricultural and Food Chemistry, 34, pp. 904-907.

Yang, Y., Gharaibeh, A., Hawthorne, S.B. and Miller, D.J. **1995**. Combined Temperature/Modifier Effects on Supercritical CO_2 Extraction Efficiencies of Polycyclic Aromatic Hydrocarbons from Environmental Samples. Analytical Chemistry, 67, pp. 641-646.