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Direct Supercritical Fluid Extraction of Contaminants from Water

by

Sharon E. Brewer

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of the
requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University
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the Faculty of Graduate Studies and Research
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submitted by Sharon E. Brewer, M.Sc.
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the Doctor of Philosophy degree

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Abstract

A method and apparatus for the direct supercritical carbon dioxide extraction from water for analytical purposes has been developed. Polar and nonpolar organic analytes have been extracted at part-per-billion (ppb) levels. The effects of changes in both the extraction vessel and experimental conditions have been studied. The principal factors which affected analyte recovery were fluid inlet design, fluid volume, and nature of the analyte and aqueous matrix.

Extraction vessels have been designed and built which are suitable for the analytical extraction of liquid samples using supercritical carbon dioxide. The apparatus can accommodate water sample sizes of 25 and 75 mL. A method has been developed using the apparatus to quantitatively extract pentachlorophenol (PCP) from water at ppb levels. The amount of analyte extracted increased as supercritical carbon dioxide volume was increased, therefore total fluid volume was an important experimental variable. It was determined that a maximum of 1.5 times the sample volume was required to obtain quantitative analyte recovery under the conditions studied. The design of the fluid inlet was found to influence extraction recovery.

Carbon dioxide flow rate and density were also varied to determine their effect on extraction efficiency, and were found to have no significant effect at the conditions studied. This is in agreement with the first approximation of a theoretical model.

Extractions were performed from water containing natural organic matter (fulvic acid) known to adsorb analytes. The extraction effectiveness was not altered appreciably with the presence of organic matter at 200 times the level of a spiked analyte, PCP; it was slightly less effective when the organic matter concentration was 2000 times the analyte concentration. Co-extraction of the organic matter was not observed.

An in-situ derivatization and supercritical carbon dioxide extraction method was also developed and applied to water containing organic matter and PCP. This combined derivatization and extraction was found to recover more analyte than extraction of the same samples with supercritical carbon dioxide alone. The extraction of the derivative using carbon dioxide was also more efficient than extracting the derivative with hexane.

The extraction method developed was applied to water containing several chemically different analytes spiked at ppb levels: PCP, 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenoxy acetic acid (2,4-D), dieldrin, 2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane (DDT), and phenanthrene. High recoveries were observed for PCP ($97 \pm 7.0\%$), dieldrin ($99 \pm 6.8\%$), and DDT ($85 \pm 6.3\%$), while lower recoveries were observed for 2,4,6-TCP ($52 \pm 4.0\%$). It was not possible to extract 2,4-D under the conditions tested.

The extraction method does not require organic solvents for extraction purpose, shows potential for selective extraction, and has been applied to water containing dissolved fulvic acid.

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CHAPTER ONE

INTRODUCTION

1.1 Research Objectives

The major objective of this research project was to develop a method for the direct quantitative extraction of contaminants present at part per billion levels from water by using supercritical CO₂. To complete this research required the following tasks:

- design and manufacture an extraction vessel suitable for the direct extraction of water samples of minimum volume 20 mL
- develop an extraction apparatus and method using this extraction vessel for the analysis of pentachlorophenol in water
- determine how the efficiency of the extraction method is affected by changes in extraction conditions
- determine the efficiency of the extraction method for synthetic water samples containing natural organic matter and inorganic solids
- investigate the extraction of 2,4,6-trichlorophenol, 2,4-dichlorophenoxy acetic acid, dieldrin, 2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane, and phenanthrene.

A relatively polar, acidic compound, pentachlorophenol (PCP) was used as a model analyte throughout this study. Other analytes used in this study are described in chapter four. PCP is commonly found as a water pollutant in both drinking and surface water (CCREM 1987). The relevant physical and chemical

properties of the analytes are given in section 4.14.

Currently there are two principal techniques for the analysis of PCP in drinking water. The water sample is either put through a clean-up step, acidified, and extracted with ethyl ether as in EPA method 515.1 (EPA 1991); or it is passed through a solid phase where the analyte is absorbed and subsequently eluted using dichloromethane as in EPA method 525.1 (EPA 1991). The objective of this research is to develop a method which will allow the direct extraction of PCP with supercritical CO₂ as the extraction solvent instead of organic solvents. Such alternative extraction methods are desirable due to the increased concern over toxicity and disposal costs of traditional solvents.

1.2 General Introduction

The extraction of organics from water samples usually involves either thorough mixing with an organic solvent (liquid-liquid extraction), or sample contact with a solid phase which adsorbs analytes, followed by extraction of the solid phase with an organic solvent. Advantages and disadvantages of these methods are discussed in chapter two.

Supercritical fluids have replaced organic solvents as extractants in a number of applications reported over the past few years, due mainly to the desire to reduce the quantities of toxic organic solvents used. Although most applications have involved solid matrices, A number of researchers have

applied supercritical fluids to the direct extraction of liquids. The present study was aimed at extending this work to accomplish the objectives presented in the previous section.

The main difficulty in applying supercritical fluids to the direct extraction of liquid samples is the need to construct a suitable extraction vessel. While the design of a vessel for the supercritical fluid extraction of solid samples is fairly straightforward, this is not the case with liquid samples. The principal factors which must be considered are sample size, dead volume, and supercritical fluid inlet. The design of the fluid inlet has a profound influence on extraction efficiency, as it determines how the aqueous and fluid phases interact with each other. This governs the mass transfer of a solute between the two phases.

Despite the difficulty inherent in extraction from liquid samples, the potential advantages of such a method include greatly reduced use of traditional organic solvents, increased potential for selective extraction, and the ability to completely extract a water sample containing suspended solids in a single step. Reduced use of organic solvents may also reduce the cost of analysis, and is better for environmental reasons as some commonly used organic solvents are considered to be toxic.

CHAPTER TWO

BACKGROUND

2.1 Extraction

2.1.1 Extraction in Analytical Chemistry

The purpose of extraction in analytical chemistry is to isolate the desired analytes from a sample matrix in order to allow their chemical identification and quantitation. The extraction process must generally accomplish two objectives, isolation and concentration of the analytes. The specific extraction technique chosen for a given application depends on the nature of the sample matrix, and the properties and concentration ranges of the analytes. The method of analyte detection to be used must also be considered, because the analytes must be presented to the detector in a manner that is compatible with the detector.

2.1.2 Analytical Supercritical Fluid Extraction

A supercritical fluid extraction (SFE) apparatus consists of a source of the pressurized extraction fluid, an extraction cell, and a collection device for isolating the extract. SFE can be performed on-line, which means that it is coupled with some type of chromatographic instrumentation; or off-line, in which the extraction is independent of other subsequent analytical steps. One of the reasons that SFE has become such a viable alternative to conventional

extraction techniques is the increased disposal costs of traditional solvents. Another reason is that the solubility of compounds in supercritical fluids (SFs) can be affected by changes in the density of the fluid. This makes selective extractions a possibility depending on the nature of the analytes and the matrix.

Most environmental sample SFE applications involve solid matrices such as soils and sediments, foods, and tissues. A number of reviews on the use of SFE have been published which summarize this area (Chester 1992 & 1994, Janda 1993).

Recent work has allowed SFE of many types of polar analytes from solids using supercritical CO₂ as the solvent by combining a sample derivatization step prior to, or as part of the extraction process for solid samples. Some examples are given below in table 2.1.

Table 2.1 Literature examples of combined derivatization and supercritical fluid extraction of polar analytes from solid samples.

Analyte	Derivatization Agent	Reference
organic acids	silylation reagent	Hill et al. 1991
acid pesticides, fatty acids, sulfonates	boron trifluoride and trimethylphenyl-ammonium hydroxide	Hawthorne et al. 1992a and 1992b
chlorinated phenolics	acetic anhydride	Lee et al. 1993

2.1.3 Extraction from Water

The principal methods of extracting analytes from water are liquid-liquid extraction, adsorption onto a solid phase, and gas stripping. Gas stripping is mainly applied to volatile analytes, and will not be discussed further.

The success of a liquid-liquid extraction in isolating and concentrating the analyte depends on the relative affinities of the analyte for water and the extraction solvent. This is expressed quantitatively in terms of the partition coefficient, K_p . For the case of extraction of a solute from water by an organic solvent,

$$K_p = C_{\text{org}} / C_{\text{aq}} \quad 2.1$$

where C_{org} is the equilibrium concentration of the analyte in the organic phase, and C_{aq} is the equilibrium concentration of the analyte in the aqueous phase.

When liquid-liquid extraction is done as a batch process, a fixed amount of solvent is contacted with a water sample for a fixed length of time, the phases are allowed to separate, and the organic solvent recovered. The process must generally be repeated a number of times to ensure quantitative recovery of the analyte in the organic phase. More efficient extractions are obtained when the value of K_p is large. For example, in EPA method 508 (EPA 1991) for the determination of chlorinated pesticides in water, a separatory funnel extraction of a water sample is performed three times, by using 60 mL

aliquots of methylene chloride for each extraction. Liquid-liquid extraction can also be performed as a flow-through process, where the solvent phase is continuously renewed as the extraction proceeds. Equilibrium is never reached in this type of extraction, and analytes continuously partition into the solvent phase. There are many types of apparatus designed for continuous liquid-liquid extraction (Cusack 1991). Liquid-liquid extraction may be done at ambient temperatures with a large range of sample volumes, depending on the apparatus used. Organic solvents are required, and the extract may need to be concentrated in order to permit detection of the extracted analytes. The organic solvents used for liquid-liquid extraction are generally not selective, and chemical clean-up of the extract to isolate analytes from potential co-extracted interfering compounds is often required.

Solid phase extraction (SPE) involves isolating the desired analytes from a water sample by contacting the sample with a solid phase. Analytes are retained by the solid phase, while the water matrix passes through, which accomplishes the isolation step. The solid phase is usually washed by a solvent mixture that selectively removes non-analyte sample components which can be potential interferences, and then analytes are recovered from the solid phase by using a different solvent. The efficiency of the SPE method for isolating analytes from the water is determined by the nature of the solid phase. Analytes must have a greater affinity for the solid phase than for the aqueous phase. EPA method 525.1 (EPA 1991) is one example of an SPE method for

the determination of a range of organic compounds in drinking water. The extraction stage of the method involves passing a one liter water sample through a C₁₈ solid phase disk or cartridge. The solid phase is then eluted with dichloromethane. The main advantages of SPE are its ability to handle various sample volumes, the convenience of the technique, the elimination of large volumes of organic solvent, the possibility of incorporating a clean-up step, and its operation at ambient temperatures. In addition, SPE methods are ideally suited for on-site application. Its disadvantages are the potential for analyte breakthrough and the possibility of limited recovery of some analytes strongly adsorbed to the solid phase.

A novel version of SPE is solid phase microextraction (SPME) which uses a coated silica optical fibre to partition analytes from an aqueous sample (Louch 1992). Analytes adsorbed onto the fibre can then be desorbed directly into the injection port of a gas chromatograph. This technique has been used to extract a wide range of analytes from aqueous samples, including nonpolar organics (Arthur 1992) and phenolic compounds (Buchholz 1994).

2.1.4 Analytical Supercritical Fluid Extraction of Water

The methods used to remove analytes from water systems by SFs can be divided into three classes. The first class is similar to SPE, and involves a two step process where the contaminants are first adsorbed onto a solid support such as activated carbon. This solid is then extracted using a

supercritical fluid. This method was used by Pawliszyn et al. (1989) to remove polychlorinated benzenes from water. They reported high analyte recoveries for SF extraction times of one hour. Supercritical fluids have also been used to dissolve and degrade toxic materials in one step; this is sometimes called "active" extraction (Groves 1985). The SF used for this process is usually supercritical water, and extreme conditions ($p \geq 218$ atm, $T \geq 274$ °C) are thus required in order for the supercritical state to be obtained. These conditions can be difficult to work with, and equipment maintenance can be a problem. The third class of extractions consists of a single step process whereby organic contaminants are extracted from the water by direct contact with the SF. This could be done by a batch-type extraction where a fixed volume of SF is contacted with a water sample for a specific length of time and then the two phases are separated. Direct extraction could also be accomplished by a flow-through extraction whereby fresh SF is continuously passed through a water sample for a certain length of time.

The study of SF extraction from aqueous samples is becoming more popular, with an increasing number of studies focusing on this application. Much of the research has focused on how to optimize the extraction vessel design so that it would keep the water sample in the extraction vessel, minimize the water carried out of the extraction vessel, and to provide an efficient extraction. A number of papers have been published by a group from Texas A&M University on extraction from water. Roop et al. (1988) extracted creosote

from water with both near-critical and supercritical CO₂ using a batch type extraction. The efficiency of the extractions was determined by toxicological assay; there was no appreciable extraction of the toxic components until the critical pressure of CO₂ was exceeded. The same group (Roop 1989a) reported a three-part batch extraction study of water contaminated with phenol. The distribution coefficient for phenol between the aqueous and CO₂ phases for a range of pressures and temperatures was determined; compared with predictions from theory; and correlated with sample toxic activity.

Roop and Akgerman (1989b and 1990) have also investigated the effect of the addition of a small amount of an entrainer or modifier to the supercritical CO₂ on the batch extraction of an aqueous solution containing 6.8% phenol. The three entrainers investigated were methanol, chlorobenzene and benzene. Benzene caused the greatest increase in extraction efficiency. A thermodynamic model was developed to predict the entrainer effect on the extraction. Yeo and Akgerman (1990) published the results of a study of the determination of the partition coefficient between supercritical CO₂ and water of four different organic contaminants individually, and also for a mixture of all four in the same water sample. The organics chosen to represent different classes of contaminants were benzene, toluene, naphthalene, and parathion. The results showed that the presence of benzene and toluene seemed to increase the extraction of each other and the other contaminants. This may be due to entrainer effects as discussed above.

Another group that has been working on extraction of organics from water is from Yugoslavia. They have shown that supercritical CO₂ can be used to extract various pesticides from water (Knez 1988 & 1989) and they suggest that this is more economical than other methods which are more commonly used.

Ehnholt et al. (1983 and 1987) have used supercritical CO₂ to isolate a number of organic compounds present in small amounts in water. Twenty-three different compounds were chosen to represent a range of possible analytes usually encountered in drinking water. The results showed that in general compounds that were considered volatile and not highly soluble in water were easily extracted. Trapping the extracted analytes was shown to be difficult. Some inorganic salts were also studied; these did not show evidence of extraction. For the total organic content of samples, an extraction efficiency of 90% was reported.

Taylor et al. (1989, 1990, 1992) have also produced a number of papers dealing with direct flow-through SFE from liquid samples using supercritical CO₂ as the solvent. Their extraction set-up involved on-line SFE and chromatography. Both dynamic and equilibrium extraction modes could thus be performed with the aqueous samples. They reported the extraction of phenol from sulphuric acid, and the extraction of phosphonates and nitrogenous bases from aqueous samples (Taylor 1989 & 1990). When NaCl was added to the sample, the equilibration time was found to decrease. In another paper, the

same group studied the supercritical CO₂ extraction of phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 3-methyl-4-chlorophenol, and 2,4-dimethylphenol from water where each analyte was at a concentration level of 160 ppm (Hedrick 1992). The sample size was 3 mL, and the extraction vessel used was a commercially available one which was modified for use with liquid samples. For each phenol tested, the percent recovery decreased as pressure was increased at constant temperature. Due to use of the same restrictor in all experiments, flow rate also changed as pressure was varied.

Ong et al (1989 & 1991) have also developed an extraction vessel for direct extraction of liquid samples, in their study of the extraction of cholesterol from blood serum (Ong 1989) and PAHs from wastewater (Ong 1991) by using supercritical CO₂ as the solvent.

Work has also been done on the extraction of alcohols from water, for which CO₂ has been used in many of the reported studies (Brignole 1987, Inomata 1990, Kuk 1983). It has been shown that carbon dioxide may not be the preferred solvent, depending on the application (Brignole 1987). Light hydrocarbons such as propane and butane may be favoured as SFs for supercritical and near-critical extractions due to their extracting capability and lack of water entrainment.

Thiebaut et al. (1989) have used supercritical CO₂ to extract µg quantities of phenol and 4-chlorophenol from 5 µL aqueous samples. The extraction

system was coupled on-line with supercritical fluid chromatography using a phase separator to ensure removal of the water that was present in the CO₂ phase. The use of the phase separator was adopted from liquid-liquid extraction technology, but for the case of SF extraction it was mounted upside down. Phase separators of various materials were tested to evaluate their usefulness. The efficiency of the extraction for the compounds tested was determined to be 85%.

One novel study was carried out by Alzaga et al. (1994), who compared the supercritical CO₂ extraction of pesticides from freeze dried water samples and the liquid-liquid extraction of the same reconstituted water samples. By this approach, they effectively transformed the problem of direct SFE of liquids to the simpler one of performing SFE on a solid matrix. SFE was found to improve recoveries, reduce analysis time and be more cost effective, compared to conventional liquid-liquid extraction. Croft et al. (1994) used a similar approach when combining the simultaneous supercritical CO₂ extraction and methylation of chlorophenoxy acetic acids. The aqueous sample was transferred onto a solid support so that the extraction/derivatization was actually being done from a solid phase.

A recent study by Barnabas et al. (1994) compares the direct SFE of organochlorine pesticides (lindane, aldrin and dieldrin) from water with indirect SFE using empore disks as the solid phase. Supercritical CO₂ was the solvent

in both cases. The solid phase approach was found to give higher recoveries. When salt was added to the water sample prior to direct SFE, it was found to have no effect on extraction recovery and actually increased the carry-over of water. Typical direct SFE times of 100 minutes were required to recover 50 - 70% of the analytes. Flow rate was not found to affect extraction recovery.

Shimoda et al. (1994) also published a recent study of the direct extraction of volatile compounds from water comparing gaseous, liquid and supercritical carbon dioxide as the solvent. Supercritical carbon dioxide was found to give quantitative recovery of the volatiles studied, and to remove the odour from a soy sauce sample. The extraction vessels used in both of these studies (Barnabas 1994, Shimoda 1994) will be described further in chapter three.

There has been recent interest in the direct extraction of inorganic compounds from water. Wang et al. (1994) have published an interesting study of the in-situ derivatization and SFE of various metals. Detection was accomplished by connecting the extraction system on-line to an atomic absorption spectrometer.

2.2 Supercritical Fluids

This section discusses the properties of supercritical fluids (SFs) which make them useful solvents for extraction procedures.

The pressure-temperature diagram of a substance shows the relationship of the vapour, liquid, and solid states of a substance as a function of temperature and pressure. A supercritical fluid is defined as a substance that is above its critical temperature and pressure (see figure 2.1). The critical point on this diagram is defined by the critical temperature and pressure. The critical temperature, T_c , is the temperature above which it is not possible to liquefy the vapour by increasing the pressure. The critical pressure, p_c is the pressure of the vapour at the critical temperature. The SF above this point can have a density and solvent power approaching that of a liquid, while the transport properties can resemble those of a gas. This region is labelled in figure 2.1, which gives a schematic phase diagram for carbon dioxide. The supercritical fluid region is defined as the area above and to the right of the critical point. The near-critical fluid (NCF) region is also important for certain applications, and is defined as the region where $T < T_c$, but $p > p_c$.

To define the region around the critical point that is of interest in SF extraction, it is useful to use the reduced temperature (T_r) and pressure (p_r) parameters. These are expressed as

$$T_r = T / T_c, \quad p_r = p / p_c.$$

Figure 2.1 Schematic phase diagram for carbon dioxide.

The critical temperatures and pressures for some compounds are given in table 2.2.

Table 2.2 Critical pressures and temperatures for various compounds.

Compound	p_c/atm	$T_c/^\circ\text{C}$
Methane	45.4	-82.6
Xenon	57.9	16.5
Carbon Dioxide	72.9	31.0
Nitrous Oxide	71.9	36.0
Water	218.3	374.1

The region where variation of temperature and pressure cause the most change in the fluid density is seen in figure 2.2 for carbon dioxide. It is in the range

$$0.9 < T_r < 1.2, \text{ and } 0.9 < p_r < 3.$$

Such large changes in the SF density allow for the solvent power of the SF to be varied. As the solvent power changes, so does the extent of the solubility of different analytes in the SF. This ability to control the solvent power is important in the process of extraction. The properties of SFs which favour their use as solvents are their high densities, which allow liquid-like solubilities, and their transport properties, viscosity and diffusion coefficient, which are between those of liquids and gases. Table 2.3 compares some of the relevant properties of SFs, liquids, and gases.

Figure 2.2 Plots of density as a function of reduced pressure for carbon dioxide in the critical region (adapted from Burk 1990).

Table 2.3 Order of magnitude comparison of physicochemical properties of supercritical fluids, liquids and gases.

property	Gas	SF	Liquid
density g mL ⁻¹	10 ⁻³	<1	1
viscosity kg m ⁻¹ s ⁻¹	10 ⁻⁵	10 ⁻⁴	10 ⁻³
diffusion coefficient m ² s ⁻¹	10 ⁻⁵	10 ⁻⁷	10 ⁻⁹

The viscosity of a fluid can be defined as that property which causes a fluid under stress to resist flow. The viscosity of a liquid generally decreases as temperature is increased, whereas the viscosity of a gas is generally independent of pressure at lower pressures, and increases with temperature (Geankoplis 1978). Figure 2.3 shows the viscosity of CO₂ at various temperatures as a function of pressure. CO₂ behaves like a normal gas below its critical pressure, while above p_c as shown on figure 2.3, viscosity increases. Also, above p_c carbon dioxide behaves like a liquid in that viscosity decreases as temperature is increased. Generally, the viscosities of SFs have values intermediate to liquids and gases, depending on the temperature and pressure considered. This means that one can expect improved mass transfer leading to more efficient extraction when using a SF solvent rather than a liquid one.

Figure 2.3 Viscosity as a function of pressure at various temperatures for carbon dioxide (adapted from Burk 1990).

Another property that gives SFs an advantage for use as extraction solvents is their diffusion coefficients. The diffusion coefficient is a measure of how fast the molecules move relative to each other, and is closely related to viscosity. SFs have diffusion coefficients that are intermediate between the diffusion coefficients of gases and liquids. The fact that SF diffusion coefficients are greater than those of liquids is one reason why extractions are generally faster when SFs are used as solvents. The diffusion coefficient for CO_2 is plotted as a function of pressure in figure 2.4 for two temperatures. As can be seen from the diagram, even at a temperature of 40°C , the diffusion coefficient for CO_2 is an order of magnitude greater than the values observed for liquids.

Yet another advantage of SFs which applies especially to extraction from solids is that they can completely wet a solid surface. For example, when a drop of a liquid is placed on a solid surface, the drop will spread out along the surface at an angle which depends on the surface tension of the interfaces involved. In many cases, there can be difficulties in having the liquid wet the solid surface. For a SF, there is no resistance to spreading of the SF along the surface, and the surface is completely "wetted" by the fluid. This may not have any implications for the extraction of contaminants from liquids, except in the case where the contaminants are adsorbed onto suspended solids. The point has also been made that there may be considerable energy savings in using SFs rather than conventional extraction techniques. Several studies have

Figure 2.4 Self-diffusion coefficient for carbon dioxide as a function of pressure (adapted from Lee 1990).

evaluated SF extraction in terms of cost/benefit analysis (Lenhard 1989, Knez, 1988).

The equation of state which describes the behaviour of an ideal gas is

$$pV_m = RT \quad 2.2$$

where V_m is the molar volume of an ideal gas, and R denotes the universal gas constant, $8.314 \text{ J K}^{-1}\text{mol}^{-1}$. This ideal equation of state is obeyed only at low densities. The compressibility factor, Z , is often used to express the deviation from ideality, where

$$Z(p,T) = pV_m/RT \quad 2.3$$

For an ideal gas the value of Z would be 1.0 for all temperatures and pressures. The SF-Solver™ program developed by Isco Inc. uses the ideas developed by Pitzer (1955a & 1955b) to evaluate the compressibility factor in terms of the acentric factor, ω , which takes into account the non-sphericity of the molecule. The acentric factor can be determined from the vapour pressure, critical temperature, and critical pressure.

2.3 Carbon dioxide

2.3.1 Properties

Carbon dioxide has been used as a solvent for extraction in both the liquid and supercritical form. As seen in figure 2.1, liquid CO₂ exists from -55 °C to 31 °C and between 5.1 and 72.8 atm. The critical point of CO₂ is 31 °C and 72.8 atm. The gaseous form of CO₂ at ambient pressure has such a low density that it has essentially no solvent power. Any solute which remains in the gaseous phase after expansion of CO₂ does so simply due to its vapour pressure.

Supercritical carbon dioxide has been the solvent of choice for many extraction applications due to a variety of reasons. Carbon dioxide is non-toxic, non-flammable and environmentally safe, as well as having all of the other advantages of supercritical fluids discussed in section 2.2. It also has a relatively low critical temperature and pressure, which makes it favorable because more extreme conditions of pressure and temperature may be difficult to maintain. CO₂ is easily separated from solutes because of its extreme volatility at ambient conditions. It is inexpensive. It has favorable transport properties due to its relatively low viscosity and large diffusion coefficients.

Other SFs often have disadvantages due to unfavorable physical properties, cost, and reactivity. The properties of supercritical CO₂ can be

compared with those of liquid solvents under ambient conditions as shown in table 2.4. The CO₂ properties were determined at 55°C and 200 atm (Lee 1990).

Table 2.4 Physical property comparison of supercritical carbon dioxide with liquid solvents at 25°C (Lee 1990)

Parameter	CO ₂ 200 atm 55°C	Hexane	Dichloro- methane	Methanol
density g mL ⁻¹	0.746	0.660	1.326	0.791
kinematic viscosity m ² s ⁻¹ x10 ⁷	1.00	4.45	3.09	6.91
diffusivity of benzoic acid m ² s ⁻¹ x10 ⁹	6.0	4.0	2.9	1.8
$\frac{p_{v,sat} \text{ solvent}}{p_{v,sat} \text{ phenol}}$	1.4×10^5	4.2×10^2	1.2×10^3	3.6×10^2

It can be seen that the CO₂ density is comparable to those of common liquid solvents, while its kinematic viscosity (ratio of viscosity to density) is lower, and the diffusivity of benzoic acid is higher. The final parameter,

$p_{v,sat}^{solvent}/p_{v,sat}^{phenol}$, is the ratio of solvent and phenol vapour pressure at ambient conditions. The large value of $p_{v,sat}^{solvent}/p_{v,sat}^{phenol}$ for CO_2 compared to the other common solvents emphasizes the ease with which CO_2 can be removed from the solute after extraction by simple decompression.

One of the first extensive studies of the solvent properties of liquefied gases was reported by Francis (1954). He determined the phase diagrams of several ternary systems involving liquid CO_2 and both organic and inorganic compounds. The suitability of liquid CO_2 along with various co-solvents for the purposes of solvent extraction was indirectly evaluated by studying the CO_2 systems at or near room temperature. A large body of work was accumulated by Hyatt (1984) in an attempt to classify CO_2 relative to conventional organic solvents. Solubilities of various organics were given, and the properties of CO_2 that favours its use as a solvent are summarized. Hyatt concluded that both liquid and SF CO_2 behave similarly to a hydrocarbon solvent with very low polarizability (ie. hexane). Solute diffusion coefficients in SFs generally have values between those found in gaseous and liquid solvents. It has been noted that solute diffusion coefficients tend to follow the same trends as the self-diffusion coefficients of the extracting fluids. In general, the self-diffusion coefficient for supercritical CO_2 is greater than that for liquid CO_2 (see table 2.3). This suggests that the solute mass transfer rates in supercritical CO_2 will be much higher than that for liquid CO_2 ; this has been experimentally verified for

certain compounds such as naphthalene (Lee, 1990). Therefore, supercritical CO₂ would be a preferred extraction solvent than liquid CO₂.

The main advantage of supercritical CO₂ was noted to be the variation in its solvating power through changes in density (Hyatt 1984). It was found that the general solvent behaviour of supercritical CO₂ is very much the same as CO₂ liquid. Materials completely insoluble in CO₂ liquid are not expected to be soluble in supercritical CO₂. Table 2.5 shows the solubility in weight percent of selected compounds in liquid carbon dioxide.

Table 2.5 Solubility of selected compounds in liquid carbon dioxide.

Compound	Solubility	Reference
Benzene	miscible	Francis 1954
Water	0.1 weight%	Francis 1954
Anthracene	<0.02 weight %	Hyatt 1984
Dicarboxylic Acids	insoluble	Schultz 1970

The solubilities of several organic compounds in both liquid and supercritical CO₂ have also been studied by Dandge et al. (1985) in an attempt to generalize the relationship between solute structure and solubility in carbon dioxide. A number of structural properties were determined to have an effect on the solubility, and generally it was seen that as the molecular mass of

members of a homologous or oligomeric series increases, a decrease in the solubility of the solute in the supercritical CO₂ is observed. A general rule is that large polar compounds (molecular weight > 200 Dalton) will most likely have negligible solubility in supercritical CO₂. This means that it is possible to separate nonpolar from polar solutes, and low molecular weight from high molecular weight solutes, by supercritical CO₂ extraction.

Stahl et al. (1978) suggested a number of generalizations regarding pure supercritical CO₂ extraction:

- at pressure ranges of 70-100 atm, low polarity hydrocarbons and lipophilic organic compounds were extracted;
- polar functional groups on molecules made the extraction more difficult;
- phenols with one carboxyl and more than two hydroxyl groups were not able to be extracted;
- more highly polar compounds such as sugars were not extracted at all up to 400 atm.

A number of researchers have studied the solubility of a wide range of solutes in modified SF carbon dioxide. The effect of modifiers (also called co-solvents) on solubilities can be difficult to predict. Generally, the addition of a polar modifier such as methanol will increase the solubility of polar solutes. It may also increase the solubility of nonpolar solutes due to dipole-induced dipole interactions. However, as this project does not involve the use of modifiers,

they will not be discussed further in this document. Interested readers may refer to the paper by Levy et al. (1993) for further information on the subject.

2.3.2 The Carbon Dioxide and Water System

When considering the extraction of compounds from water with supercritical CO₂, it is important to understand how the two fluids interact. The two compounds have a mutual solubility which must be considered. There have been numerous studies of the water-CO₂ system which have characterized the mutual solubilities and phase compositions as a function of pressure.

Wiebe and Gaddy (1941) studied the binary system CO₂-water at various temperatures and pressures. The extent of the mutual solubilities of the two phases was investigated. This study was extended by King et al. (1992) to also determine the phase densities. Figures 2.5 illustrates how the solubility (expressed in mole fraction x 1000) of water in liquid and supercritical carbon dioxide changes with pressure and temperature. The amount of water dissolved increases as pressure and temperature are increased. The solubility according to figure 2.5 of water in CO₂ at the experimental conditions used in this study is less than 0.6 mole %. The amount of water carried out of the extraction vessel during an extraction would be expected to be even less than this amount. Figure 2.6 shows how the solubility of liquid CO₂ in water increases as pressure is increased and decreases as temperature is increased.

Figure 2.5 Solubility (mole fraction) of water in carbon dioxide as a function of temperature (data from King 1992).

Figure 2.6 Solubility (mole fraction) of liquid carbon dioxide in water as a function of temperature (data from King 1992).

These observations for liquid CO₂ exhibit the same trend observed for supercritical CO₂ by Weibe and Gaddy (1941). The solubility of CO₂ in water is small, and therefore is not expected to affect the water matrix during an extraction.

An extensive review of previous work on the CO₂-water system was carried out by Takenouchi and Kennedy (1964). Their work also included further study on this system at higher temperatures and pressures, as their primary interest was to obtain information on the behaviour of the CO₂-water system at extreme conditions, such as those of interest in geochemical studies. Their studies included pressures of up to 3000 atm and a temperature range of 110-350°C; these are above those of interest for the process of supercritical extraction. The critical temperature of this binary system (31 mol% CO₂) was determined to be 265°C; below this complete miscibility of the two phases will not be seen. The critical pressure was determined to be 2122 atm.

Hough et al. (1959) have studied the interfacial tension between water and CO₂ using a high pressure pendant drop interfacial tension apparatus. The system was studied for a pressure range between 1 and 1000 atm, and temperatures from 38 to 138 °C. The variation of interfacial tension with pressure is shown in figure 2.7 for temperatures of 38 and 71°C. In both cases the interfacial tension reaches a minimum by 125 atm, and there is no further change with increasing pressure. The values of the interfacial tension between

Figure 2.7 The interfacial tension of the water-carbon dioxide system at 38 and 71 °C as a function of pressure (adapted from Hough 1959).

water and CO₂ for specific experimental conditions affect the efficiency of the mass transfer between the two phases. More efficient extraction will be expected when the interfacial tension is smaller.

2.3.3 Partition Coefficients

Solubility data for a pure analyte in a SF may have limited use when extraction of the analyte is being done from an aqueous matrix, or when there is more than one analyte being extracted. As a result, interest has been focussed on determining experimental values for the equilibrium partition coefficient for various analytes between a SF and water. This discussion will present some of these results, where supercritical carbon dioxide is the fluid. The partition coefficient, K_p , is then expressed as the ratio of the concentrations in the two phases,

$$K_p = C_{SF} / C_{aq} \quad 2.4$$

and can be approximated as the ratio of the solubilities where data are available:

$$K_p \approx S_{SF} / S_{aq} \quad 2.5$$

Ghonasgi et al. (1991a, 1991b, 1991c) have studied single solute and multi-solute partition coefficients between water and supercritical CO₂ for a range of experimental conditions. In their studies aqueous solutions of the desired analyte(s) were fed into a batch type extraction apparatus along with a known volume of supercritical carbon dioxide. The components were then mixed until equilibrium was reached, the phases were allowed to separate, and both the aqueous and fluid phase were sampled. The partition coefficient was determined as the ratio of the mole fraction of the analyte in the supercritical carbon dioxide phase to the mole fraction of the analyte in the aqueous phase. The analytes studied were phenol, *m*-cresol, *p*-chlorophenol, and benzene. Results obtained for phenol agreed with earlier studies by Roop and Akgerman (1989b). The data obtained for *p*-chlorophenol shown in table 2.6 illustrate the changes observed in partitioning as experimental conditions were varied.

Table 2.6 Experimental partition coefficient (K_p) for *p*-chlorophenol between supercritical carbon dioxide and water (data from Ghonasgi 1991b)

pressure atm	K_p at 40 °C	density g mL ⁻¹	K_p at 50 °C	density g mL ⁻¹
95	1.94	0.55	0.44	0.34
109	3.00	0.69	0.68	0.50
122	3.47	0.74	1.32	0.60
136	4.96	0.77	2.00	0.67
150	5.24	0.79	2.40	0.71
163	5.38	0.81	2.75	0.73

The interesting trend observed from these data is that the amount of *p*-chlorophenol in the carbon dioxide phase increases as pressure is increased, and decreases as temperature is increased. K_p follows the same trend as density of the supercritical CO₂, but density alone does not govern the partition coefficient. The amount of analyte in each phase is controlled by two competing effects, the analyte interaction with the aqueous phase and the analyte interaction with the carbon dioxide phase. For other analytes studied by Ghonasgi et al. (1991b), partition coefficients followed the same trend as pure analyte solubility did with changes in temperature and pressure. This suggests that the strength of the interaction between the analyte and supercritical carbon dioxide is the dominant factor controlling the partition coefficient data for the analytes studied.

Hedrick et al. (1992) investigated the effect of pressure, temperature and density of CO₂ on the partition coefficient of phenol. The initial concentration of phenol in the water was 200 ppm, and K_p was determined by sampling the CO₂ phase after the system came to equilibrium. They also observed that K_p increases as pressure is increased and decreases as temperature is increased. In other experiments, density was held constant and temperature increased. At each temperature studied until approximately 60°C, K_p decreased. As temperature was increased past 60°C, however, K_p began to increase. The initial decrease (below 60°C) was attributed to the greater solubility of phenol in

water, which around 60°C must be overcome by the increased solubility in CO₂ due to a rise in the analyte vapour pressure. More data in this temperature region would help to further illustrate this effect.

Research into the influence of additional analytes on the values of the single solute distribution coefficients has also been done (Gupta 1991). This study showed that for the analytes chosen (phenol, *m*-cresol, *p*-chlorophenol, benzene) there was no difference between the experimental distribution coefficient for the analyte determined individually or in a mixture. Yeo and Akgerman (1990) did a similar multi-solute study with different analytes (benzene, toluene, naphthalene and parathion). In this study it was found that the distribution coefficient for both naphthalene and parathion increased on going from a single solute to a multi-solute system. Ghonasgi et al. (1991c) suggested that in order for a solute to favourably influence another's solubility there would have to be both strong solute-solute interactions, and different single solute distribution coefficients, which could explain the results of Yeo and Akgerman (1990). There has been some work done on determining the partitioning of an analyte in a three phase system consisting of supercritical carbon dioxide, water and a solid. Yeo and Akgerman (1993) used phenol and naphthalene as analytes and activated carbon, alumina and soil as solids. Their preliminary results indicate that the main parameters important when extracting analytes from a water-solid mixture with a supercritical fluid are the affinity of

the analyte for water and the solid. The nature of the solid and the analyte both affected the analyte's partitioning into the supercritical phase. Analytes with a high affinity for the solid phase and/or a high solubility in water are more difficult to extract.

2.4 Extraction Apparatus

In order to understand the types of apparatus needed to perform direct supercritical fluid extractions, it is helpful to first examine apparatus used for liquid-liquid extractions and then to decide what modifications are necessary in order to perform the same types of extractions with SFs.

In liquid-liquid extraction, the two phases must be brought into intimate contact with a high degree of turbulence in order to obtain high mass-transfer rates. This may be done as in a one-stage process, known as static or batch extraction. In the case where an SF is involved, the two phases are combined, pressurized and vigorously mixed. They are then allowed to reach equilibrium and separate. This type of system has been used to obtain partition coefficients by a number of researchers as discussed in section 2.3.3. The fact that the solvent amount is fixed means that incomplete extractions are a possibility.

An alternative to the static process is dynamic extraction. In this case the equilibrium contact is not single-stage, as the solvent is allowed to flow

through the extraction vessel. As the solvent is being continuously renewed, these extractions are generally more efficient than batch mode extractions. The solvent used generally flows into the extraction vessel through a porous frit. The frit produces fine droplets of the solvent which then flow through the sample solution. The design of the solvent inlet system affects the solvent bubble size and its dispersion through the sample. For efficient extraction, there must be an intimate interdispersion of the two phases. The finer this dispersion is, the greater the interfacial area, and therefore the faster the mass transfer of analyte from the sample to the SF extraction solvent. The rate of rise of the solvent droplets is controlled by the rate of stirring, the density difference between the sample and SF phases, the continuous phase viscosity, and the droplet size. A third type of extraction involves a counter-current flow apparatus. In this system, both the sample and the solvent are passed through the extraction vessel in opposite directions.

When extracting from aqueous samples, the configuration of the extraction vessel is not always straightforward. The extraction vessel design must be optimized to improve extraction efficiency. The main concern is to keep the sample in the extraction vessel and minimize the removal of water. Hedrick and Taylor (1989) modified a standard extraction vessel for use in SF extractions from aqueous samples. The vessel is a tube sealed at each end with a length of narrow bore tubing extending almost the length of the vessel

from each end. The SF is bubbled into the aqueous phase through one tube, rises, and collects at the top of the extraction vessel. The SF exits the cell through the second tube which is above the level of the liquid in the vessel. A diagram of this flow through type extraction vessel is shown in figure 2.8a. This vessel was designed to reduce the amount of water that would exit with the SF. One other way of minimizing the amount of water exiting the extraction vessel with the solvent was the method described by Thiebaut et al. (1989), and involved placing a phase separator after the extraction vessel, which removed any aqueous phase from the fluid before depressurization.

One of the most important parameters relating to apparatus design is the method of introduction of the SF into the extraction vessel. Figure 2.8 illustrates two extraction vessels which have been designed specifically for the direct extraction of liquid samples. In figure 2.8a, the SF inlet is simply a 1/16 inch stainless steel tube, and the vessel has an internal volume of 6 mL which can accommodate a 3 mL aqueous sample (Hedrick 1989). In figure 2.8b, the SF inlet is a liquid chromatography solvent filter. The filter is a frit type, which does not have a specific hole size, simply an average porosity (Barnabas 1994). The internal volume of the vessel is 50 mL, and the sample size used was 45 mL. A frit type inlet similar to that of SF extraction vessels for solids will not work since the optimum frit porosity for extraction purposes will not hold the water sample in the extraction vessel, as has been tested in our laboratory. There is

Figure 2.8 Schematic diagrams of two extraction vessels designed for liquid samples (a from Hedrick 1989, b from Barnabas 1994).

thus no assurance that contact between the two phases is taking place in the vessel, and there may be incomplete recovery of the sample after extraction has finished.

In order to understand SF extractions and predict their efficiency, data regarding their mass transfer behaviour are needed. Models which successfully predict the efficiency of SF extractions have yet to be developed. There have been studies, however, in which mathematical models of conventional extractions have been applied to SF systems with some degree of success. Lahiere et al. (1987a, b) have studied mass transfer in counter-current supercritical fluid extraction. Various types of liquid-liquid contacting devices were evaluated by using supercritical solvents. The systems studied were alcohol-water mixtures, and the solvent was supercritical carbon dioxide. A liquid-liquid mass transfer model was used to predict the efficiency of SF extractions. For an isopropanol-water solution the extraction efficiency was predicted to be 20% less than the actual, and for ethanol the efficiency was overpredicted by 40%. The failure of the model was attributed to inaccurate values of the distribution coefficients and interfacial tension. A later study by Bartolomeo et al. (1990) studied mass transfer in flow through systems for SFE of liquids. The extraction system was the same as the one described above. In this case, the system was evaluated using two theoretical models, one based on a liquid-liquid system, and the second based on a gas-liquid system. The

liquid-liquid model did not accurately predict the extraction results, and therefore was not considered applicable. The gas-liquid model was used in two forms, one rigorous and one simplified. Both gave reasonable results compared with experiment for an ethanol mixture, while for isopropanol, neither predicted accurate results. This was attributed to the more ideal behaviour of ethanol compared to isopropanol. The conclusion reached was that the model would need to have a better description of resistance to mass transfer in the gas phase.

CHAPTER THREE

APPARATUS

3.1 Experimental Extraction Apparatus

A schematic diagram of the total extraction system used in the present study is shown in figure 4.1 (page 64) and described in section 4.1 (page 63). The main components of the apparatus that required development during this work were the extraction vessel, and the methods of pressure release and trapping.

3.1.1 Extraction Vessels

3.1.1.1 First Extraction Vessel

Two types extraction vessels suitable for the extraction of liquid samples have been designed, built and used in the course of this project. The first extraction vessel (figure 3.1) has an internal volume of approximately 86 mL, and both the top and bottom end caps are removable. Replaceable teflon gaskets were used to provide a sealing surface between the main body of the extraction vessel and the end caps.

The supercritical CO₂ inlet is passed through a hole in the centre of the cap, and also through a 1/8 inch pipe - 1/8 inch swagelock union which has been welded to the inner side of the cap. The position of the inlet is fixed by tightening a 1/8 inch swagelock nut onto the union. The vessel outlet consists

Figure 3.1 Cross sectional schematic diagram of extraction vessel with an internal volume of 86 mL.

of a hole bored through the cap. A modified 1/16 inch pipe fitting into which a 1/8 inch stainless steel tube is welded is screwed into the outside of the cap. A viton o-ring under a spacer attached to the fitting ensures that the system is sealed and prevents leaking. The number of seals on this extraction vessel made it time consuming to use, and this was taken into consideration when designing the second extraction vessel..

3.1.1.2 Second Extraction Vessel

The second extraction vessel (figure 3.2) has an internal volume of 30 mL, and is suitable for a maximum 25 mL volume water sample. It is similar in design to the first one, but with a few improvements. There is only a single cap on the top of the vessel to decrease the number of seals required. The main body of the vessel below the cap is a single unit, and the sealing mechanism is the same as in the previous vessel. The CO₂ inlet is permanently attached to the vessel cap, as is the inlet and outlet tubing. The fluid outlet is a hole in the cap to which on the outside is welded to a short piece of 1/4 inch tubing (included in the volume). It is easier to use than the first vessel, because the water sample can be placed in the extraction vessel through the outlet. The machine schematic diagrams of this extraction vessel design are given in Appendix I. Two versions of this type of extraction vessel were used in this study, with the only difference between them being the size and uniformity of holes in the CO₂ inlet (as discussed in 3.1.1.3). The extraction vessels were

Figure 3.2 Cross sectional schematic diagram of extraction vessel with an internal volume of 30 mL.

constructed by the Science and Technology Centre at Carleton University.

3.1.1.3 Fluid Inlet

For this work, a suitable type of inlet was determined to be a hollow disk with small holes drilled into it, that could be positioned near the bottom of the extraction vessel (see figures 3.1 and 3.2). The CO₂ enters the disk at the centre through a narrow bore 1/8 inch tube which passes through the top of the extraction vessel. The fluid can then be forced out the holes of the hollow disk into the extraction vessel, and the "drubbles" (droplets/bubbles) pass through the water sample. The supercritical CO₂ in the extraction vessel passing through the water sample was described as being in the form of "drubbles" (droplets or bubbles). This term is used throughout this thesis to describe supercritical CO₂ from the extraction vessel inlet passing through water.

Calculations were done to determine the effect of hole size on the pressure drop across the disk using the Hagen-Poiseuille equation (Geankoplis 1978),

$$\Delta p = (32 \mu / D_o^2) (\Delta L \ v) \quad 3.1$$

where μ is the fluid viscosity, D_o is the hole diameter, ΔL is the length of the hole, and v is the average flow velocity of the fluid in the hole. The Hagen-Poiseuille equation was developed for laminar flow in a cylindrical pipe. Since

the holes have a small length compared to their diameter, the Hagen-Poiseuille equation will not accurately determine the pressure drop, but should give the correct order of magnitude. The pressure drop was determined to be in the order of 10^{-6} atm for 0.30 mm hole diameters (see Appendix II.A for detailed calculation), which is negligible. Since the value determined is small, more elaborate calculations were not pursued. An example of such calculations is for flow through perforated plates, page 5-37 of Perry and Green (1984). A significant pressure drop is not desirable because this would cause the SF drubbles to expand as they entered the extraction vessel.

Models of the SF "drubbler" inlet system were constructed out of copper, and then used to determine the optimum number and placement of holes on the disk. The "drubblers" were tested by passing both a liquid solvent (hexane), and a gas (air or carbon dioxide) through them while they were immersed in water. This was done to observe the differences between the two fluids as properties of the drubbler were changed. This was a useful exercise, since it could be assumed that the SF behaviour will be intermediate between a liquid and a gas, and it is not possible to observe the SF passing through water in the pressurized extraction cell. Hexane has a density and other properties close to those of the supercritical CO_2 used in the extraction experiments at pressures of the order of hundreds of atmospheres. The behaviour of supercritical CO_2 can be expected to be between that of hexane and that of either gas (air or carbon dioxide).

As the drubbler holes are made smaller in size, more drubbles will be produced at any one time period. This increases the surface volume available for contact between the two phases. The disadvantage is that the smaller the drubbler hole size, the larger the pressure difference will be across the hole. This will actually cause the drubble size to increase due to expansion upon formation, resulting in the same size drubbles as could be formed from a larger hole with less of a pressure drop. The other disadvantage as hole size is decreased is that it becomes more difficult to reproducibly manufacture. If one hole is larger than the rest, drubbles will be formed preferentially at that hole and the advantages of smaller holes are greatly reduced.

The drubbler holes specified in the final design had a diameter of 0.30 mm. Upon examination after manufacture, it was determined that the drubblers constructed for each vessel were different. The 86 mL vessel had drubbler holes with diameter 0.46 mm; the first 30 mL vessel had a wide range of drubbler holes sizes with the average being 0.46 mm; the second 30 mL vessel had drubbler holes with diameter 0.30 mm. The disk itself in each case was 5.5 mm high, and had a diameter of 19.7 mm. The top of the disk had three concentric rings of 20, 12, and 6 holes, with 8 holes on the bottom of the disk (in a ring pattern for extraction vessel one, star pattern for extraction vessel two; as determined after manufacture). Since the bottom of the inlet disk was in contact with the bottom of the extraction vessel when sealed, any differences between the holes in the bottom of the disk were assumed to have a negligible

Figure 3.3 Top view of supercritical CO₂ inlet (drubbler).

affect. A top view of the drubbler is shown above in figure 3.3.

Further visual studies with hexane and the drubbler were done after SFE method was developed. In these studies, the flow rate was maintained between 0.5 - 1.0 mL min⁻¹, which is in the range of flow rates used in the SF experiments. These studies showed that the following factors are important in the determination of extraction efficiency:

- a. At flow rates between 0.5 - 1.0 mL min⁻¹ the hexane (and presumably the supercritical CO₂) comes through in discrete drubbles, rising at rates which

make accurate determination of rise speed by ordinary photography impossible.

- b. The water volume is not expanded to a significant extent due to the presence of the hexane.
- c. Using the drubbler with hole sizes of 0.3 and 0.46 mm, the range in sizes of the drubbles formed are of the order of 0.5 - 5 mm in diameter (determined from photographs).
- d. At flow rates less than 0.5 mL min^{-1} , the drubbles appear to come from one particular hole.
- e. The drubbles at times crawled up the stainless steel stem of the drubbler, especially when released from holes in close proximity to the stem.

3.1.2 Pressure Release

Once the SF extraction is complete, the extracted materials need to be separated from the CO_2 . The most common method of doing this involves reducing the density of the fluid, which allows the extracted components to precipitate out. This can be done by either increasing the temperature or decreasing the pressure. The pressure decrease method is the most widely used, partially because the temperature cycling method can cause stress on the extraction vessel after repeated use.

Depressurization of the fluid can be accomplished by using a narrow-bore tube connected at one end to the extraction vessel, with the other end at

ambient conditions. The common choice of narrow-bore tubing used for SFE pressure reduction is silica capillary tubing. Narrow-bore tubing made of other materials in dimensions suitable for SFE pressure reduction is not commercially available. The advantage of using a silica capillary is that many sizes are commercially available, and the flow rate can be pre-determined by appropriate choice of the length and inside diameter of the capillary. A disadvantage is that the pressure decrease is more gradual, and the capillary system can get plugged by solute precipitating before exiting the capillary (Burk, 1990).

Silica capillary tubing is commonly used as a restrictor when SFE from solid matrices is being performed. This becomes more difficult to use as a restrictor when water is present in the samples because the water tends to plug the capillary as it freezes due to adiabatic cooling of the CO₂. Breakage occurs due to hydrolysis of the silica. For this reason silica capillary tubing was not used as a restrictor with the aqueous extraction system constructed for the current research described here. There are several designs of restrictors incorporated into existing commercial extraction apparatus. The advantages of some of these have been discussed (Ashraf-Khorassani 1992, Porter 1992). As these restrictors are not easily adaptable to other extraction systems, use of any existing commercial restrictor was not chosen for the apparatus designed in the current research.

The type of restrictor used in this study was a 1/16 inch stainless steel tube which was crimped near one end. The crimping was accomplished by

using a device designed to pinch tubing gradually by adjusting a micrometer. In this manner, reproducible ($\pm 10\%$ of flow rate) restrictors could be made. One disadvantage to using this type of restrictor is that the pressure reduction occurs over a short distance. The flowrate is therefore dependent on the pressure of the system because the restrictor has fixed dimensions. The rapid depressurization causes adiabatic cooling of the CO_2 , which may lead to plugging of the restrictor due to freezing of residual water or CO_2 . The restrictor must therefore be heated. The restrictors can also become partially plugged during use due to contaminants in the system, so they must also be visually inspected often.

3.1.3 Trapping

There are several ways of collecting the extracted components. The simplest involves collecting them in a small amount of liquid solvent. This is best accomplished when the restrictor is a piece of silica capillary tubing. Another collection method involves trapping of the CO_2 and analyte in cooled vessels (either one single vessel or a series), followed by evaporation of the CO_2 . Methods in which analyte trapping is done by simply allowing the CO_2 to flow an empty vessel can experience analyte loss due to aerosol formation. A third extract recovery method consists of analyte sorption from the SF onto a solid phase, which is then extracted by conventional means.

Another way of direct extract collection combined directly with analysis

involves coupling the pressure let-down device with a gas chromatograph. The advantages of on-line sample collection are that any intermediate handling of the sample between extraction and analysis is eliminated. The extracted analytes are therefore quantitatively transferred onto the chromatographic column. Other advantages include speed of the method, low detection limits, and possible cost savings. The disadvantage of this approach is that because the entire extract is injected onto the column, only a single determination per sample can be performed.

There were three types of trapping system tested in the current research, each of which is illustrated in figure 3.4. Figure 3.4a shows a long pyrex tube which contains solvent and is heated at the bottom to reduce restrictor plugging, and cooled at the top to eliminate analyte loss. The depressurization from the restrictor was found to be too violent, and the fluid flow was erratic with this system. Figure 3.4b illustrates a pyrex tube with a heater around the restrictor tip, and a coolant bath farther along the trap. This design was adapted from Burk (1990). The trap was initially cooled to 0°C with an ice-water bath, but the residence time of the gaseous carbon dioxide stream was not found to be long enough to allow sufficient recovery of the analytes at the fluid flows desired to be used in this study. When a colder bath was used (acetone/dry ice, -76°C; and chloroform/liquid nitrogen, -60°C) problems with freezing of carbon dioxide in the trap occurred which caused erratic flow over the duration of the extraction. The other problem with this trap design involved the difficulty

Figure 3.4 Schematic diagrams of trapping systems used in this study.

connecting the restrictor to the pyrex tube and preventing leaks at the flow rates used in this work (0.5 - 1.3 mL supercritical CO₂ min⁻¹). The third trap, illustrated in figure 3.4c, was a 4 ft length of 1/4 inch stainless steel tubing flattened and formed into a coil. This trapping system was used in all subsequent experiments. The restrictor was connected to the heated end of the trap via a 1/16 - 1/4 inch union, constructed to allow insertion of the 1/16 inch tube 3 inches into the 1/4 inch tube. The temperature of the heated external portion of the trap had to be at least 160°C to prevent restrictor plugging. The internal volume of the trap was 5 mL. The flattened area of the trap was placed in an ice-water bath. Flow of the expanded CO₂ was measured by connecting a soap bubble flow meter to the open end of the trap. For each new analyte studied, the trapping efficiency was determined by attaching a tube filled with a suitable solid phase to the end of the stainless steel trap to collect any analytes passing through the first system.

3.2 Model Calculations

The extraction process can be thought of as being comprised of three parts: (i) the formation of drubbles, (ii) the rise of drubbles up the column of water, and (iii) the transfer during this rise of contaminants from the water to the SF drubbles. An idealized model of the formation of drops/bubbles from holes can be developed from Tate's law (Soo 1967). This model assumes that the buoyant force equals the surface force at the point where the drubble breaks

free. The hole is assumed to be perfectly cylindrical and surface forces between the solid and the drubble are neglected. Under these conditions,

$$D = \{(6 D_o \sigma) / (\Delta\rho g)\}^{1/3} \quad 3.2$$

Here D is the drubble diameter, D_o the hole diameter, σ the interfacial tension between the drubble fluid and the water, $\Delta\rho$ the difference in density between the fluid and the water, and g the acceleration due to gravity. Tate's law predicts drubbles of a diameter of 3.4 mm from holes of diameter 0.3 mm under experimental conditions of 40°C, 300 atm, if the σ for water - supercritical CO₂ is 22 dyne cm⁻¹ as extrapolated from figure 2.7 (see Appendix II.B for detailed calculation). This value for drubble diameter is in the range of the visual observations of hexane rising in water through 0.3 mm and 0.46 mm holes discussed in 3.1.1.3.

The simplest model for estimating the rate of rise of drubbles is Stokes' law. It assumes spherical particles moving slowly enough to produce laminar flow. The terminal steady velocity u (or rate of rise of drubbles) is then given as (Geankoplis 1978),

$$u = \{ (4 g D \Delta\rho) / (3 \rho C) \}^{1/2} = (g D^2 \Delta\rho) / (18 \mu) \quad 3.3$$

Here C is the drag coefficient, which for laminar flow equals $24/N_{Re}$, where N_{Re}

is the Reynolds number for spheres in motion, given as $N_{Re} = (D u \rho)/\mu$, where μ is the viscosity of the water, and ρ is the density of the water. The rate of rise of supercritical CO_2 drubbles of diameter 3.4 mm, for the above experimental conditions predicted by equation 3.3 is 0.95 m s^{-1} (see Appendix II.C). For such a case, N_{Re} is in the order of 4900, indicating turbulent flow exists around the drubble, which makes the use of equation 3.3 inappropriate. Three empirical correction methods (Perry 1984, Griskey 1979) give values for u of approximately 0.10 m s^{-1} (see Appendix II.D). As the drubbles rise, they encounter water in which contaminants are not locally depleted. Turbulent flow is nevertheless advantageous, as the mass transport across the water - drubble surface is enhanced by it. However, a rapid rise decreases the contact time between the drubble and the water. The extraction effectiveness is to a first approximation (for constant total SF volume) independent of flow rate. An increase in the flow rate increases the rate of formation of the drubbles but does not alter the size of the drubbles or their rate of rise. The total number of drubbles passing through the aqueous phase is independent of flow rate. Thus the surface area and time of contact remain the same. These are two factors which strongly influence the rate of mass transport of the contaminant from the water to the carbon dioxide.

An interesting result is obtained if equations 3.2 and 3.3 are assumed valid. The time and surface area of contact between a drubble and the water is governed by the drubble diameter, which to a first approximation is given by

equation 3.2. The diameter governs the rate of drubble rise (equation 3.3), its surface area, its volume, and the rate of drubble formation at constant flow. At a higher CO₂ density (lower $\Delta\rho$), the diameter will be greater. The net result of applying these two equations is that the effectiveness of the extraction is predicted to be independent of CO₂ density for constant total CO₂ volume. This is a surprising result of a first approximation only, as variations in the mass transfer and the partition coefficient are not considered in this simplistic model.

The rate of mass transfer (N) of PCP between water and supercritical CO₂ drubbles can be estimated from the following relationship (Geankoplis 1978):

$$N = k_c \Delta C_{PCP} A_S \quad 3.4$$

where k_c is the mass transfer coefficient, ΔC_{PCP} is the change in the concentration of PCP between the bulk solution and the interface ($C_{PCP, aq} - C_{PCP, surface}$), and A_S is the total surface area available for mass transfer. When considering the initial rate of mass transfer to fresh drops of SF, the ΔC_{PCP} term is simply reduced to $C_{PCP, aq}$, the initial concentration of PCP in the aqueous phase.

In order to estimate the initial rate of mass transfer for this extraction system, it is necessary to use an empirical relationship to evaluate the mass transfer coefficient, k_c , such as the following derived from expressions for

moving drops (Geankoplis 1978),

$$k_c = 1.13 [u (D_{AB} / D)]^{1/2} \quad 3.5$$

where u is the rise rate of drubbles (equation 3.3) corrected for turbulent flow, D_{AB} is the diffusion rate of PCP through water, and D is the diameter of a drubble. D_{AB} can be expected to be in the order of that for benzoic acid in water, $1.0 \times 10^{-9} \text{ m s}^{-1}$ (Geankoplis 1978), due to their similar structures since D_{AB} depends on the cross-sectional area of the molecule. The total area available for mass transfer, A_s , can be determined from the following relationship,

$$A_s = (Q/V) (h/u) A \quad 3.6$$

where Q is the fluid flow rate, V is the drubble volume, h is the height of the water column, u is the drubble rise rate and A is the drubble area. The Q/V term represents the rate of drubble formation, while the h/u factor represents the contact time between the two phases.

If equations 3.4, 3.5 and 3.6 are combined, the estimated initial rate of mass transport from water to supercritical CO_2 is $1.0 \times 10^{-12} \text{ mol s}^{-1}$ for an extraction temperature and pressure of 40°C and 300 atm , supercritical CO_2 flowrate of 1 mL min^{-1} , and initial PCP concentration of 100 ppb (see Appendix

II.E for detailed calculation). This would indicate that for a 20 mL water sample extracted using the stated conditions one could expect approximately 25% extraction in 20 min, if the previous relationships hold. This model also assumes that uniform drubbles are being formed at all holes on the surface of the inlet. The change in ΔC_{PCP} over time was not considered. Other parameters are of course operative, for example the mass transport from water to supercritical CO₂ should be greater at higher density due to a more favourable partition coefficient. However, as density decreases, the diffusivity in the supercritical fluid increases, enhancing mass transport. The diffusivity of the analytes in the SF drubbles is about ten times greater than in liquid drops.

CHAPTER FOUR

EXPERIMENTAL

4.1 Extraction System and General Procedure

A schematic diagram of the extraction system used in this study is shown in figure 4.1. Liquid carbon dioxide (Liquid Carbonic 99.5% purity) was obtained through a dip tube and pumped to the desired pressure by a piston pump (Milton Roy model 92014903). A stainless steel frit filter (Nupro 15 micron) was placed in-line after the CO₂ tank to prevent any particulate matter from reaching the pump head. A heat exchanger was attached to the pump head, and a 0°C glycol solution was passed through it to prevent vaporization of the CO₂ in the pump head. The pulse dampener was simply a 1 m length of coiled flattened 1/8 inch outer diameter tubing, but it was not found to be necessary due to the large size of the extraction vessels. Valves (Autoclave Engineers 316SS SW2081) were used to isolate the extraction vessel after an extraction so that the sample could be retained. The extraction vessel, restrictor and trapping system are described in sections 3.1.1, 3.1.2, and 3.1.3 respectively. The extraction system was constructed by using high pressure stainless steel tubing and swagelock fittings pressure-rated to 10 000 psi. The tubing before valve one was 1/8 inch outer diameter, and from then on was 1/16 inch outer diameter. A minimum of 0.5 m length of tubing was immersed in the thermostatted water bath along with the extraction vessel. This was enough to

Figure 4.1 Schematic of extraction apparatus.

allow the CO₂ to come to thermal equilibrium before reaching the extraction vessel. The pressure gauge (Span Instruments 0-6000 psi) was connected in-line.

After spiking of the water sample, it was placed into the extraction vessel which was then sealed. The extraction vessel was then placed in the water bath, and attached to the extraction system. Valve two was closed to isolate the system from the restrictor. Valve one was opened, the CO₂ tank was opened, and the pressure was recorded. The system was immediately inspected for any leaks.

The initial temperature of the water bath was always approximately 41°C. The extraction system at this temperature required 15-20 minutes to come to thermal equilibrium. During this time, the restrictor heater was turned on (160 - 200 °C) and the trap coolant put in place. During the last 5 minutes of thermal equilibration, the pump was turned on and the system was raised to the desired operating pressure. Once this was accomplished, the valve to the restrictor was opened, timing of extraction was begun, and the pump stroke backed off in order to keep the pressure constant. Flow of gaseous CO₂ was checked approximately every 2 minutes using a soap bubble flow meter, and the pressure recorded at the same time. In extractions where the trap setup did not allow the flow to be measured throughout the extraction (preliminary work only) the flow was measured at the beginning and end of each run. When the extraction time was complete, valve two followed by valve one was closed. The

restrictor heater was then turned off, and the trap disconnected from the restrictor once the flow of gas had stopped (< 1 min). The extraction was timed from the initial opening of valve two, until this valve was closed at the completion of a run. Typical extraction times were 30 - 60 minutes.

The trap(s) were rinsed with a small amount of solvent, which was identical to the solvent used to prepare the stock solution of analytes in use for that experiment. The rinsings were collected in pre-weighed vials, and weighed immediately afterward at room temperature. The actual volume of solvent collected was determined from the solvent density at room temperature (23 °C). The volume of solvent used for each rinsing typically was between 0.5 and 1.5 mL of methanol, and each trap was rinsed through twice into separate vials which were analyzed separately.

The flow rate of supercritical CO₂ in an extraction was determined from the flow rate and density of gaseous CO₂, and the density of supercritical CO₂. The supercritical CO₂ density was calculated using the SF-Solver™ program developed by Isco Inc. for the average temperature and pressure recorded during an extraction. This program was used to calculate all density data for the supercritical CO₂ used in the present work, as it gave comparable results to other methods of density determination.

4.2 Blank Extractions

Initial experiments were conducted by using different sizes of water samples with no analyte, to determine the maximum size of the water samples which could be used for an extraction. The water was Milli-Q distilled and deionized quality. The extraction procedure as described in 4.1 was followed, and attempts were made to trap any of the water matrix which was carried-over with the CO₂ extraction solvent. The results are discussed in section 5.1.

4.3 Sample Preparation and Analysis

Stock solutions of PCP were prepared in Optima grade methanol (Fisher) in glass volumetric flasks, and stored in the dark at 4 °C. The PCP solution volume used to spike water samples prior to extraction was normally in the order of 5 µL. The prepared water samples used in these experiments had PCP concentrations ranging from 86 to 200 ppb. These concentrations were chosen for the ease of analysis. All of the water samples used in this study were prepared from Milli-Q distilled and deionized water. The actual water samples used for extraction were prepared and mixed in a teflon bottle. The extracts (trap rinsings) were analyzed the same day as the extraction. Blank methanol vials were prepared at the same time as the extracts were collected, and handled in the same manner. Calibration standards were prepared while the extraction was being carried out. These standards were prepared from the same PCP solutions used to spike water samples, and were analyzed at the

same time as the extracts. Each extract or standard was analyzed three times using the analytical method described below. The average peak area was used to determine the amount of analyte recovered through a calibration curve.

A high pressure liquid chromatograph (HPLC) was used to analyze PCP. The samples were poured directly from the collection vials into autosampler vials. No further sample treatment was required prior to analysis. The instrument used was a Varian 9010/9050 with a Zorbax reverse phase column (4.6 mm by 25 cm RP-C₁₈) and an ultra-violet detector. The mobile phase was methanol (Fisher Optima) with 0.1% acetic acid, at a flow rate of 1.5 mL min⁻¹, and a pressure of 130 atm. The retention time of PCP was 2.8 minutes and the UV detection wavelength was 220 nm. A sample calibration curve for PCP is shown in figure 4.2.

4.4 Trapping Efficiency

It is very important to verify the efficiency of the trapping system before any optimization experiments are done for SFE. This is accomplished by spiking the analyte from the stock solution in to the empty extraction vessel, and determining that the analyte is quantitatively recovered by using the experimental conditions. The trapping system described in section 3.1.3 and illustrated in figure 3.4c was tested with a 3 µg spike of PCP to determine if the analyte trapping would be successful. The experimental conditions are given below in table 4.1. The results are presented and discussed in section 5.2.

Figure 4.2 Sample calibration curve for pentachlorophenol analysis by the HPLC method described in the text.

Table 4.1 Experimental conditions for trapping efficiency experiments.

pressure	200 ± 2 atm
temperature	41.0 ± 0.2 °C
SF flow rate	0.6 ± 0.03 mL min ⁻¹

4.5 Extraction Reproducibility

Once the trapping efficiency was verified, it was necessary to test the reproducibility of the extraction technique. This was accomplished by choosing one set of extraction conditions, sample size and PCP concentration, and repeating a number of extractions to ensure that similar results were obtained. The extraction vessel used for these experiments was the 30 mL internal volume (20 mL sample) vessel with the range of hole sizes averaging to 0.46 mm. The experimental conditions are given below in table 4.2. The results are presented and discussed in section 5.3.

Table 4.2 Experimental conditions for reproducibility study.

sample volume	20 mL
PCP concentration	86 ppb
pressure	200 ± 2 atm
temperature	41.0 ± 0.2 °C
SF flow rate	0.6 ± 0.03 mL min ⁻¹
extraction time	60 minutes
total SF volume	30 ± 4 mL
SF density	0.84 ± 0.1 g mL ⁻¹

4.6 Inlet Effect

Design of the SF inlet to the extraction vessel was an important part of the work as discussed in section 3.1.1.3. Experiments were thus done to compare the effect of drubbler design on extraction efficiency. One set of experimental conditions was chosen and repeated experiments performed using the 86 mL internal volume extraction vessel. The drubbler was then removed so that the SF inlet was simply a 1/8 inch outer diameter tube (i.d. 0.025 inch). The extractions were then repeated under the same experimental conditions, given below in table 4.3. The results are presented and discussed in section 5.4.

Table 4.3 Experimental conditions for SF inlet study.

sample volume	75 mL
PCP concentration	200 ppb
pressure	200 ± 2 atm
temperature	41.0 ± 0.2 °C
SF flow rate	0.8 ± 0.04 mL min ⁻¹
time	60 min
total SF volume	48 ± 4 mL
SF density	0.84 ± 0.1 g mL ⁻¹

4.7 Volume of Supercritical Carbon Dioxide

The effect of time or volume of CO₂ used in an extraction was studied by keeping the flow rate of fluid constant during different experiments and adjusting the total extraction time. The hope was that this would give an extraction profile. The extraction conditions are given below in table 4.4. All extractions were done with the 20 mL sample extraction vessel with the drubbler holes averaging 0.46 mm. The results are presented and discussed in section 5.5.

Table 4.4 Experimental conditions for volume carbon dioxide study.

sample volume	20 mL
PCP concentration	110 ppb
pressure	200 ± 2 atm
temperature	41 ± 0.2 °C
SF density	0.84 ± 0.1 g mL ⁻¹

4.8 Flow and Density of Carbon Dioxide

The flow rate of the CO₂ through the water sample was studied to see if it would have an effect on extraction recovery. As flow rate is increased, the increased turbulence due to the presence of more drubbles in the extraction vessel may aid in increasing the extraction efficiency. To study this, different restrictors were made to give different flows under the same extraction conditions. The total SF volume was held constant for each experiment by adjusting the total extraction time.

This study was done in two parts with the two different extraction vessels that could accomodate 20 mL samples. The first set of experiments used the vessel with the drubbler having the irregular shaped holes averaging a hole diameter of 0.46 mm. The extraction conditions are given below in table 4.5. The results are presented and discussed in section 5.6.

Table 4.5 Experimental conditions for flow rate study.

sample volume	20 mL
PCP concentration	110 ppb
pressure	200 ± 2 atm
temperature	41.0 ± 0.2 °C
total SF volume	20 ± 2 mL
SF density	0.84 ± 0.1 g mL ⁻¹

The vessel used for the above experiments was lost once these experiments had been performed. This occurred in the return transportation of the extraction vessel from Sweden, where it had been used for some experiments.

A second 30 mL internal volume extraction vessel was thus constructed, having more regular 0.30 mm diameter drubbler holes. It was used to repeat the flow rate study. At this point it was also decided to vary the density of the CO₂ by changing the pressure to determine if that would influence extraction efficiency. Three different densities were studied, all other extraction conditions were kept the same as those listed in table 4.5. The results are presented and discussed in section 5.6.

4.9 Extraction from Aqueous Solutions of Inorganics

The inorganic solid Fe_2O_3 , was obtained in aqueous suspension from the Department of Water and Environmental Studies in Linköping Sweden. The solids had been ground, separated by size, and prepared in solution in Milli-Q quality distilled and deionized water (Ledin 1993). The usual size definition for colloidal matter is a diameter of less than 0.45 microns. The average diameter of the solids used in these experiments was 0.5 microns, and was therefore termed particulate matter. The concentration of the stock solution had been determined by photon correlation spectroscopy (Ledin 1993) to be Fe_2O_3 3.6 g L^{-1} . When samples were prepared with the inorganic solids for solution, the desired aliquot of the stock solids solution was obtained using an eppendorf pipette after manually shaking the solution for 5 minutes. The solution was then made up to volume with distilled deionized water.

Once the sample was prepared, it was transferred into the extraction vessel and the extraction procedure detailed in section 4.1 was followed. The objective of attempting extractions from solutions containing suspended inorganic matter was to try to simulate the extraction of a difficult sample. Many organic compounds of environmental interest may occur in water sorbed to inorganic material. The results of these extractions are discussed in section 5.7.

4.10 Extraction from Aqueous Solutions of Humic Acid

The humic acid used in this work was obtained in purified form (Pettersson 1992) from the Department of Water and Environmental Studies in Linköping Sweden. Solutions prepared for extraction containing humic acid were made up in large volume, prepared directly from the purified solids and extracted the same day of preparation. The objective of these extractions was to test the developed SFE method on a more difficult aqueous sample. There have been many studies of the complexation of organic analytes in water to natural organic matter, so that it would be interesting to see if supercritical CO₂ would be able to extract an analyte from this more difficult matrix. The results are discussed in section 5.8.

4.11 Extraction from Aqueous Solutions of Fulvic Acid

The fulvic acid used in this work was obtained in purified form (Pettersson 1992) from the Department of Water and Environmental Studies in Linköping Sweden. The number average molecular weight of the fulvic acid (FA) was $M_n = 1190$, the weight average molecular weight, M_w was 1810, thus the ratio of M_n to M_w was 1.52. This indicates that it is in a low molecular weight fulvic acid. The molecular weights had been determined by gel filtration (Pettersson 1992). Solutions prepared for extraction containing dissolved fulvic acid were made up in large volume and prepared directly from the purified solids. They were extracted the same day of preparation. The objective of

these extractions was again to test the developed SFE method on a more difficult aqueous sample.

4.11.1 Blank Extractions

Aqueous solutions containing 20 ppm of fulvic acid were prepared, and extracted with the extraction procedure detailed in section 4.1 and by using the 30 mL internal volume vessel with the 0.30 mm drubbler holes. The objective in this case was to determine if the SFE would cause any change in the solution, or cause any of the fulvic acid to be extracted. The results are discussed in section 5.9.

4.11.2 Extraction of Pentachlorophenol

Extractions were performed with the same vessel and under identical experimental conditions to compare the extraction of PCP from water with the extraction of PCP from fulvic acid solution. The experimental conditions are given below in table 4.6, and the extraction procedure was the same as described in section 4.1. These extractions were done with fulvic acid concentrations of 20 and 200 ppm, which are values typical of real environmental samples. The analysis of the extracts was done in the same manner as described in section 4.3. The results of these extractions are presented and discussed in section 5.9.

Table 4.6 Experimental conditions for fulvic acid extractions.

sample volume	20 mL
PCP concentration	100 ppb
pressure	300 ± 2 atm
temperature	41.5 ± 0.2 °C
SF flow rate	0.6 ± 0.03 mL min ⁻¹
time	33 min
total SF volume	20 ± 2 mL
SF density	0.90 ± 0.1 g mL ⁻¹

It has been shown for 2,4,6-TCP (Robinson 1994) that as a water sample is aged the amount of analyte bound to humic matter increases. It is reasonable to assume that water samples containing dissolved PCP would exhibit a similar trend, which means an aged water sample would be a more difficult matrix to extract. Unfortunately, due to the difficulties applying the SFE method to the humic acid experiment (see section 5.8), this type of study was possible only with FA. Prepared samples were aged in glass containers for three weeks, in the dark at 4 °C. The experimental conditions were the same as given in table 4.6. The results of these extractions are discussed in section 5.9.

4.12 Extraction Combined with In-situ Derivatization

4.12.1 Extraction and Derivatization Method

One part of this study involved adaptation of a method for the combined derivatization and extraction of phenolics from water when using supercritical CO₂ as the extraction solvent. The advantages of this procedure are a reduction in the amount of time required for analysis and the ability to analyze the extract directly by GC, thereby lowering the detection limit by using the entire extract for detection.

The method was developed from those described in the literature by Renberg et al. (1981) and Coutts et al. (1979). The in-situ derivatization and extraction was performed as follows:

- the water sample was prepared as described in section 4.3, except the spiking was done into a 0.5 M solution of NaHCO₃
- the water sample was transferred to the extraction vessel
- 90 µL of acetic anhydride was added into the water sample in the extraction vessel
- the extraction procedure continued as normal, using the experimental conditions given in table 4.6

The addition of NaHCO₃ ensures that the PCP is in the de-protonated form, and ensures that the acetylation will take place. The extract analysis was done by GC-ECD, with confirmation of product formation done by GC-MS. The

GC analytical details are described below in section 4.12.2. Standards were prepared during the extraction, by adding NaHCO_3 to 10 mL water samples containing various phenol concentrations, adding acetic anhydride, and then extracting with 1 mL hexane. The hexane extracts were then analyzed at the same time as the SF extracts. The product of the derivatization reaction was pentachlorophenyl acetate (PCPA). The water sample was collected after the extraction, and re-extracted according to the method for preparing standards, and analyzed by the same method to determine if any un-derivatized PCP remained in the solution.

4.12.2 Gas Chromatographic Analyses

For the gas chromatographic analyses, sample aliquots were taken directly from the collection vials. The sample volume injected in each case was 1 μL . Gas chromatographic (GC) analysis using a mass spectrometric (MS) detector was used to analyze the above extract and confirm the formation of the PCPA. The extract was first concentrated by directing a gentle stream of nitrogen gas over the extract. The instrument used was a Varian Saturn II (ion trap), equipped with a DB5 capillary column (30 m by 0.25 mm id, 0.25 μm film thickness). The carrier gas was helium (Air Products chromatographic grade), flowing at 5 mL min^{-1} .

The normal analysis program used was as follows:

injector temperature: 300 °C

MS detector temperature: 220 °C

GC temperature program:

hold at 150 °C for 2 min

ramp 10 °C min⁻¹ to 240 °C

hold at 240 °C for 4 min

total time: 15 min

GC analysis using an electron capture detector (ECD) was used for the quantitative analysis of the PCPA extracts. The instrument was a Varian 3400, equipped with a DB5 capillary column (30 m by 0.25 mm id, 0.25 µm film thickness). The carrier gas was helium (Air Products chromatographic grade) with a flowrate of 5 mL min⁻¹, and the make-up gas was nitrogen (Central Oxygen zero grade) with a flowrate of 30 mL min⁻¹. The normal conditions and temperature program for analysis was the same as that described above for MS detection, except the detector was at 300 °C. Quantification was done using an external standard calibration curve prepared with peak areas.

4.13 Extraction from Aqueous Solutions of Fulvic Acid Combined with In-situ Derivatization

The applicability of the in-situ derivatization method described in section 4.12.1 was also tested on aqueous solutions of PCP containing dissolved fulvic acid. The in-situ derivatization method was applied to the aged fulvic acid solutions described in 4.11.2. NaHCO_3 was added to the solutions to give a concentration of 0.5 M. The in-situ method as listed in 4.12.1 was followed, and the same experimental conditions were used as those described in table 4.6. The results are presented and discussed in section 5.11.

4.14 Extraction of Multiple Analytes

Stock solutions were prepared in either methanol or acetone in glass volumetric flasks, and stored in the dark at 4 °C. All solvents used for preparing stock solutions were Optima grade from Fisher. The spike volume for each water sample was normally in the order of 5 μL , the analytes were spiked into aqueous solutions containing 20 ppm fulvic acid to increase their water solubility. The multiple analytes used for spiking at this stage were pentachlorophenol (PCP), 2,4,6-trichlorophenol (2,4,6-TCP), phenanthrene, 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT), 2,4-dichlorophenoxy acetic acid (2,4-D), and dieldrin. The relevant physical properties of the analytes are listed in table 4.7. The analytes chosen should have a wide range of solubilities in supercritical CO_2 as discussed in section 2.3.1. The individual aqueous

analyte concentrations are given in table 5.6. Pentachlorothioanisole (PCTA) was used as an internal standard to correct for changes in detector response.

The extraction conditions are listed below in table 4.8. The total amount of SF used in this case was increased to 40 mL to allow for complete extraction of PCP under these conditions. This was done so that any differences in analyte recovery could be noted. The results are presented and discussed in section 5.12.

Table 4.7 Relevant properties^a of analytes in the multiple analyte extractions.

Name	Formula	Molecular Weight g mol⁻¹	Purity %	Water Solubility mg L⁻¹ (25°C)^b	Vapour Pressure atm (25°C)^b
PCP	C ₆ HCl ₅ O	266.34	>93%	14.9	2.4 x 10 ⁻⁵
2,4,6-TCP	C ₆ H ₃ Cl ₃ O	197.45	98%	434.4	1.3 x 10 ⁻³ (76.5°C)
phenanthrene	C ₁₄ H ₁₀	178.2	93%	1.0 - 1.8	9.9 x 10 ⁻⁷
DDT	C ₁₄ H ₉ Cl ₅	353.25	93%	<2.5 x10 ⁻²	2 x 10 ⁻¹⁰
2,4-D	C ₈ H ₆ Cl ₂ O ₃	221.04	99%	890	
dieldrin	C ₁₂ H ₈ Cl ₆ O	380.7	93%	0.186 (20°C)	3.9 x 10 ⁻⁵ (20°C)
PCTA ^c	C ₇ H ₃ Cl ₅ S	296.45	99.1%		

^a data taken from Canadian Water Quality Guidelines 1987, and the CRC Handbook 1973

^b unless stated otherwise

^c internal standard

Table 4.8 Experimental conditions for multiple analyte extractions.

sample volume	20 mL
fulvic acid	20 ppm
pressure	300 ± 2 atm
temperature	41.5 ± 0.2 °C
SF flow rate	0.8 ± 0.04 mL min ⁻¹
time	50 min
total SF volume	40 ± 4 mL
SF density	0.90 ± 0.1 g mL ⁻¹

In order to analyze peritachlorophenol and the complete mixture of multiple analytes it was necessary to derivatize the extracts so they all could be detected in a single GC analysis. Diazomethane was chosen as the derivatization agent. In order to prepare it, nitrosomethylurea was first prepared in a large quantity from an aqueous solution of methylamine and urea, as it is stable over longer time periods than the CH_3N_2 itself.

The diazomethane solution was prepared as required according to the following procedure (Burk 1990). In a 50 mL erlenmeyer flask, 20 mL diethyl ether and 6 mL of 50% aqueous KOH solution are mixed. Added to this was 2 g nitrosomethylurea. The ether layer turned yellow quickly, which indicated diazomethane had been produced. When the reaction had finished, the ether layer was drawn off, and stored in the freezer. The solution was stable for up

to two weeks. This method of preparation did not introduce any interferences at the concentration levels used in this study.

Extracts were derivatized according to the following method. The sample was first evaporated to dryness, then approximately 0.5 mL of diazomethane solution was added. The solution was then mixed and allowed to stand for at least 20 minutes to ensure complete methylation. The solution was then again evaporated to dryness, and 1 mL of the chosen solvent added. The internal standard was then added. The product of the derivatization reaction for PCP was pentachloromethoxybenzene (PCMB). PCP standards were treated in the same manner.

The multiple analyte extracts were analyzed using GC-ECD as described in section 4.12.2 with the following GC temperature program:

hold at 80 °C for 2 min

ramp 10 °C min⁻¹ to 300 °C

hold at 300 °C for 2 min

total time 26 min

Quantification of analytes was done using both external and internal standard methods based on peak area.

In order to analyze phenanthrene in this mixture, it was decided to do GC analysis by flame ionization detection (FID). The column was a DB-5, using helium as the carrier gas. The FID had hydrogen at a flowrate of 30 mL min⁻¹ and air at a flowrate of 300 mL min⁻¹ (both Central Oxygen zero grade). A

calibration curve was not able to be constructed due to difficulties with the analysis mainly caused by irreproducible phenanthrene peak areas; however when the extracts were concentrated phenanthrene was identified and confirmed to be present using the GC-MS.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Sample Size from Blank Extractions

Initial experiments were conducted by using different sample sizes of blank water, to determine the maximum sample size which could be used for an extraction. Samples were extracted under the experimental conditions described in section 4.2. For the large extraction vessel, the maximum sample size was 75 mL, leaving an additional dead volume of 11 mL. For both smaller extraction vessels, the maximum sample size was 25 mL, leaving an additional dead volume of 5 mL. When larger sample sizes than these were used, it was found that water was forced out of the extraction vessel and into the restrictor, which caused the flow of supercritical CO₂ to become blocked. The amount of dead volume required to prevent this depends only on the design of the extraction vessel. When these maximum water sample sizes were used, no water carry-over was observed. This agrees with the observations discussed in section 3.1.1.3, where the water sample was not expanded to a significant extent by the presence of solvent during extraction.

5.2 Trapping Efficiency

To verify the efficiency of the trapping system prior to performing the SFE optimization experiments, PCP was spiked into an empty vessel as described in section 4.4, and an extraction performed to determine the efficiency of PCP recovery. The trapping system used for all experiments was illustrated in figure 3.4c. The extracts were analyzed as described in section 4.3. The results of these experiments are shown below in table 5.1.

Table 5.1 Trapping efficiency of pentachlorophenol.

Trial	Recovery (μg)	Percent Recovery
1	2.99	99.6
2	2.60	86.5
3	2.93	97.5
average	2.84	$94.5 \pm 5.0\%$

5.3 Reproducibility

Table 5.2 presents results from seven extractions of PCP spiked into 20 mL water samples at a concentration of 86 ppb. Extraction conditions were described in section 4.5. Good reproducibility for PCP extraction and recovery was observed, with an average recovery of 97% (rsd 3.7%).

The extraction system was cleaned between runs with a small amount of methanol, and tested for residual analyte; none was found. With identical

supercritical CO₂ flow rates, reproducible results were obtained. The main source of irreproducibility was change in the restrictor due to plugging of the hole as discussed in section 3.1.2. When a restrictor was replaced, there would be some change in the flow rate due to the method of crimping the metal to prepare the restrictor.

Table 5.2 Reproducibility of extractions of pentachlorophenol.

Trial	Percent Recovery
1	103
2	105
3	86.1
4	88.5
5	98.0
6	108
7	90.5
average	97.0 ± 3.5%

5.4 Inlet Effect

Design of the SF inlet to the extraction vessel was an important part of this work as discussed in section 3.1.1.3. Experiments were thus done to compare the effect of the drubbler on extraction efficiency. Three extractions were done on a 75 mL water sample containing 200 ppb of pentachlorophenol

using the large extraction vessel with 0.46 mm holes in the drubbler. The extraction conditions were given in section 4.6. The drubbler disk was then removed from the extraction vessel so that the SF inlet was simply a 1/8 inch outer diameter tube (i.d. 0.025 inch). A tube inlet similar to the second type had been used in the literature for extractions from water samples (Taylor 1989). The extraction conditions listed in table 4.3 were chosen so that the PCP recovery would be less than 50%. The time of the extraction was not long enough to completely extract the PCP from the water sample at the stated conditions. This ensures that any change in extraction recovery due to the nature of the inlet will be clearly identified, which would not be the case if PCP recovery had reached 100% in both cases. The results are given below in table 5.3.

Table 5.3 Experimental comparison of fluid inlet to extraction vessel.

SF Inlet	Percent Recovery	Average Percent Recovery	rsd	Total Runs
Drubbler	37.3 37.3 39.8 34.9 39.8 37.5	38 ± 2.0	5.3%	6
Tube	21.5 20.7 23.4	23 ± 1.0	4.3%	3

The results shown in table 5.3 indicate that there is indeed a significant increase in extraction efficiency with use of the drubbler. The tube type inlet will form large discreet drubbles, and it may be difficult to achieve efficient contact between the two phases for large sample sizes. Under the stated experimental conditions, the efficiency increase can be determined by taking the ratio of the average percent recovery values. This finds that the efficiency has been increased by a factor of 1.6.

5.5 Volume of Supercritical Carbon Dioxide

The effect of total SF volume passed through the water sample was studied by conducting separate extractions of different length under the identical experimental conditions. The water sample size was 20 mL and the extraction vessel used was shown in figure 3.2 with drubbler holes 0.30 mm in diameter. The extraction conditions were given in section 4.7. The water sample volume was 20 mL and the concentration of PCP was 110 ppb. Results are shown in figure 5.1. Each point is the average of three extractions, and the standard deviations of both the percent recovery and total SF volume are shown on the graph. The data represented in this graph are given in appendix IV, table IV.A. This profile is typical for those observed for extractions performed by using other conditions. These results suggest that for greater than 90% extraction of PCP under the experimental conditions listed in table 4.4 (section 4.7), a volume of SF of at least 1.5 times the water sample volume must be passed

Figure 5.1 Percent recovery of PCP versus total volume of supercritical carbon dioxide (200 atm, 41 °C, 0.8 mL min⁻¹, and 20 mL sample with 110 ppb PCP).

through the sample. This estimate was found to hold for both extraction vessels with the same drubbler type under these conditions when PCP was the analyte. The data in figure 5.1 also indicate an order of magnitude agreement with the simple mass transfer model presented in section 3.2. This order of magnitude agreement is reasonable, considering the simplicity of the model and the possible ranges in the values used. More sophisticated models developed for other studies (Lahiere 1987a and 1987b, Bartalomeo 1990) do not provide much better agreement with their experiments. The data from table 5.3 indicates that 2.5 times the water sample volume would be required if the drubbler was absent, assuming that the SF inlet was the only factor affecting the rate of extraction.

5.6 Effect of Flow and Density of Supercritical Carbon Dioxide

Studies of the effect of SF flow rate were done by doing separate experiments using the same conditions but with different restrictors. The extraction time was adjusted to keep the total CO₂ volume passed through the water sample constant for each flow rate. The experimental conditions were given in section 4.8. The total supercritical CO₂ volume was 20 mL in each case. The results are shown in figure 5.2. Each point is an average of two extractions, and the standard deviations of both recovery and flow are shown as error bars on the graph. The data points are documented in appendix IV, table IV.B.

Figure 5.2 Percent recovery of PCP versus supercritical carbon dioxide flow rate (200 atm, 41 °C, and 20 mL sample with 110 ppb PCP).

The results illustrated in figure 5.2 show the extraction efficiency increasing as the CO₂ flow rate is increased. The drubbler used for these extractions had holes which upon closer inspection were found to be somewhat irregular in shape. The average hole diameter was 0.46, with the hole sizes ranging from 0.30 to 0.47 mm. This extraction vessel was lost during the course of this study, therefore no further experimentation with it was possible.

Similar experiments were done by using the extraction vessel with a different drubbler which had slightly smaller (0.30 mm) diameter and more uniform holes. This is the same hole size used for the analyses reported in section 3.2. The range of flow rates studied were the same as described above, as were the experimental conditions. The experiments were expanded to include three different supercritical CO₂ densities, 0.64 g mL⁻¹, 0.76 g mL⁻¹, 0.90 g mL⁻¹. The density was varied by keeping the temperature constant and changing the pressure. The total supercritical CO₂ volume for each experiment was 20 mL. These results are shown in figure 5.3. Error estimates are of the same magnitude as those shown in figure 5.2. The data points are documented in appendix IV, table IV.C. The data in figure 5.3 show no increase in extraction efficiency as flow rate was varied. This is in agreement with recent results obtained by Barnabas et al. (1994).

The apparent contradiction of the data in figures 5.2 and 5.3 concerning the effect of flow rate can be explained through a "weakest link" principle. If the drubbler holes are not all uniform, then at low flow rates it is likely that drubbles

Figure 5.3 Percent recovery of PCP as a function of fluid flow and density (41 °C, 20 mL sample with 110 ppb PCP).

will only be formed at the largest hole. This alone will cause lower flow rates to have a lower extraction efficiency. If the largest hole happens to be close to the drubbler stem, then the fluid could actually rise up the stem and not achieve maximum contact with the water sample, which would cause a further decrease in extraction efficiency. Higher flow rates would give a better distribution of drubbles in the water, and therefore cause more efficient extraction to take place through better contact. The differences in figure 5.2 and 5.3 also illustrate that differences in drubbler machining can have an effect. It is important to note that the rate of rise of drubbles is not affected to a first approximation by flow rate. Only the rate of formation of drubbles is affected. The contact time between the SF and water is thus independent of flow rate.

The results in figure 5.3 also show that there was no appreciable change in the extraction efficiency with density, within experimental error. This agrees to a first approximation with the analyses in section 3.2. The analyses in 3.2 neglect the changes with density of the CO₂ dynamic properties and the partition coefficient of PCP between CO₂ and water. At lower density, the diffusion of the PCP in the SF would be greater, which would increase the rate of transfer of PCP from the water sample to the supercritical CO₂. The partition coefficient would, however, be smaller as discussed in section 2.3.2, resulting in a lower solubility of PCP in the SF. This may not be a critical factor if the density of the SF is sufficiently high to give favourable partitioning. Further modelling calculations based on those presented in section 3.2 to illustrate these effects

were not attempted, due to the inability of the model to describe this non-uniform system.

It is also interesting to note by comparing figures 5.2 and 5.3, that for the small holed drubbler (0.30 mm), 20 mL of SF recovers an average of 50% of the PCP at each set of conditions. This is less than with the irregular holed drubbler under similar conditions (figures 5.1 and 5.2) which would be expected to produce some drubbles of a slightly larger diameter. These differences may be due to hole size irregularity (in both drubblers), or surface effects, and illustrate the importance of consistent drubbler machining. All remaining experiments were performed with the 30 mL internal volume extraction vessel having the drubbler with regular hole sizes of 0.30 mm.

5.7 Extraction from Aqueous Solutions of Inorganics

Blank extractions were attempted from aqueous solutions containing low ppm amounts of Fe_2O_3 prepared as described in section 4.9. Fe_2O_3 was chosen as a typical inorganic solid which may be present in natural water. In each case at the end of the extraction, there was a solid material was on the bottom of the extraction vessel which was very difficult to remove. It seems that the solids were not remaining suspended during the extraction runs, and therefore these experiments were not pursued any further. The difficulty with sample preparation of this type could be overcome by obtaining a real sample

containing dissolved solids for extraction.

5.8 Extraction from Aqueous Solutions of Humic Acid

Blank extractions were performed from aqueous solutions containing low ppm amounts of humic acid prepared as described in section 4.10. In each case humic acid material was seen on the bottom of the extraction vessel at the end of an extraction. The humic acids were at least partially precipitated during the extraction run. The pH of the aqueous solution pressurized with CO₂ must therefore be low enough to cause some humic material precipitation. This agrees with the observations seen by Enholt et al. (1987). The pH of water with 100 atmospheres pressure of CO₂ has been determined to be less than 3 (Fell 1993), therefore it is quite feasible that the pH of the water sample could be low enough to cause precipitation of humic acids, which occur completely by pH 2. These experiments were not pursued any further during the course of this study. These observations mean that precipitation of humic material will occur during the extraction of real water samples containing dissolved humic acids using this technique.

5.9 Extractions from Aqueous Solutions of Fulvic Acid

Blank extractions were performed on aqueous solutions containing 20 ppm of a fulvic acid prepared as described in section 4.11. No visual change was observed in the water sample after extraction, and there was no

precipitation of any solid matter. The aqueous solution containing the dissolved fulvic acid was also passed through a size exclusion chromatography column both before and after the extraction, and no visual change was observed in the peak size distribution. No organic matter was trapped during the extraction. The fulvic acid should be quite polar due to the presence of carboxylic acid groups, and also has a high molecular weight, therefore it would have poor solubility in CO₂. Aqueous fulvic acid solutions were therefore used to study how the presence of a dissolved fulvic acid would affect the extraction efficiency of PCP.

The percent recovery of PCP in water alone was compared to that recovered from water containing 20 ppm FA and 100 ppb PCP prepared as described in section 4.11.2. The extraction conditions were given in section 4.11.2. In each case only 20 mL of SF was used for the extraction so that differences in extraction efficiency could be observed. Results are shown in table 5.4. The data represent an average of three extractions. There was no difference in the observed PCP recoveries within experimental error. Further extractions were done from aqueous solutions containing 200 ppm FA (2000 times the PCP concentration) to check for any change in extraction efficiency. The higher concentration of FA should cause more of the PCP to be sorbed on the organic matter, making the extraction potentially more difficult. These results are also shown in table 5.4 (average of two extractions). In this case the percent recovery has decreased, due to increased interactions between the

FA and the PCP as discussed in section 4.11.2.

The effect that aging of the FA-PCP aqueous solution has on extraction efficiency was also studied, for the case where the FA concentration was 200 ppm. This was of interest because as the sample ages, more of the analyte will likely be sorbed on the organic matter (Robinson 1994). This is expected to mimic the more difficult extractions expected for real environmental samples. The sample was prepared, and stored at 4°C and in the dark for three weeks before the extraction was done. In this case, there was minimal further decrease in extraction efficiency as illustrated by the results in table 5.4.

Table 5.4 Effect of dissolved fulvic acid on pentachlorophenol recovery.

Sample	Percent PCP Recovered (rsd)
blank water	47 ± 3.2 (6.8%)
20 ppm FA	45 ± 3.0 (8.0%)
200 ppm FA	30 ± 2.0 (6.7%)
200 ppm FA aged 3 weeks	26 ± 1.5 (5.8%)

5.10 In-situ Derivatization

Development of a combined derivatization and extraction method which would use supercritical CO₂ as a solvent was done based on the experimental method described in section 4.12.1 The analyte was PCP, and the derivative was pentachlorophenol acetate. The average percent recovery over four trials

was found to be $71.0 \pm 4.0\%$ (rsd 5.6%).

The trapping system was not optimized for recovery of the derivative. This may be why the average recovery for the developed method did not reach 90 - 100%. The recovery results were reproducible, but complete recovery was never attained. The extracts were also tested by HPLC to check for the presence of underivatized PCP; none was detected. Figure 5.4 compares GC-ECD chromatograms of both a standard and an extract.

After CO₂ extraction, the water matrix was re-extracted by applying the conventional derivatization technique, and analyzed for remaining PCP. No trace of unextracted PCP was found, which leads to the conclusion that analyte loss occurred during the trapping stage. Further work in this area is needed to optimize the trapping system. Literature recovery values for the extraction of derivatized phenolic compounds at ppb levels prepared by the same reaction are in the order of 100% when hexane is the extraction solvent (Coutts 1979). Recoveries of this magnitude for PCP should be expected if the trapping stage was optimized.

Figure 5.4 GC-ECD of chromatogram of an in-situ derivatization extract and standard prepared by the method described in the text. The pentachlorophenyl acetate (PCPA) peak is labelled.

5.11 Extractions from Fulvic Acid Solution Combined with In-situ

Derivatization

The applicability of the in-situ derivatization method described in section 4.12.1 to samples containing FA was also tested. In this case, it was the aged samples that were used. The extraction conditions were not changed from those used in the extraction of fulvic acid-spike water samples. Extractions of the sample by using the in-situ extraction method and hexane extraction were also done so that the SFE result could be compared with results obtained by using a traditional method. Results are shown in table 5.5.

Table 5.5 Combined derivatization and extraction of pentachlorophenol from aged aqueous solutions of fulvic acid.

Extraction method	Perecent Recovery (individual runs)	Average Percent recovery PCPA (rsd)
SFE	30 32 28	30 ± 2.0 (6.7%)
in-situ derivatization and SFE	46 51	48 ± 3.0 (6.3%)
in-situ derivatization and hexane extraction	30 26	28 ± 2.0 (7.1%)

The interesting result suggested by the data in table 5.5, is that the combination of in-situ derivatization and extraction using supercritical CO₂ recovers more of

the pentachlorophenol derivative than when the derivatization is combined with hexane extraction. In either case, there was no contamination of the extracts by the extraction of derivatized organic matter. As the lesser pH of the water sample pressurized with CO₂ should cause an increase in the complexation of PCP and FA, the increased recovery of pentachlorophenyl acetate must be due to the enhanced extraction of adsorbed analyte. This is one area where the advantageous properties of SFs have the potential to really increase extraction efficiency, when the analyte is adsorbed on dissolved natural organic matter. The extraction efficiency may be further increased if the difficulties discussed in section 5.10 with the recovery of the derivatized phenol are overcome.

5.12 Extraction of Multiple Analytes

The extraction method developed was used to analyze aqueous solutions that contained a number of analytes prepared from stock solutions as described in section 4.14. The analytes were spiked into an aqueous solution containing 20 ppm FA, to increase their water solubility. It is not possible to introduce some of the contaminants of interest in the absence of FA or other materials which complex or adsorb the contaminants. For DDT and phenanthrene, the literature pure water solubility is exceeded (table 4.5), but the "apparent solubility" of many hydrophobic compounds is increased in the presence of dissolved organic matter. The extraction conditions were given in section 4.14. The total amount of CO₂ used for the extraction for these experiments was

increased to 40 mL to allow complete extraction of PCP. This was done so that any differences between analyte recovery could be noted. A chromatogram of an extract is shown in figure 5.5. The recovery of each analyte along with the initial aqueous concentration is given in table 5.6. The data represent an average of three extractions. The recovery data from individual trial is given in appendic IV, table IV.D.

Table 5.6 Aqueous concentration and percent recovery for extractions of multiple analytes.

Analyte	Aqueous Concentration (ppb)	Percent Recovered (rsd)
PCP	106	97 ± 7.0 (7.2%)
2,4,6-TCP	115	52 ± 4.0 (7.7%)
Dieldrin	122	99 ± 6.8 (6.9%)
DDT	161	85 ± 6.3 (7.4%)
phenanthrene	124	detected
2,4-D	118	not detected

Since all analytes were contained in the same extract, they were all subject to the derivatization method described in section 4.14, as the analysis was done by using GC-ECD. The low recovery of 2,4,6-TCP may have been due to loss during the derivatization step. Quantification was done by using the

Figure 5.5 GC-ECD chromatogram of an extract containing the multiple analyte mixture described in the text.

external standard method only; use of an internal standard method may result in improved analytical results. The identification of analytes was confirmed by GC-MS. Recoveries of the analytes quantified are in the same order as were observed in the other aqueous SFE studies discussed in section 2.1.4.

Phenanthrene was qualitatively detected as described in section 4.14, but it was not quantifiable due to difficulty with the GC-FID analysis discussed in section 4.14. It was expected to be completely extracted since it is neutral and nonpolar, and should not have been lost in the trapping stage therefore high recoveries would be expected. There was no 2,4-D detected. This may be due to incomplete extraction due to the acidity of the compound ($pK_a \approx 3$). The important result from the data in table 5.6 is that the developed SFE method is applicable to other analytes and analyte mixtures. Optimization of the trapping stage and the use of recovery standards should allow the quantitative extraction and analysis of a wider range of analytes.

CHAPTER SIX

CONCLUSIONS

Extraction vessels have been designed and built which are suitable for the extraction of aqueous samples for analytical purposes using supercritical fluids. The apparatus can accommodate 20 and 75 mL samples. The main ways that the extraction vessel may be improved in the future are elimination of the drubbler stem, and scaling up the extraction vessel to accommodate larger sample sizes.

Extraction of pentachlorophenol from water has been shown to be quantitative at sample concentrations 80 - 100 ppb. The average recovery over seven experiments was shown to be $97 \pm 3.5\%$. To achieve quantitative recovery of PCP, a volume of supercritical CO_2 which was 1.5 times the water sample volume was sufficient. This result depends on the drubbler design developed, and recoveries may be decreased with increased turbulence during extraction.

The design of the supercritical fluid inlet does have an effect on extraction recovery. Optimization of this inlet design is important, especially for the extraction of large samples. The importance of uniform machining in the design of the drubbler has been demonstrated. One possible improvement on this inlet design would be to remove the drubbler stem from the main column of the extraction vessel. This could be accomplished by means of a bottom cap

with a teflon disk with holes in it acting as both a drubbler and a gasket.

Flow rate does not have a noticeable effect on extraction efficiency for the experimental conditions studied in this work, as long as the drubbler holes are uniform. This agrees with recent observations by Barnabas et al. (1994). The advantage of faster flow rates is a decrease in extraction time, and a potential increase in turbulence which may increase extraction efficiency. The contact time between the supercritical carbon dioxide and water is independent of CO₂ flow rate, which is contrary to the effect showed when extractions from solid matrices are performed.

The density of supercritical carbon dioxide was not found to influence extraction efficiency in the ranges studied, from 0.6 to 0.9 g mL⁻¹, despite the fact that partition coefficients have been shown to increase as density is increased. This is most likely due to the fact that equilibrium between the two phases is not established in a dynamic extraction, and therefore the factors controlling the contact between the two phases are more important. It is expected however that at very low densities one would observe a decrease in extraction efficiency due to the much lower "solubility" of the analyte in the supercritical phase. A wider range of CO₂ densities would have to be experimentally studied in order to verify the effect of CO₂ density on extraction efficiency.

A range of analytes was able to be extracted from water during this study. Pentachlorophenol, DDT, and dieldrin were recovered in high amounts,

while 2,4,6-TCP was recovered to a lesser extent. Phenanthrene was extracted but not able to be quantified due to difficulties with the analytical method, while 2,4-D was not able to be detected.

An in-situ derivatization method was combined with direct extraction of pentachlorophenol from water. The trapping of the analyte was not optimized, but the possible advantages of such a method were indicated, including increased extraction of absorbed analytes, and direct analysis by GC.

Supercritical CO₂ was found to extract PCP from an aqueous fulvic acid solution, where the analyte will be partially bound to the fulvic acid. The in-situ derivatization method mentioned above was also found to be applicable to this type of sample, and to give higher recoveries of the derivative than when hexane was the solvent.

Extractions were not able to be performed from sample matrices containing humic acid or suspended inorganic solids due to their precipitation when pressurized with carbon dioxide. The precipitation of the inorganic solids is likely due to the size of the particulate matter. The precipitation of the humic acid is likely due the lowered pH of the aqueous solution when pressurized with CO₂. Complete precipitation of the humic acid would occur at a pH of 2, and the pH of the aqueous solution pressurized with CO₂ would be less than 3 (Fell 1993).

In summary, the notable original contributions of this work are:

- the construction of a unique extraction vessel shown to be useful for analytical SFE from liquids;
- the investigation of the extractability of polar and nonpolar analytes from water at ppb levels using supercritical CO₂;
- the investigation of analyte extractability from complex aqueous matrices containing dissolved fulvic acid at levels up to 2000 times analyte concentration;
- in-situ derivatization and extraction from water using supercritical CO₂.

Future work on this project should include further detailed characterization of the drubbler holes since their characteristics have been shown to be an important factor. Further optimization of the extraction vessel could be accomplished by replacing the drubbler material and removing the drubbler stem in the middle of the extraction vessel. This would hopefully further improve the extraction efficiency. It would also be worthwhile to do a detailed comparison of the direct supercritical fluid extraction of water with current accepted extraction methods. This could involve a study of how the aqueous concentration levels of the analytes influence extraction recovery.

The extraction of real complex samples containing natural organic matter and inorganic solids should be investigated. The present work indicates that supercritical fluids may have an advantage over traditional organic solvents when extracting from water samples containing dissolved fulvic acids. It may

also be interesting to investigate the ability of supercritical carbon dioxide to precipitate natural organic matter.

The scale-up of the extraction apparatus to allow the extraction of larger sample sizes should also be investigated. It would be useful to be able to extract two litre water samples as this is the size is used in many EPA methods, and the two extraction techniques could be directly compared. The best way to enlarge the extraction vessel would be to make the vessel taller. This is fairly simple due to the availability of large inner diameter high pressure tubing. The advantage of this would also be to increase the contact time between the supercritical and aqueous phases. It may also be possible to improve the apparatus so that it is less time-consuming to use by eliminating some of the fittings, and using finger-tight fittings where possible. The potential of counter-current extraction could also be investigated.

It may also be interesting to study the effect of certain additives on extraction efficiency. Salts have been shown to increase the partition coefficient of polar analytes, but also increase the extraction of water as discussed in section 2.1.4. It may be possible to include a water trap before the depressurization stage to eliminate this potential problem.

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APPENDIX I

EXTRACTION VESSEL MACHINING SCHEMATICS

NUT - MATERIAL : ST. ST. 304

APPENDIX II

DETAILED MODEL CALCULATIONS

II.A Pressure drop calculation using the Hagen-Poiseuille equation.

$$\Delta p = \frac{32 \mu}{D_o^2} (\Delta L \ v) \quad 3.1$$

μ = fluid viscosity = 8.0×10^{-5} Pa s; extrapolated from figure 2.3 for 300 atm and 40 °C

D_o = hole diameter = 3.0×10^{-4} m; chosen to represent a typical hole size

ΔL = length of hole = 1.0×10^{-3} m; determined from drubbler top thickness

$v = 7.8 \times 10^{-3}$ m s⁻¹ = average fluid flow velocity in the hole; calculated as shown below

$$v = \frac{Q}{n} \times \frac{1}{(\pi D_o/2)^2}$$

Q = overall SF flow = 1 mL min⁻¹ = $(10^{-6} / 60)$ m³ s⁻¹; typical flow rate

n = number of holes = 30

D_o = hole diameter = 3.0×10^{-4} m

$$v = \frac{(10^{-6} / 60) \text{ m}^3 \text{ s}^{-1}}{30} \times \frac{1}{3.14 (3 \times 10^{-4} \text{ m}/2)^2} = 7.8 \times 10^{-3} \text{ m s}^{-1}$$

therefore,

$$\Delta p = \frac{32 (8.0 \times 10^{-5} \text{ Pa s}) (1.0 \times 10^{-3} \text{ m}) (7.8 \times 10^{-3} \text{ m s}^{-1})}{(3.0 \times 10^{-4} \text{ m})^2}$$

$$= 0.22 \text{ Pa}$$

$$= 2.2 \times 10^{-6} \text{ atm}$$

II.B Calculation of drubble size using Tate's Law.

$$D = \{(6 D_o \sigma) / (\Delta \rho g)\}^{1/2} \quad 3.2$$

$$D_o = \text{hole diameter} = 3.0 \times 10^{-4} \text{ m}$$

$$\sigma = \text{interfacial tension} = 22 \text{ dyne cm}^{-1} = 22 \times 10^{-3} \text{ N m}^{-1}; \text{ extrapolated from figure 2.7 for 300 atm and } 40^\circ\text{C}$$

$$\begin{aligned} \Delta \rho &= \text{density difference between water and SF} \\ &= 1000 \text{ kg m}^{-3} - 900 \text{ kg m}^{-3} = 100 \text{ kg m}^{-3} \end{aligned}$$

$$g = \text{acceleration due to gravity} = 9.8 \text{ m s}^{-2}$$

$$D = \left[\frac{6 (3.0 \times 10^{-4} \text{ m}) (22 \times 10^{-3} \text{ N m}^{-1})}{(100 \text{ kg m}^{-3}) (9.8 \text{ m s}^{-2})} \right]^{1/2}$$

$$= 3.4 \times 10^{-3} \text{ m}$$

$$= 3.4 \text{ mm}$$

II.C Calculation of drubble rate of rise or terminal steady velocity.

$$u = \frac{g D^2 \Delta \rho}{18 \mu} \quad 3.3$$

g = acceleration due to gravity = 9.8 m s^{-2}

D = drubble diameter = $3.4 \times 10^{-3} \text{ m}$; calculated in II.B

$\Delta \rho$ = density difference between water and SF = 100 kg m^{-3}

μ = viscosity of water = $0.66 \times 10^{-3} \text{ Pa s}$; taken from Geankoplis (1978) for 40°C

$$\begin{aligned} u &= \frac{9.8 \text{ m s}^{-2} (3.4 \times 10^{-3} \text{ m})^2 (100 \text{ kg m}^{-3})}{18 (0.66 \times 10^{-3} \text{ Pa s})} \\ &= 0.95 \text{ m s}^{-1} \end{aligned}$$

$N_{\text{Re}} = (D u \rho) / \mu$ (see page 62)

D = drubble diameter = $3.4 \times 10^{-3} \text{ m}$; calculated in II.B

u = terminal steady velocity = 0.95 m s^{-1} ; calculated above

ρ = density of water = 1000 kg m^{-3}

μ = viscosity of water = $0.66 \times 10^{-3} \text{ Pa s}$; taken from Geankoplis (1978) for 40°C

$$\begin{aligned} N_{\text{Re}} &= (3.4 \times 10^{-3} \text{ m})(0.95 \text{ m s}^{-1})(1000 \text{ kg m}^{-3}) / (0.66 \times 10^{-3} \text{ Pa s}) \\ &= 4894 \end{aligned}$$

II.D Empirical correction methods for turbulent flow.

i) calculate u using drag coefficient for turbulent flow:

$$u = \frac{\left[4 g D \Delta \rho \right]^{1/2}}{3 \rho C} \quad 3.3$$

g = acceleration due to gravity = 9.8 m s^{-2}

D = drubble diameter = $3.4 \times 10^{-3} \text{ m}$; calculated in II.B

$\Delta \rho$ = density difference between water and SF = 100 kg m^{-3}

ρ = density of water = 1000 kg m^{-3}

C = drag coefficient = 0.4; extrapolated from Perry (1984) page 5-64 for $N_{Re} = 4894$

$$u = \frac{\left[4(9.8 \text{ m s}^{-2})(3.4 \times 10^{-3} \text{ m})(100 \text{ kg m}^{-3}) \right]^{1/2}}{3(1000 \text{ kg m}^{-3})(0.4)}$$

$$= 0.11 \text{ m s}^{-1}$$

recalculate N_{Re} for current velocity

$$N_{Re} = (D u \rho) / \mu$$

$$= (3.4 \times 10^{-3} \text{ m})(0.11 \text{ m s}^{-1})(1000 \text{ kg m}^{-3}) / (0.66 \times 10^{-3} \text{ Pa s})$$

$$= 567$$

ii) when $N_{Re} < 1000$, C can be determined using the following correction formula from Perry (1984) page 5-63:

$$C = \frac{24}{N_{Re}} (1 + 0.14(N_{Re})^{0.70})$$

$$= \frac{24}{567} (1 + 0.14(567)^{0.70})$$

$$= 0.54$$

recalculate u:

$$u = \frac{\left[4 g D \Delta p \right]^{1/2}}{\left[3 \rho C \right]} \quad 3.3$$

$$u = \frac{\left[4(9.8 \text{ m s}^{-2})(3.4 \times 10^{-3} \text{ m})(100 \text{ kg m}^{-3}) \right]^{1/2}}{\left[3(1000 \text{ kg m}^{-3})(0.54) \right]}$$

$$= 0.091 \text{ m s}^{-1}$$

recalculate N_{Re} for current velocity

$$N_{Re} = (D u \rho) / \mu$$

$$= (3.4 \times 10^{-3} \text{ m})(0.091 \text{ m s}^{-1})(1000 \text{ kg m}^{-3}) / (0.66 \times 10^{-3} \text{ Pa s})$$

$$= 469$$

iii) when $2 < N_{Re} < 500$ C can be determined using the following correction formula from Griskey (1979):

$$C = \frac{18.5}{(N_{Re})^{0.6}}$$

$$= 0.46$$

recalculate u :

$$u = \left[\frac{4 g D \Delta \rho}{3 \rho C} \right]^{1/2} \quad 3.3$$

$$u = \left[\frac{4(9.8 \text{ m s}^{-2})(3.4 \times 10^{-3} \text{ m})(100 \text{ kg m}^{-3})}{3(1000 \text{ kg m}^{-3})(0.46)} \right]^{1/2}$$

$$= 0.099 \text{ m s}^{-1}$$

recalculate N_{Re} for current velocity

$$N_{Re} = (D u \rho) / \mu$$

$$= (3.4 \times 10^{-3} \text{ m})(0.099 \text{ m s}^{-1})(1000 \text{ kg m}^{-3}) / (0.66 \times 10^{-3} \text{ Pa s})$$

$$= 510$$

II.E Calculation of rate of mass transfer using the following equations from chapter 3.

$$\text{rate of mass transfer, } N = k_c \Delta C_{\text{PCP}} A_s \quad 3.4$$

$$k_c = \text{mass transfer coefficient} = 1.13 [u(D_{AB}/D)]^{1/2} \quad 3.5$$

u = terminal steady velocity = 0.10 m s^{-1} ; chosen as a typical value based on those calculated above in appendix II.D

D_{AB} = diffusion rate of PCP through water = $1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; see page 64

D = drubble diameter = $3.4 \times 10^{-3} \text{ m}$; calculated in II.B

$$\Delta C_{\text{PCP}} = \text{change in PCP concentration} = C_{\text{PCP, aq}} - C_{\text{PCP, SF}}$$

$$= C_{\text{PCP, aq}} \text{ initially}$$

$$= 100 \text{ ppb}$$

$$= 3.70 \times 10^{-4} \text{ mol m}^{-3}$$

$$A_s = \text{area available for mass transfer} = (Q/V) (h/u) A \quad 3.6$$

$$Q = \text{overall SF flow} = 1 \text{ mL min}^{-1} = (10^{-6} / 60) \text{ m}^3 \text{ s}^{-1}; \text{ typical flow rate}$$

$$V = \text{drubble volume} = 4/3(\pi)(D/2)^3 = 1.8 \times 10^{-8} \text{ m}^3$$

$$h = \text{height of water column} = 0.10 \text{ m}; \text{ determined by measurement}$$

u = terminal steady velocity = 0.10 m s^{-1} ; chosen as a typical value based on those calculated above in appendix II.D

$$A = \text{drubble area} = 4\pi(D/2)^2 = 1.7 \times 10^{-5} \text{ m}^2$$

combining 3.4, 3.5, 3.6:

$$N = 1.13 [u(D_{AB}/D)]^{1/2} \Delta C_{PCP} (Q/V) (h/u) A$$

substituting in values from previous page:

$$= \frac{1.13 [(0.10\text{ms}^{-1})(1.0 \times 10^{-9}\text{ms}^{-1})]^{1/2} \times [3.7 \times 10^{-4}\text{mol m}^{-3}]}{3.4 \times 10^{-3}\text{m}} \times \frac{10^{-6}\text{m}^3\text{s}^{-1} \ 0.10\text{m} \ 1.7 \times 10^{-5}\text{m}^2}{60 (1.8 \times 10^{-8}\text{m}^3) (0.10\text{ms}^{-1})}$$

$$= 1.1 \times 10^{-12} \text{mol s}^{-1}$$

APPENDIX III

SAMPLE EXPERIMENTAL CALCULATION

The average area is determined from repeat HPLC injections of the same sample:

$$\begin{aligned}
 A_{\text{AVG}} &= \frac{(A_1 + A_2 + A_3 + A_4)}{4} \\
 &= \frac{(19\,816 + 19\,627 + 20\,025 + 20\,389)}{4} \\
 &= 19\,964 \text{ counts}
 \end{aligned}$$

The average area is used to determine the extract concentration from the calibration curve:

$$\text{extract concentration} = 1.05 \mu\text{g mL}^{-1}$$

The extract concentration is multiplied by the extract volume to give the total amount of analyte extracted:

$$\begin{aligned}
 \text{amount extracted} &= 1.05 \mu\text{g mL}^{-1} (3.00 \text{ mL}) \\
 &= 3.17 \mu\text{g}
 \end{aligned}$$

This total amount extracted would then be averaged for the number of replicate extractions. The error in the total amount extracted was calculated as the standard deviation of the averaged extraction results.

$$\begin{aligned}
 \text{Tot}_{\text{AVG}} &= \frac{(E_1 + E_2 + E_3)}{3} \\
 &= \frac{(3.17 + 3.30 + 3.58)}{3} \\
 &= 3.35
 \end{aligned}$$

$$\text{sd} = 0.15$$

APPENDIX IV

EXPERIMENTAL DATA

IV.A Data corresponding to figure 5.1:

Volume CO ₂ (mL)	Percent Recovery (individual runs)	Average Percent Recovery	rsd
6.6 ± 1.0	27.0 33.0 29.0	30.0 ± 2.2	7.3
12.6 ± 1.0	51.0 58.3 52.5	53.9 ± 2.7	5.0
18.8 ± 1.0	87.4 70.5 75.6	77.8 ± 6.1	7.8
28.5 ± 1.0	105 95 97	99 ± 5.1	5.2

IV.B Data corresponding to figure 5.2:

Flow CO ₂ mL min ⁻¹	Percent Recovery (individual runs)	Average Percent Recovery	rsd
0.3 ± 0.03	38.1 33.9	36.2 ± 1.5	4.1
0.4 ± 0.03	48.0 42.5	45.3 ± 2.0	4.4
0.6 ± 0.03	69.0 62.0	65.5 ± 2.5	3.8
0.8 ± 0.04	82.1 73.9	78.0 ± 2.8	3.6
1.3 ± 0.09	108.0 97.0	102.5 ± 4.0	3.9

IV.C Data corresponding to figure 5.3:

0.64 g mL ⁻¹		0.76 g mL ⁻¹		0.90 g mL ⁻¹	
flow mL min ⁻¹	average percent recovery	flow mL min ⁻¹	average percent recovery	flow mL min ⁻¹	average percent recovery
0.16	55	0.22	47	0.19	54
0.60	37.1	0.71	45	0.41	47
0.98	45	1.3	40	0.94	55.5
		1.8	50	1.7	46.5

IV.D Data corresponding to table 5.6:

Analyte	Percent Recovery Run 1	Percent Recovery Run 2	Percent Recovery Run 3
PCP	95	105	91
2,4,6-TCP	57	52	48
Dieldrin	106	94	95
DDT	79	90	88