LIQUID COLLECTION EFFICIENCIES AFTER SUPERCRITICAL FLUID EXTRACTION

by

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(ABSTRACT)

The design of any supercritical fluid extraction (SFE) experiment should break down into two parts: 1) removal of the analytes of interest from the bulk matrix and 2) deposition of those analytes in a user friendly manner for further studies (spectroscopy or chromatography). While great attention has been paid to the extraction of analytes, less attention has been paid for their efficient collection after extraction. Currently solid phase trapping and liquid trapping are available for off-line collection of analytes after SFE.

A polarity test mix consisting of acetophenone, *N,N*-dimethylaniline, naphthalene, *n*-decanoic acid, 2-naphthol, and *n*-tetracosane was spiked onto sand and extracted with supercritical carbon dioxide to evaluate the collection efficiency of various solvents and solvent mixtures. Nine single collection solvents and four mixed collection solvent systems were studied. When one-component collection solvents were employed, quantitative (above 90%) recovery of all analytes was not possible. With mixed collection solvents, recoveries of 90% or better with all analytes were possible.

Additional studies were performed with carbon dioxide modified with 1, or 4% acetonitrile or 1, 4, or 8% methanol or toluene. With these extraction fluids, quantitative collection of the analytes with a mixed collection solvent was not possible, but excellent collection efficiencies were observed for hexane and methanol collection.

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There are many people who should be thanked for all their help along the way. First, I would like to thank my mom for all of her support along the way. She may not have understood all of the chemistry involved, but she was very much interested in seeing me succeed. I would have liked to have had my father and stepfather present when this thesis was signed, but hopefully they have gotten the word. I would like to thank Dr. Taylor for all of his support over the years. I would also like to thank my committee members for their support. To Dr. Taylor's research group, a big thank you. Last, but certainly not least, I would like to thank Phyllis for keeping me sane at the end of all of this work.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1
INTRODUCTION

PROPERTIES OF SUPERCRITICAL FLUIDS:

A supercritical fluid has been described as any substance that is above its critical parameters. The critical temperature, Tc, is defined as the maximum temperature at which a gas can be converted to a liquid by an increase in pressure. The critical pressure, Pc, is defined as the maximum pressure at which a liquid can be converted to a gas by an increase in temperature. **Figure 1** shows the phase diagram of a single component system. As can be seen, once the critical point has been reached, there exists a thermodynamic state in which the gaseous and liquid phases of a substance are indistinguishable. This is unlike the triple point of a substance in which a solid, liquid, and a gas phase exist in equilibrium, but, in three different phases.

Supercritical fluids possess some unique properties which make them attractive for use in separation processes. Diffusion, viscosity, and density of supercritical fluids fall between the values of liquids and gases, **Table I**. Diffusivity in supercritical fluids is higher than in liquids, this leads to more rapid equilibration and extraction of analytes from the bulk matrix. The lower viscosity of supercritical fluids compared to liquids leads to improved mass transfer of analytes between the bulk matrix to the solvent (fluid). This leads to faster, and possibly more efficient extractions compared to classical liquid extractions, due to a more complete penetration of the

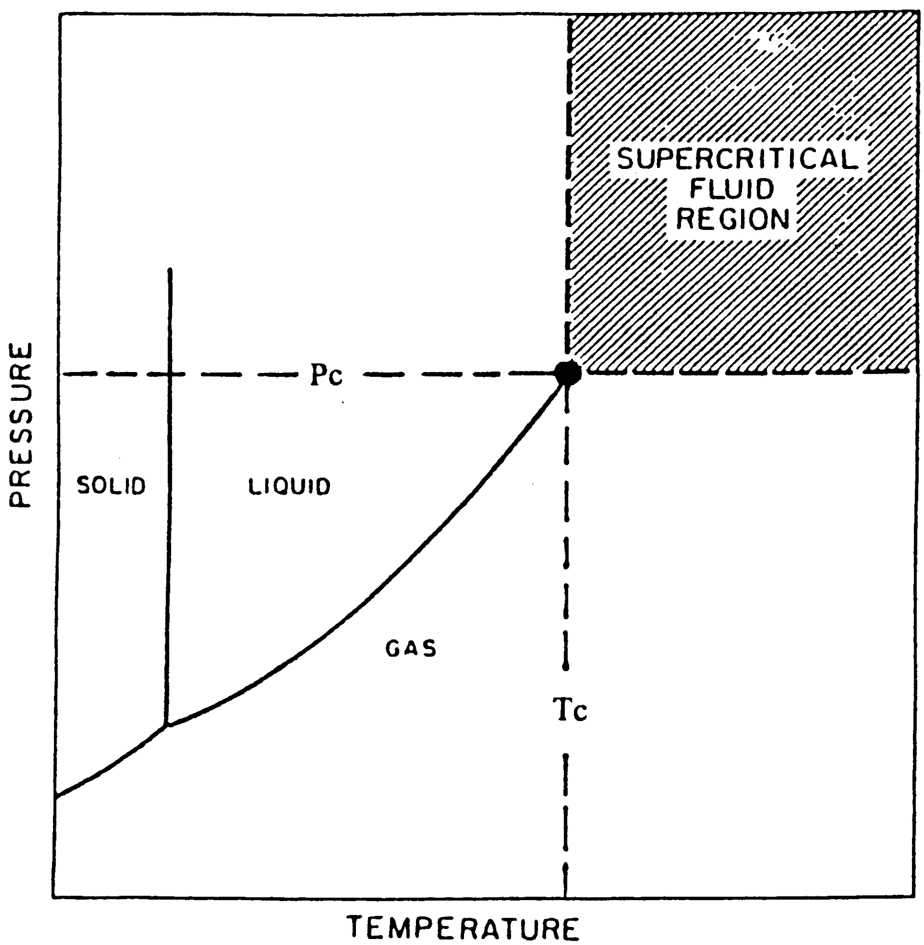


FIGURE 1:

SINGLE COMPONENT PHASE DIAGRAM

TABLE I*

SUPERCRITICAL FLUID PROPERTIES

Mobile Phase	Density (g/mL)	Viscosity (poise)	Diffusivity (cm^2 / s)
Gas	0.001	0.00005 - 0.00035	0.01 - 1.0
Supercritical Fluid#	0.2 - 0.9	0.0002 - 0.001	0.00033 - 0.00001
Liquid	0.8 - 1.0	0.003 - 0.024	0.000005 - 0.00002

* Reference #1

Typical range of values.

matrix. The densities of supercritical fluids, at high pressure and low temperature, are comparable to liquids. This property (density) is the closest to solvating strength. Solvating power, diffusivity and viscosity are functions of the density of the supercritical fluid. Unlike liquids, supercritical fluid densities can be changed easily. Supercritical fluids have densities that are 100 to 1000 times greater than gases, which should give supercritical fluids solvating powers close to liquids. Positive density programming can be brought about in two different ways; by increasing the pressure and/or by decreasing the temperature. **Figure 2** shows this effect for various pressures and temperatures for CO_2. By following an isotherm, it can clearly be seen that as the pressure is increased, the density of CO_2 increases. The largest change is brought about when the supercritical fluid is held near its critical temperature. By following an isobar, it can be seen that by keeping a constant pressure but increasing the temperature, the density of the supercritical fluid drops. Another unique aspect of supercritical fluids is that they possess no surface tension. This helps in permeating matrices to remove analytes not bound to the surface.

COLLECTION OPTIMIZATION:

The design of supercritical fluid extraction experiments should be divided into two parts, the removal of the analytes of interest from the bulk matrix and the accumulation of the analytes in a user friendly manner for

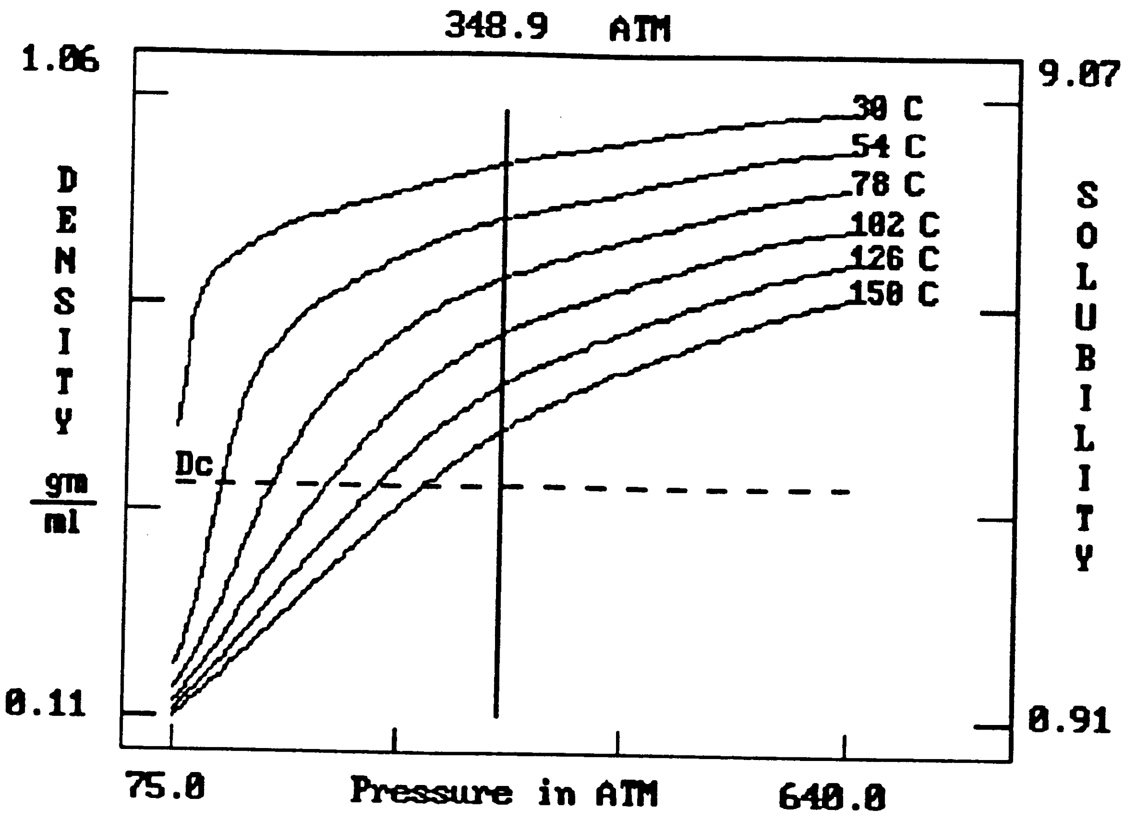


FIGURE 2:

PRESSURE AND TEMPERATURE EFFECTS ON CARBON DIOXIDE DENSITY (Reference #2) detection, identification, and quantification. There are many ways to go about optimizing the extraction of analytes. Several articles have been published describing statistical optimization of SFE experiments (*3 - 9*). These papers do not however discuss how to optimize the trapping of the analytes. Even though extraction parameters may be optimized, if the collection system is not efficient then valuable information could be lost.

After SFE, collection of the analytes can either be on-line or off-line. SFE has been coupled to several chromatographic techniques for on-line collection. SFE has been interfaced with high performance liquid chromatography HPLC (*10 - 13*). This seems to be the most difficult of methods to combine. This is noted by the relatively few articles published for this hyphenated technique. Articles describing SFE interfaced to GC have been published since 1986 (*14 - 20*). There have been numerous reports of on-line SFE coupled to SFC (*21 - 24*). Both Suprex and Dionex offer on-line SFE/SFC systems for sale.

For off-line collection of analytes after SFE, there are currently two choices: (a) trapping on solid inert or sorbent matrices and then flushing with solvents and (b) liquid solvent collection. There have been several articles describing collection problems or pitfalls and solutions to overcome them (*25 - 38*). *Wright et al.* looked at the comparison of trapping efficiencies between collecting analytes in an open 100 mL volumetric flask cooled to 0 °C and in a sealed 100 mL volumetric collection flask cooled by liquid nitrogen (*25*). A 50 μm stainless steel restrictor, heated by an electrical current, was used to allow the CO_2 to decompress. Several

PAH's (polynuclear aromatic hydrocarbons) were used (chrysene, benzanthrone, 1-nitropyrene, dibenzo[*a,i*]carbazole, coronene, rubrene) to study the collection efficiencies. The open flask recoveries ranged from a high of 8.2% for coronene to a low of 0% for rubrene. When the collection flask was closed and cooled by liquid nitrogen, recoveries were from 95% for dibenzo[*a,i*]carbazole to a low of 25% for rubrene (*25*). Rubrene recoveries are probably low due to incomplete extraction from the matrix, which was XAD-2 resin. These data suggest that cooling the collection flask and sealing the collection flask are very important for good analyte recovery. *Sandra* and coworkers in Belgium wrote an article entitled "*Recovery Studies by Off-Line SFE*" (*26*). They have pointed out that several factors should be kept in mind when extracting and collecting analytes: 1) density of CO_2 used for extraction, 2) polarity of supercritical fluid, 3) volume of supercritical fluid per unit time, flow rate, 4) volume and dimensions of extraction vessel, 5) extraction time, 6) sample amount, particle size, pore structure of solid material, and 7) matrix to which analytes are bound. *McNair* and *Frazier (27)* looked at 3 PAH's (anthracene, chrysene, benzo[a]pyrene) and 2 pesticides (dursban, pentachlorophenol) to study liquid collection. For their study they used a 50 µm tapered fused silica restrictor, which was heated by nichrome wire, and placed in a collection vial containing methylene chloride. A solvent pump was used to introduce methylene chloride into the collection vessel at a rate of 20 µ L/min to replace methylene chloride lost from the trap by evaporation. When an empty collection vial was used, recoveries for the analytes ranged from a high of 32% for anthracene to a low of 6% for dursban. When methylene chloride was used as a collection solvent, recoveries ranged from a low of 75% for dursban to a high of 97% for anthracene (*27*). These data show the importance of liquid collection compared to an empty collection trap.

Thomson and *Chesney* (*28*) used a 0.02 in I.D. stainless steel crimped tube as a restrictor and studied CO_2 flow rates when extracting triticale straw, barley straw, triticale seed, and barley seed. They used a solvent flush of the restrictor to prevent plugging. Before the collection vial, a tee was placed in line and the CO_2 flow could be turned off to allow a solvent flush of the restrictor, and then the CO_2 flow was continued. When no solvent flush was used, the restrictors would plug, which is common for high organic content compounds and stainless steel restrictors. Iso-octane was the solvent flush and the collection solvent. This system solved their restrictor plugging problems.

Hawthorne and coworkers at the University of North Dakota have studied collection efficiencies for 66 semi-volatile pollutants and fragrance/flavor compounds (*29*). Methylene chloride, chloroform, acetone, methanol, and hexane were studied as collection solvents when mild heating of the 26 μm fused silica restrictor was used to prevent plugging . Acetone, chloroform, and methylene chloride yielded similar recoveries with analyte loses of 10 to 25% (*29*). Methanol showed analyte loses of 35 to 50 % and hexane was the poorest solvent for the more volatile components. It, however, showed better recoveries of higher weight components than methanol, but not as good as acetone, chloroform, or methylene chloride. A temperature controlled aluminum block, to keep the collection solvent at 5 °C, was used to prevent restrictor plugging and to remove the need to externally heat the restrictors. With this design, recoveries ranging from 92 to 104% with RSD's of 6% or less for the pollutants were achieved when methylene chloride was used as the collection solvent which was the only solvent tested (*29*). These data suggest that keeping the collection solvent cool is important for good analyte trapping.

Dionex Corporation studied liquid collection of analytes after decompression through linear restrictors (*30*). With their design, the restrictor was not in direct contact with the collection solvent. This is the same set-up as employed by the Dionex SFE-723 extractor described in the next chapter. Their results showed that higher solvent volumes were beneficial to analyte recovery. Heating the restrictors to prevent plugging and analyte condensation in the restrictor was also important in analyte recovery. They showed that a cool collection solvent improved analyte collection as opposed to solvents at room temperature or higher, which agrees with the work done by *Hawthorne, et al.* (*29*).

Suprex Corporation has published a series of articles dealing with collection of analytes after supercritical fluid extraction (*31 - 33*). In their studies they compared collection efficiencies under three different trapping schemes: 1) collection into an empty vial after depressurizing the CO_2 through a 50 μm fused silica linear restrictor, 2) collection in 2 mL methylene chloride using the fused silica linear restrictor, and 3) collection on a cryogenically cooled trap filled with glass beads using a DuraFlow (i.e. plastic) restrictor. A range of PAH's were used to study the traps (1-methyl naphthalene, 2-methyl naphthalene, 1-methyl fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and chrysene). Collection in the dry vial resulted in recoveries from a low of 5% for both methyl naphthalenes to a high of 23% for chrysene. Collecting in methylene chloride modestly improved recoveries from a low of 19% for the methyl naphthalenes to a high of 38% for pyrene. The cyrogenically cooled trap of glass beads at a temperature of -30°C showed recoveries from a low of 93% for both methylnaphthalenes to a high of 107% recovery of chrysene. A study was done to see if the rinse solvent played any effect on recoveries of the analytes. With a solid phase trap, analytes are deposited onto the trap when the CO_2 decompresses and the analytes must be rinsed off of the trap into a collection vial if further analysis is to be performed. Once again, PAH's were studied and methylene chloride and methanol were used as rinse solvents to remove the analytes from the cryogenically cooled glass beads. The recoveries of the PAH's with a methylene chloride rinse solvent were 93% for the methyl naphthalenes for a low to 107% recovery of chrysene for a high. When methanol was employed as the rinse solvent, recoveries dropped to 51% for chrysene for a low to 104% for a high for 1- methyl fluorene. All other recoveries were below 87%. Another factor considered in this study was the temperature of the trap, which could be cooled from 40 to - 50 °C. A range of hydrocarbons (C_{10}, C_{15}, C_{20}, C_{28}, C_{40}) was used to study trap temperature effects. When the trap was cooled to - 20 °C, recovery of C_{10} was only 15% while the other hydrocarbons had recoveries of 87 to 96%. With a decrease in trap temperature to -45 °C, recovery of C_{10} was 75% with all other analytes studied at 89 to 95% recovery. Besides considering the temperature of the trap when depositing the analytes onto the trap, trap temperature when rinsing with a solvent to remove the analytes must be taken into account. Suprex showed that recovery of C_{36} improved from 32% at a trap desorption temperature (when rinsing with methylene chloride) of - 10 °C to 97% recovery at a trap desorption temperature of 35 °C (*32*). These data show that for solid phase trapping, trap temperature during analyte deposition and trap temperature during analyte desorption with the rinse solvent are critical.

Hawthorne and *McNally* recently studied the feasibility of performing solventless collection of analytes, by rapidly depressurizing CO_2 after a static extraction (*34*). In this case a dynamic extraction could not be performed and only analytes highly soluble in the extraction fluid and not tightly bound to a matrix could be extracted and collected quantitatively.

Mulcahey has studied a number of compounds varying in polarity when evaluating trapping efficiencies on solid phase extraction (SPE) tubes (*35*) packed with phenyl, octyl, diol, cyano, and amino bonded silicas. A polarity test mix containing acetophenone, *N,N*-dimethylaniline, *n*-decanoic acid, 2-naphthol, and *n*-tetracosane (C_{24}) was employed. *Mulcahey* used a sample loop, with sufficient dead volume to insure analytes were solubilized in the CO_2 and mixed thoroughly prior to introduction of analytes to the solid matrix trap. The sample loop was used to introduce 50 μL of a 1 mg/mL per analyte solution to the CO_2 stream, this resulted in 50 μg of each analyte introduced into the system. Trap temperature was kept at - 20 ^oC. When reversed-phase traps (octyl and phenyl) were studied, recoveries of decanoic acid were never greater than 55%. The diol SPE trap yielded recoveries in the low 70%'s for acetophenone and *N,N*-dimethylaniline, 28% for decanoic acid, and quantitative recovery (greater than 90%) for 2-naphthol and C_{24}. When a cyano trap was studied the recoveries of the light components (acetophenone and *N,N*-dimethylaniline) improved and reached 80 and 83% respectively, while the heavier components (2-naphthol and C_{24}) dropped in recovery to 85 and 84%. The amino SPE trap showed the worst recoveries for any of the normal-phase traps studied. These data suggest that trap composition can play a role in analyte recovery.

Later *Mulcahey* evaluated a commercial extraction system (Hewlett Packard 7680A SFE) employing both stainless steel and octadecylsilica (ODS) solid matrix traps (*36*). *Mulcahey* employed the same polarity test mix to study these two traps. Once again, a sample loop was used to introduce the analytes to the trap. The analytes were introduced, again, at 50 μg per component. In these experiments, the traps were tested at different temperatures ranging from 5 to 80 ^oC. When ODS was employed as a solid matrix trap for the polarity mixture studied, complete recovery of all analytes was not possible with 100% CO_2 at any one given trap condition (*36*). Acetophenone and *N,N*-dimethylaniline were only quantitatively recovered when a trap temperature of 20 ^{o}C or lower was employed. Decanoic acid was only efficiently trapped and recovered when a trap temperature of 80 ^{o}C was used. 2-Naphthol and C_{24} were effectively trapped and quantitatively recovered at all trap temperatures studied. Recoveries of the analytes when a stainless steel trap was employed were lower than those obtained with an ODS trap (*36*). The more volatile analytes, acetophenone and *N,N*-dimethylaniline, never had a recovery greater than 12% at any trap temperature studied. Decanoic acid had recoveries ranging from 26% to 59%. 2-Naphthol had recoveries ranging from 78% to 89%. C_{24} was quantitatively recovered (93% to 99%) at all trap temperatures. These data back up Suprex's data stating that trap deposition and desorption are important for quantitative extraction.

Yoo and *Taylor* looked at the same analytes and also used the Hewlett Packard SFE to study trapping efficiencies of several solid phase traps (*37*). For this study, a solution of acetophenone, *N,N*-dimethylaniline, naphthalene, 2-naphthol, and C_{24} was prepared in acetone and spiked onto Ottawa cement testing sand. The following instrumental conditions were used, CO_2 flow of 2 mL/min at a density of 0.8 g/mL (340 bar or 336 atm at a temperature of 75 °C) for 15 minutes. Restrictor (HP calls it a nozzle) temperature was 50 °C. The solid phase trap was at 30 °C for analyte desorption and an acetone rinse was used (1.5 mL total rinse solvent). Three different traps were investigated, cyanopropyl bonded silica, diol bonded silica, and Tenax®. The trapping temperature was also investigated at 5, 30 and 60 °C. When cyanopropyl was employed as a trap, only *N,N*-

dimethylaniline gave a recovery below 90% (recovery was 50%) when the trap was at a temperature of 5 °C. When the trap was raised to 60 °C, recoveries of acetophenone, *N,N*-dimethylaniline, and naphthalene declined to 10, 20, and 5% respectively. When diol was used as a trap, recovery of all analytes at all temperatures was 95% or greater except for *N,N*-dimethylaniline which had recoveries of 60, 70, and 70% at 5, 30 and 60 °C respectively. This trend is followed for the Tenax® trap. Recovery of all analytes was 90% or greater at all temperatures except, once again, for *N,N*-dimethylaniline, which had recoveries of 60, 30, and 35% for trap temperatures of 5, 30, and 60 °C respectively. Recovery of *N,N*-dimethylaniline was never greater than 70% for any trap studied at any temperature studied. It is possible that the conditions used for extraction were not strong enough to extract quantitatively *N,N*-dimethylaniline off of the sand. The general trapping trend that was followed was, cooler trap temperatures showed better recoveries off of all the traps.

Thomas, Taylor, Levy, and *Cardimone* studied these same analytes using a Suprex extractor and solid phase trapping (*38*). In this study, extraction conditions were, CO_2 flow of 2 mL/min at a density of 0.9 g/mL (435 atm at a temperature of 65 °C) for 15 minutes. Once again, the analytes were extracted off sand. Three different traps were investigated, stainless steel balls, Unibeads (amorphous fused silica) and a 50/50 mixture (by weight) of C_{18} and Unibeads. Trap temperatures of 5, 25, 45, 65 and 85 °C were studied. Traps were rinsed with 1.7 mL of methylene chloride three times and the rinses combined and then analyzed by GC. The trap temperature was held at 25 °C when rinsing. When the Unibead trap was investigated, acetophenone and *N,N*-dimethylaniline recoveries were never greater than 16% at any temperature. At 5 °C, recovery of naphthalene was 84%, at higher trap temperatures, recovery dropped to below 35%. When stainless steel balls were used as a trap, recoveries of acetophenone, *N,N*-dimethylaniline, and naphthalene ranged from a high of 20% to a low of 1% at the trap temperatures studied. 2-Naphthol recoveries ranged from a low of 73% to a high of 83%, depending on the trap temperature. When the mixed trap was investigated, recoveries of acetophenone and *N,N*-dimethylaniline ranged from 34% to 75% over the trap temperature range studied. 2-Naphthol recoveries ranged from 67 to 77%. Recovery of C_{24} was always above 90% at every trap temperature studied and every trap composition studied.

As was pointed out above, quantitative recovery of all analytes of the polarity mix was not possible on any of the solid phase traps at any one condition previously studied (trap/rinse solvent/trap temperature) by *Mulcahey* (*35,36*). To mimic the simulated extractions done by *Mulcahey* (*35,36*), the Dionex-723 was replumbed by *Ezzel* at Dionex, to closely match *Mulcahey's* experiment (*39*). A sample loop was employed, using a 1 mL extraction cell to provide sufficient dead volume, to introduce 50 µL of a 1 mg/mL per analyte solution to the carbon dioxide stream, resulting in 50 µg of each analyte in the system. The oven was maintained at 75 °C and a pressure of 300 atmospheres was used to produce a CO_2 density of 0.77 g/mL. A restrictor heated to 80 °C was used to maintain a flow rate of

1200 - 1300 mL/min expanded CO_2, or approximately 2 - 2.4 mL/ min liquid CO_2 flow.

The Dionex-723 trap employs a solid glass surface and a liquid collection solvent for tandem trapping, **Figure 3**. The analytes and CO_2 exiting the restrictor first contact a glass transfer tube (6-mm I.D.) and then are bubbled through the collection solvent. Dionex has previously performed studies to see if different transfer tube geometries would affect trapping efficiencies; spiral, tapered, bent tubes, and tubes with frits or screens were tested and none of these configurations showed any improvements over the straight tube (*30*). Approximately 10 psi of backpressure is maintained in the collection vial from the flow meters. An outlet vent, not shown in **Figure 3**, leads to gas flow meters, which measure the decompressed CO_2 flows for each extraction vessel.

Table II shows the recovery of the analytes in the three traps investigated (*39*). Trap 1 was an empty vial that was cooled to 5 °C. Only acetophenone and *N,N*-dimethylaniline had recoveries below 90 %. These two analytes are the most volatile of the analytes studied and are not quantitatively trapped without the presence of a liquid collection solvent. When 1 mL of chloroform was added to the trap (Trap 2) over 90 % recoveries for all analytes was realized. When 5 mL of chloroform was added to the trap (Trap 3) the recoveries were identical to Trap 2. It is possible that the analytes, when introduced into the liquid trap in this manner, are never solubilized into the supercritical CO_2 phase, but rather remain associated with the 50 µL of methylene chloride in which they were

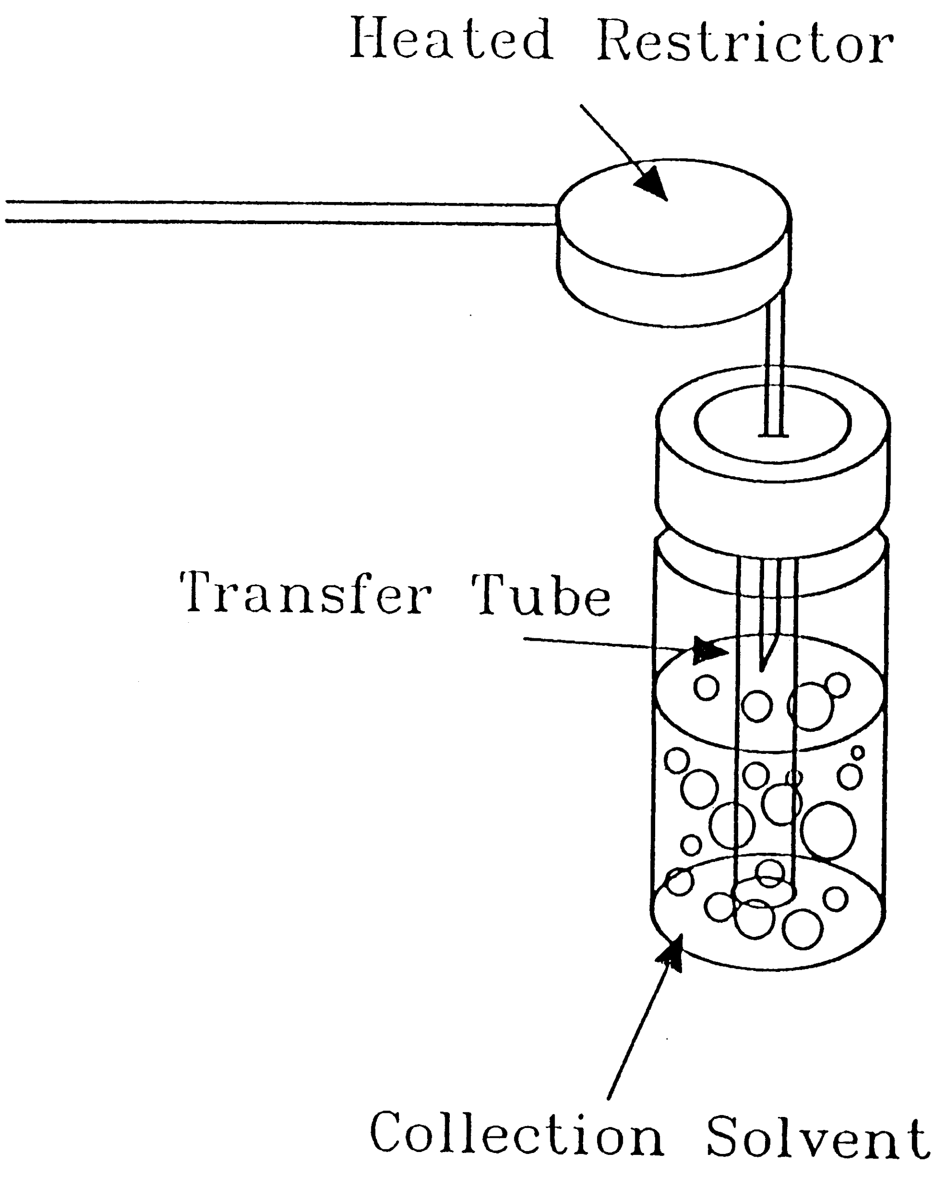


FIGURE 3:

COLLECTION TRAP EMPLOYED ON DIONEX-723

TABLE II

ON-LINE ANALYTE RECOVERY BY EZZEL[#]

ANALYTE	TRAP 1 [(a)]	TRAP 2 [(b)]	TRAP 3 [(c)]
Acetophenone	85 % (1.1)	93 % (3.1)	92 % (2.8)
N,N-Dimethylaniline	77 % (3.2)	91 % (2.9)	88 % (7)
Decanoic Acid	100 % (2.3)	103 % (2.0)	101 % (7.4)
2-Naphthol	101 % (0.5)	100 % (4.0)	99 % (5.2)
n-Tetracosane	101 % (6.1)	98 % (7.0)	104 % (8.5)

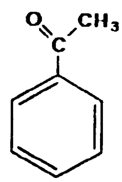
a) Empty Vial
b) 1 mL Chloroform
c) 5 mL Chloroform
Numbers in parenthesis are RSD's (n=3).

introduced into the system, and simply fall out onto the cold vial surface (*39*). This theory is backed up with experiments, in this thesis, where the analytes were spiked onto sand and then extracted for 30 minutes and collected in 5 mL of chloroform. In this case acetophenone, *N,N*-dimethylaniline, and naphthalene recoveries were all below 50%. If this hypothesis is correct, this system does not accurately simulate real extraction conditions. Therefore evaluations of trapping conditions via the recoveries of standards spiked onto a solid matrix have been performed, and are described in this thesis which should simulate a "real" extraction more closely.

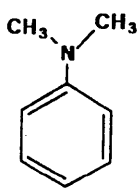
Since a single solid phase trap can not trap quantitatively all of the analytes in the polarity mix, from spikes onto sand or via a sample loop, at any given temperature, the goal of our study was to evaluate the use of liquid trapping for quantitative analyte recovery of the polarity mix. The polarity test mix used by *Mulcahey*, with the addition of naphthalene, was employed for this study, **Table III** shows the physical properties of the analytes. Single component and multi-component trapping solvents were employed.

TABLE III

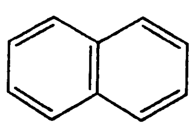
ANALYTE PHYSICAL PROPERTIES *



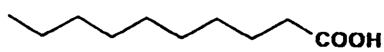
ACETOPHENONE MW = 120.15
m.p. = 20.5 °C
b.p. = 202 °C
Soluble — Organic Solvents



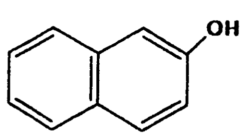
N,N-DIMETHYLANILINE MW = 121.18
m.p. = 2 °C
b.p. = 193 °C
Soluble — Alcohol, Ether, Chloroform



NAPHTHALENE MW = 128.16
m.p. = 80.2 °C
b.p. = 218 °C
Soluble — Benzene, Alcohol, Ether, Chloroform



DECANOIC ACID MW = 172.26
m.p. = 31.4 °C
b. p. = 270 °C
Soluble — Ethanol, Chloroform, Benzene, Carbon Disulfide, Ether



2-NAPHTHOL MW = 144.16
m.p. = 122 °C
b.p. = 285 °C
Soluble — Alcohol, Ether, Chloroform, Oils

TETRACOSANE $CH_3(CH_2)_{22}CH_3$ MW = 338.66
m.p. = 51.1 °C
b.p. = 391 °C
Soluble — Alcohol, Chloroform

* Properties from reference #43: the Merck Index.

CHAPTER 2

LIQUID COLLECTION EFFICIENCIES AFTER EXTRACTION WITH 100% CARBON DIOXIDE

EXPERIMENTAL:

EXTRACTION:

The extractions were performed on a multi-vessel Dionex SFE-723 supercritical fluid extractor (Dionex Corporation, Sunnyvale, CA). **Figure 4** shows the schematic of the Dionex-723 which can run eight extractions simultaneously. Carbon dioxide (SFE/SFC grade) with helium headspace (2000 psi) was obtained from both Air Products and Chemicals (Allentown, PA) and Scott Specialty Gases (Plumsteadville, PA) in aluminum cylinders (39 pounds).

Approximately 5.6 grams of Ottawa Cement Testing Sand (Fisher Scientific, Houston, TX) was placed in a 3.5 mL Keystone Scientific extraction vessel (Bellefonte, PA). The sand was used as received and no clean-up steps or preliminary extractions were performed. A spiking solution of acetophenone, *N,N*-dimethylaniline, naphthalene, *n*-decanoic acid, 2-naphthol, and *n*-tetracosane (C_{24}) was prepared in methylene chloride (all analytes were purchased from Aldrich Chemical Company, Milwaukee, WI). A solution of the polarity test mix, approximately 7 mg/mL

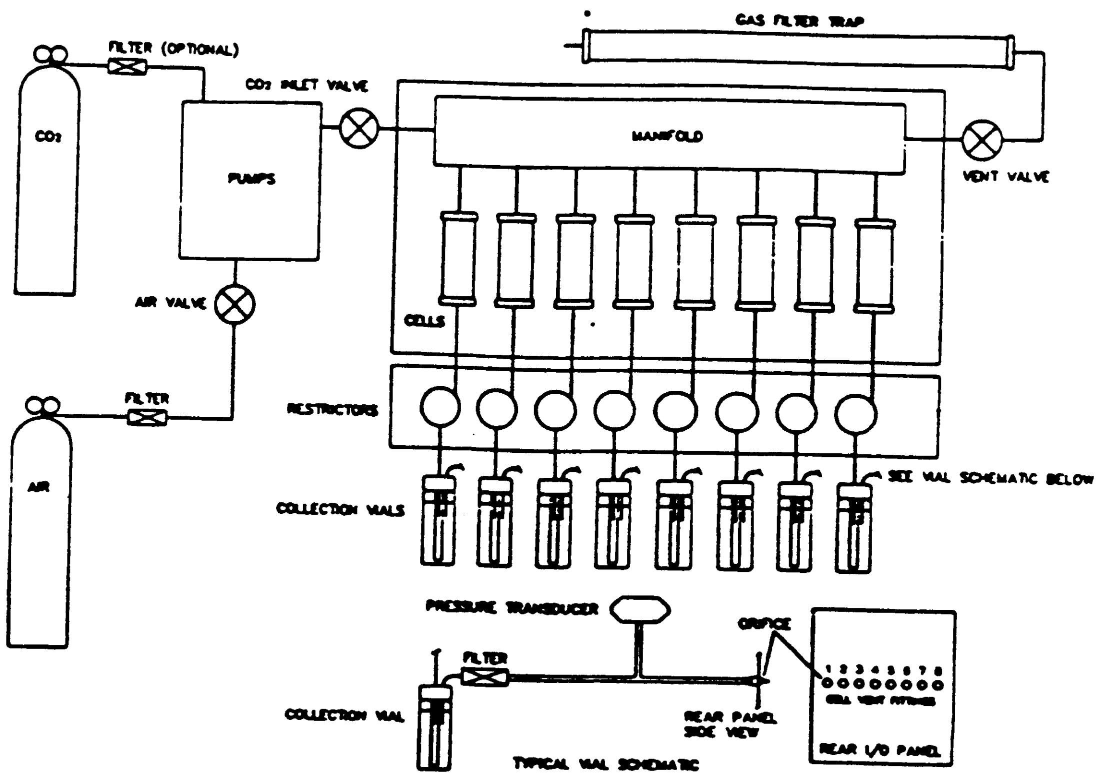


FIGURE 4:

DIONEX-723 SCHEMATIC

per component (7000 ppm), was then spiked onto the sand (100 μL spike volume) to yield 700 μg of each component.

All extractions were performed at an oven temperature of 35 °C. The total extraction time was 30 minutes, 10 minutes at a CO_2 pressure of 150 atmospheres (0.83 g/mL CO_2 density) and then 20 minutes at 340 atmospheres (0.95 g/mL CO_2 density). The fixed restrictors, rated at 250 mL/min decompressed CO_2 flow, were heated to 125 °C. The extracts were collected in 15 mL of the various solvents, each of which was thermostatted to 5 °C, via peltier cooling chips in the Dionex-723. All solvents (acetone, acetonitrile, carbon tetrachloride, chloroform, cyclohexane, hexane, methanol, and methylene chloride) were from Fisher Scientific and were ACS grade or better, except for IR grade tetrachloroethylene (*i.e.* perchloroethylene or Perc) which was purchased from Fluka (Ronkonkoma, NY).

EXTRACT ANALYSIS:

After the extraction was completed, the collection vials were removed from the Dionex-723 and sonicated for 5 minutes to help remove any dissolved CO_2 and solid analyte which was trapped on the inner glass tube of the trap. Sonication has been shown to help improve reproducibility for GC injections following off-line SFE (*40*). After sonication, a 100 μL spike of 7000 ppm pyrene internal standard was added to each collection vial, and a portion of the solution was transferred to a gas chromatographic (GC) vial for analysis. To establish an equivalent 100% recovery, 100 μL of the same analyte polarity mix solution was added to an empty collection vial and diluted to 15 mL with the appropriate solvent. The internal standard (100 µL of 7000 ppm pyrene) was added to the solution, and a portion was transferred to a GC vial for analysis. Each standard was run six times and the peak area ratios obtained (peak area of compound/peak area of internal standard) were averaged. The ratios were then used to calculate recoveries for each analyte, each analyte solution was run three times.

The extracts were analyzed by gas chromatography on a Hewlett-Packard (Avondale, PA) 5890 Series II GC equipped with an 7673 autoinjector and a Vectra QS/20 Chemstation. Flame ionization detection was employed. An HP-5 (5%- phenylmethylsiloxane) column (25 m long x 0.2 mm i.d.) with a film thickness of 0.33 µm or a DB-5MS (5%-phenylmethylsiloxane) column (30 m long x 0.25 mm i.d.) with a film thickness of 0.25 µm (J & W Scientific, Folsom, CA) was used. A 1 µL splitless injection was used. After 0.80 minute the purge valve was opened. The initial column temperature was held at 75 °C for 1.5 minutes and ramped to 300 °C at 25 °C per minute. The column headpressure was 15 psi. The injector was held at 275 °C, and the flame ionization detector was held at 325 °C.

Statistical analysis of all of the data consisted of *analysis of variance* (*ANOVA*) and *Tukey* pairwise comparison tests (*41*). Oneway *ANOVA*s were run on each analyte individually to see if there were any differences in collection efficiencies between the different test conditions for all of the tests conducted. *Tukey* pairwise multiple comparison tests, at the 95%

confidence level, were run to determine where the differences in the different test conditions occurred. **Appendix II** shows a sample of an *ANOVA* and a *Tukey* pairwise test, typical results of the statistical tests run are shown. All statistical calculations were run on the student edition of Minitab® release 8 (Minitab, State College, PA) on a Macintosh SE computer (Apple Computer, Cupertino, CA).

There are six main components to a supercritical fluid extractor: 1) fluid tank; 2) pump; 3) oven; 4) extraction vessel; 5) restrictor; 6) analyte collection system. **Figure 4** shows the layout of the Dionex-723 extractor. The pump on the Dionex is a Haskel single piston pump. This is used to pressurize the CO_2 up to the desired setting. The oven is used to control the temperature of the CO_2, extraction vessels and the sample. The oven is large enough to accomadate 8 extraction vessels that can be run in parallel. The oven can be controlled from room temperature up to 150 °C. When vessels larger than 3.5 mL are used, the extractor pump can not run 8 vessels at a time, because the pump can not keep up with the CO_2 demand. Currently there are three choices for restrictors for this instrument rated at 250, 500, or 1200 mL/min decompressed CO_2 flow at 300 atmospheres pressure and 40 °C. The restrictor is used to provide a region for the supercritical CO_2 to depressurize into a gas. The restrictors are either 30, 40, or 50 µm i.d. fused silica housed in a stainless steel case, to provide thermal stability and protection from breakage. Restrictors rated at 250 mL/min (30 µm) were used for all of our studies. After the CO_2 has depressurized the flow is conducted through a cooled collection vial that houses an appropriate solvent.

MATRIX PREPARATION:

Table IV is a listing of the matrices studied. Loading is defined as the total weight of analytes in micrograms spiked onto the matrix divided by the weight of the matrix in grams. The Ottowa Cement Testing Sand, Boileezers, 3mm glass beads, and the silica gel were all from Fisher Scientific (Houston, TX). Celite and the silane treated glass wool were obtained from Supelco (Bellefonte, PA), the wet support matrix was obtained from ISCO (Lincoln, NE), and the glass micro beads were obtained from 3M (Minneapolis, MN). The cotton balls were obtained at a local store (Rose's, Blacksburg, VA). Both Celite and the Isco wet support matrix are diatomaceous earth. The wet support matrix is more granular than Celite. The Celite had been acid washed. Celite, Boileezers, and the Isco wet support matrix were pretreated by heating to 200 °C for 1 hour, to drive off any absorbed water, allowed to cool and then spiked. The cotton balls were pre-extracted under the following conditions: 30 minutes at a CO_2 pressure of 400 atmospheres at an oven temperature of 75 °C (CO_2 density = 0.84 g/mL). The restrictors were held at 175 °C. Approximately 4% of the total weight of the cotton balls were extracted under these conditions. **Figure 5** is the GC trace of the standard analyte solution made up in the 5:5:5 mix (5 mL methanol, 5 mL hexane, and 5 mL chloroform). **Figure 6** is

TABLE IV

MATRIX STUDY

MATRIX	PARTICLE SIZE (mm)	AMOUNT (grams of matrix)	LOADING (wt comp./wt matrix) (μg/g)
Ottowa Sand	0.84 - 0.59	5.59	670
Boileezers		2.20	1700
Celite		1.43	2600
Silica Gel	0.25 - 0.074	1.58	2400
Glass Wool		1.00	3800
Cotton Balls		0.90	4200
ISCO wet support		1.31	2900
Fisher Glass Beads	3	4.68	800
3M Glass Microbeads	0.04	9.35	400

a chromatogram of the analytes extracted off of the pre-extracted cotton balls. As can be seen, there are no problems with interfering peaks from the cotton balls that have been previously pre-extracted. All other matrices were used as is with no conditioning or pre-extraction steps.

RESULTS AND DISCUSSION:

Matrix studies were performed intially to determine the most inert support for the analytes to be studied. The extraction and extract analysis were performed as outlined in the Experimental section, with only one collection solvent which was composed of 5 mL methanol, 5 mL hexane, and 5 mL chloroform to yield a total volume of 15 mL, this was thermostatted to 5 °C. Methanol and hexane are not completely miscible with each other. When these two solvents are combined, a cloudy solution develops and there is a distinct two layer system. With the addition of 5 mL of chloroform the resulting solution returns to a clear solution and only a single layer is visible.

Acetophenone showed similiar recoveries from six of the nine matrices studied, **Table V**. Only Silica Gel, Boileezers, and the cotton balls showed statistically lower recoveries when tested at the 95% confidence interval with the *Tukey* pairwise comparison. The Boileezers showed the lowest recoveries of acetophenone at a level of 8%. This probably is due to the fact that the Boileezers are large irregular shaped pieces and spiking a volatile component like acetophenone onto the matrix can be difficult. Silica

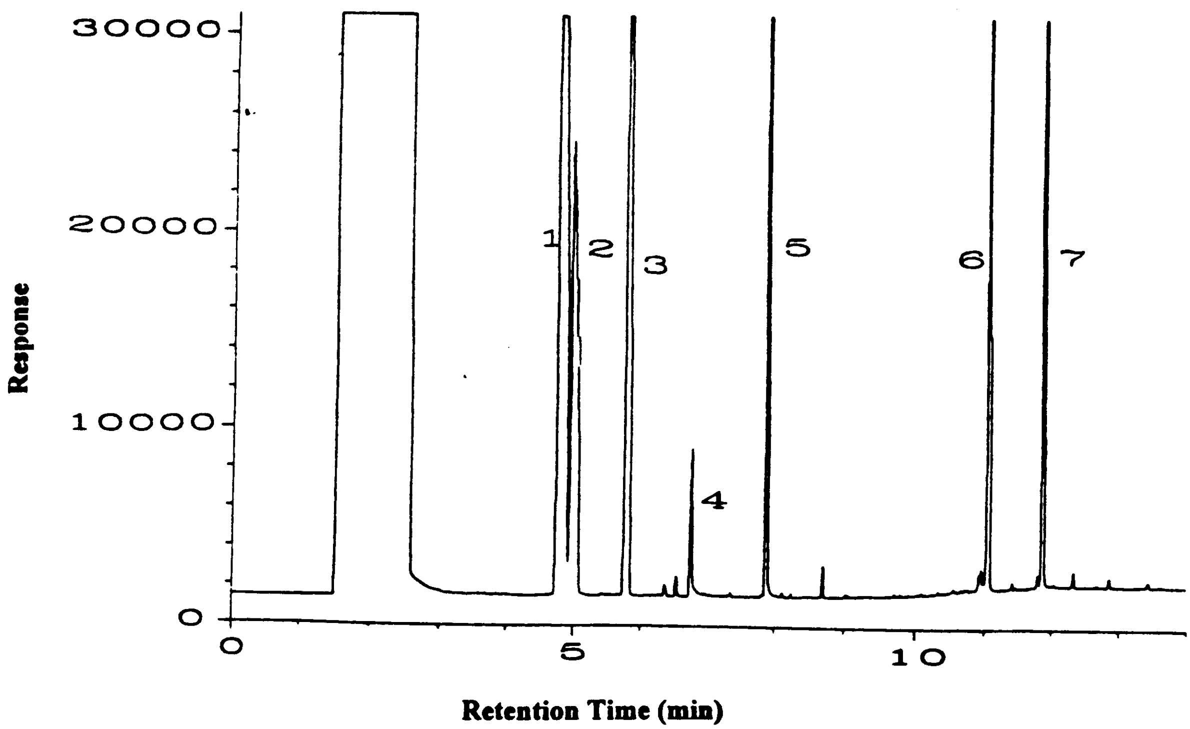


FIGURE 5:

GAS CHROMATOGRAM OF STANDARD SOLUTION.

1) Acetophenone: 2) *N,N*-Dimethylaniline: 3) Naphthalene: 4) Decanoic Acid: 5) 2-Naphthol: 6) Pyrene (I.S.): 7) Tetracosane: GC conditions given in text.

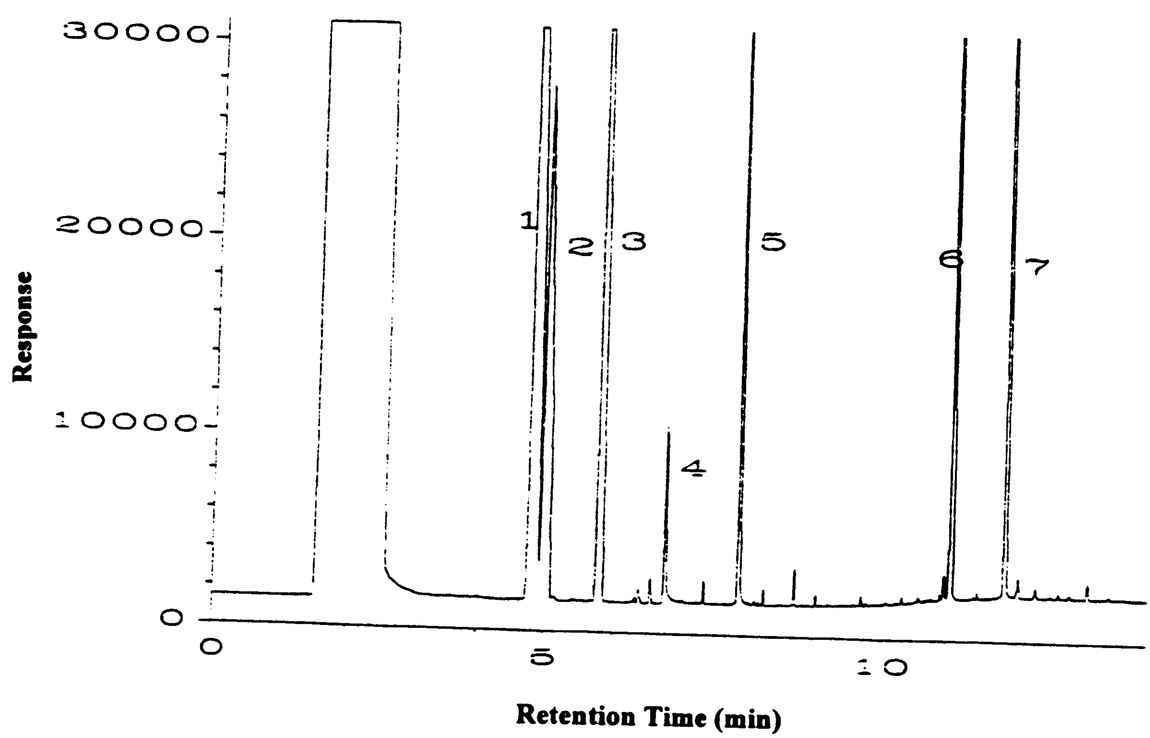


FIGURE 6:

GAS CHROMATOGRAM OF ANALYTES EXTRACTED FROM PRE-EXTRACTED COTTON BALLS.

1) Acetophenone: 2) *N,N*-Dimethylaniline: 3) Naphthalene: 4) Decanoic Acid: 5) 2-Naphthol: 6) Pyrene (I.S.): 7) Tetracosane: GC conditions given in text.

TABLE V

ANALYTE RECOVERIES FROM VARIOUS MATRICES *

Analyte	Sand	Celite	Wet Support
Acetophenone	93% (1.7)	92% (0.1)	89% (12)
N,N-Dimethylaniline	95% (1.7)	91% (0.3)	90% (8.8)
Naphthalene	95% (0.9)	93% (0.7)	91% (9.2)
Decanoic Acid	99% (5.1)	95% (4.5)	61% (13)
2-Naphthol	96% (2.2)	93% (1.6)	93% (4.2)
n-Tetracosane	96% (2.2)	94% (1.1)	95% (2.0)
# of Determinations	n = 8	n = 4	n = 4

Analyte	Silica Gel	Boileezers	Glass Wool
Acetophenone	64% (22)	8% (10)	88% (5.1)
N,N-Dimethylaniline	50% (27)	0%	89% (4.4)
Naphthalene	92% (0.9)	57% (9.6)	90% (4.3)
Decanoic Acid	0%	0%	83% (14)
2-Naphthol	0%	0%	87% (9.1)
n-Tetracosane	86% (9.8)	76% (14)	88% (7.4)
# of Determinations	n = 4	n = 3	n = 4

Analyte	Cotton Balls	Glass Beads	Micro-Glass Beads
Acetophenone	78% (10)	86% (3.7)	86% (8.9)
N,N-Dimethylaniline	82% (8.6)	88% (2.1)	88% (7.7)
Naphthalene	83% (8.3)	88% (2.3)	88% (7.2)
Decanoic Acid	100% (11)	56% (34)	51% (11)
2-Naphthol	68% (7.6)	87% (4.1)	91% (3.6)
n-Tetracosane	94% (2.7)	90% (3.2)	95% (3.5)
# of Determinations	n = 4	n = 4	n = 3

* numbers in parenthesis are RSD's.

Gel gave a recovery of 64% and cotton balls gave a recovery of 78%. *N,N*-dimethylaniline showed very similiar recoveries to acetophenone. Of the matrices tested, seven of the nine matrices had statistically similiar recoveries for *N,N*-dimethylaniline. Once again, Silica Gel and the Boileezers had lower recoveries at 50% and 0% respectively, indicating that these are two matrices which are not inert for these analytes. Naphthalene, while solid at room temperature also shows some volatility aspects. Boileezers, cotton balls, and the glass beads gave recoveries of 88% and below for naphthalene, all other supports gave recoveries above 90%.

Decanoic acid showed three groupings for recoveries. Both Silica Gel and Boileezers showed 0% recovery. The ISCO wet support matrix, Fisher glass beads, and the 3M microglass beads all had statistically similiar recoveries (61%, 56%, and 51% respectively). Sand, Celite, glass wool, and cotton balls all had statistically similiar recoveries at 100%, 95%, 83%, and 100% respectively. Since Celite and the ISCO support are both diatomaceous earth, similiar recoveries for an analyte would have been expected. Celite is a fine particle and has been acid washed while the ISCO support is coarser and has not been acid washed. It is possible that the decanoic acid is being bound by active sites on the ISCO support that acid washing would have removed from the Celite. The glass beads, both from Fisher and from 3M, could have silanol sites on them to cause decanoic acid to show reduced recoveries.

For 2-naphthol, once again, the Boileezers and Silica gel showed 0% recovery. When 2-naphthol was spiked onto cotton balls, the recovery was only 68%. Glass wool and the glass beads from Fisher both had recoveries of 87%. Sand, Celite, ISCO support, and the 3M glass beads all had recoveries of 91 to 96%.

C_{24} showed the least dependence on matrix. The Boileezers gave the lowest recoveries at 76% and the highest RSD at 14%, sand had the highest recovery at 96%. Both Silica Gel and glass wool gave the only other recoveries below 90%. Celite, ISCO support, cotton balls, Fisher glass beads, and the 3M glass beads had recoveries over 90% with RSD's at or below 3.5%.

The Ottawa Cement Testing Sand and Celite gave statistically similiar recoveries for each of the analytes studied, therefore, sand was chosen for all of the additional studies based on three factors. 1) Price,Celite costs $99 for 0.45 kilogram while sand costs $22 for 3 kilograms. 2) Ease of use, Celite needs to be heated prior to use. It also is very light and needs to be packed into the extraction vessel, while sand can be poured easily into the vessel. 3) Health, Celite, being so fine, can become a respiratory tract irritant, while sand is more innocuous.

Preliminary to our main collection efficiency study, four different restrictor temperatures (75, 125, 175, and 250 °C) and three different collection solvents (15 mL hexane, 15 mL chloroform, and 15 mL total of hexane-chloroform-methanol in a 1:1:1 mixture) were evaluated. **Table VI** shows the recoveries of the analytes. As can be seen from these data, there is an optimal restrictor temperature, or range, for the efficient

TABLE VI

ANALYTE RECOVERY Vs. RESTRICTOR TEMPERATURE*

	HEXANE COLLECTION			
ANALYTE	75 °C	125 °C	175 °C	250°C
Acetophenone	Plug	93% (3)	95% (3)	92% (3)
N,N-Dimethylaniline	Plug	89% (6)	87% (2)	84% (3)
Naphthalene	Plug	93% (4)	93% (5)	89% (3)
Decanoic Acid	Plug	82% (41)	61% (28)	36% (76)
2-Naphthol	Plug	88% (10)	93% (6)	74% (10)
n-Tetracosane	Plug	90% (8)	90% (4)	72% (17)
# of Determinations	n = 4	n = 7	n = 4	n = 4
	CHLOROFORM COLLECTION			
ANALYTE	75 °C	125 °C	175 °C	250°C
Acetophenone	Plug	81% (12)	82% (10)	69% (12)
N,N-Dimethylaniline	Plug	79% (16)	76% (9)	65% (13)
Naphthalene	Plug	87% (7)	86% (8)	74% (11)
Decanoic Acid	Plug	88% (18)	69% (6)	42% (27)
2-Naphthol	Plug	93% (4)	93% (4)	79% (17)
n-Tetracosane	Plug	95% (2)	96% (2)	78% (14)
# of Determinations	n = 4	n = 8	n = 4	n = 4
	555 MIX COLLECTION			
ANALYTE	75 °C	125 °C	175 °C	250°C
Acetophenone	Plug	93% (2)	95% (8)	78% (11)
N,N-Dimethylaniline	Plug	95% (2)	89% (6)	75% (7)
Naphthalene	Plug	95% (1)	99% (6)	82% (10)
2-Naphthol	Plug	96% (2)	98% (8)	75% (14)
n-Tetracosane	Plug	96% (2)	104% (4)	95% (3)
# of Determinations	n = 4	n = 8	n = 4	n = 4

* RSD's are in parenthesis

collection of these analytes. At a restrictor temperature of 75 °C, the restrictors became plugged. C_{24} and 2-naphthol are the most likely suspects for restrictor plugging. A 50 °C increase in restrictor temperature, to 125 °C, was sufficient to ensure that the analytes would travel through the restrictor without plugging. At 250 °C trapping of the analytes again became problematic. This is thought to be due to higher temperature differential between the oven (35 °C) and the restrictor thus producing more of an aerosol, making trapping of the analytes difficult.

Oneway *ANOVA*'s were run on the data along with *Tukey* pairwise comparisons. For hexane as the collection solvent, all restrictor temperatures, above 75 °C, were statistically equal for the recoveries of acetophenone, *N,N*-dimethylaniline, naphthalene, and decanoic acid. C_{24} and 2-naphthol statistically showed decreased recoveries with a restrictor temperature of 250 °C. Decanoic acid with huge RSD's, of 41%, 28%, and 76% at 125, 175, and 250 °C restrictor temperatures respectively, could only statistically be proven to have similiar recoveries at each temperature. For chloroform as the collection solvent, any restrictor temperature was statistically equal for the recoveries of acetophenone and *N,N*-dimethylaniline. For naphthalene, decanoic acid, 2-naphthol, and C_{24}, 125 °C and 175 °C restrictor temperatures were statistically equal for analyte recovery.

When a collection solvent consisting of 5 mL of hexane, 5 mL of chloroform, and 5 mL of methanol was studied, acetophenone, *N,N*-

dimethylaniline, naphthalene, and 2-naphthol showed decreased recoveries at a restrictor temperature of 250°C. C_{24} statistically showed better recoveries at a restrictor temperature of 175 °C than at 125 or 250 °C. A restrictor temperature range of 125 to 175 °C seemed to be optimal for these analytes with these collection solvents. *Hawthorne* and coworkers have also shown collection effficiency differences due to varying restrictor temperatures for the extraction of jet-diesel fuel and no. 5 fuel oil standards spiked onto sand (*42*). Restrictor temperatures of 70, 80, 90, and 100 °C were investigated and 90 and 100 °C restrictor temperatures were found to be optimal. Lower restrictor temperatures led to decreased recovery of heavier hydrocarbons, due to losses to the restrictor walls, and increased incidences of plugging (*42*). *Hawthorne* did not investigate restrictor temperatures above 100 °C. These data match up well with what was seen here, lower restrictor temperatures caused plugging.

Next, the effect of trap solvent volume was screened prior to our primary focus. Only hexane and chloroform were studied as collection solvents, with 0, 5, 10, 15 and 20 mL volumes used. Additional experiments were performed with (a) the inner glass tube not being employed and (b) no collection solvent placed in the trap. **Table VII** shows the recovery of analytes versus hexane and chloroform collection solvent volume. When there was no collection solvent in the vial, the lighter, more volatile components were not trapped effectively. Decanoic acid, 2-naphthol, and C_{24} were trapped almost quantitatively (83 to 88% recovery) when the inner tube was not in place. It is believed that 2-naphthol and C_{24}

fall out of solution, as solids, when the CO_2 is depressurized. This explains the high recoveries when no collection solvent is employed. The more volatile components are carried away in the CO_2 and never get a chance to stick to the trap, unless solvent is present and the depressurized CO_2 stream gets a chance to bubble through it. When hexane was investigated, it can be seen that the recoveries of the more volatile components increased when going from 5 to 10 mL of hexane. Decanoic acid was problematic in trapping with hexane at any solvent volume which is evidenced by the high RSD's. Chloroform, which has problems effectively trapping the lighter weight analytes, showed improvement for 2-naphthol and C_{24} trapping with an increase in solvent volume. 15 mL was deemed to be the best collection volume and was used throughout the rest of the experiments (*45, 46*).

Finally, the analyte mixture was spiked directly into the collection vial instead of onto the sand, to determine how well the solvent would retain the analytes while being purged with decompressed CO_2. After spiking the trap solvent, empty extraction vessels were placed in-line and a blank 30 minute extraction procedure was followed. Results for hexane and chlorofrom are shown in **Table VIII**, which indicate that these two solvents can retain these analytes during a normal extraction. This study will not tell how well a solvent will perform as a collection solvent. Spiking analytes directly into the collection solvent and then bubbling CO_2 through for 30 minutes to try and remove the analytes from the liquid collection solvent (as was done here) is an entirely different proposition than trying to have

TABLE VII

ANALYTE RECOVERY Vs. SOLVENT VOLUME*

ANALYTE	Septum Only#	0 mL Solvent##
Acetophenone	31% (74)	19% (59)
N,N-Dimethylaniline	21% (78)	12% (63)
Naphthalene	43% (32)	46% (15)
Decanoic Acid	83% (14)	99% (2)
2-Naphthol	88% (5)	99% (8)
n-Tetracosane	88% (5)	97% (5)
# of Determinations	n = 4	n = 4

	HEXANE COLLECTION			
ANALYTE	5 mL	10 mL	15 mL	20 mL
Acetophenone	72% (20)	91% (1)	93% (3)	96% (3)
N,N-Dimethylaniline	67% (22)	86% (2)	89% (6)	90% (4)
Naphthalene	73% (18)	90% (2)	93% (4)	96% (3)
Decanoic Acid	59% (26)	118% (24)	82% (41)	45% (9)
2-Naphthol	91% (6)	98% (3)	88% (10)	94% (6)
n-Tetracosane	85% (13)	91% (3)	90% (8)	96% (4)
# of Determinations	n = 3	n = 4	n = 7	n = 3

	CHLOROFORM COLLECTION			
ANALYTE	5 mL	10 mL	15 mL	20 mL
Acetophenone	74% (10)	67% (25)	81% (12)	89% (6)
N,N-Dimethylaniline	69% (8)	64% (21)	79% (16)	85% (6)
Naphthalene	78% (8)	70% (21)	87% (7)	91% (5)
Decanoic Acid	94% (9)	80% (14)	88% (18)	74% (3)
2-Naphthol	89% (7)	83% (10)	93% (4)	92% (3)
n-Tetracosane	89% (9)	87% (8)	95% (2)	95% (2)
# of Determinations	n = 4	n = 4	n = 8	n = 4

* RSD's in parenthesis
# Inner glass tube not employed, no collection solvent employed in an empty collection vial.
Inner glass tube employed, but no collection solvent employed in an empty collection vial.

TABLE VIII

TRAP SPIKING STUDY*

ANALYTE	15 mL HEXANE	15 mL CHLOROFORM
Acetophenone	98% (0.2)	96% (0.5)
N,N-Dimethylaniline	99% (0.3)	96% (0.6)
Naphthalene	99% (0.2)	96% (0.5)
2-Naphthol	106% (2)	95% (0.8)
n-Tetracosane	99% (1)	96% (1)
# of Determinations	n = 4	n = 4

* RSD's in parenthesis

the solvent remove the analytes from the decompressed CO_2 stream and trap them in the collection vial.

Our primary concern in this chapter is the effect of trap solvent composition on collection efficiency. Acetophenone and *N,N*-dimethylaniline had the highest volatility of the compounds studied. To effectively trap these compounds the collection solvent should be one in which the analytes have high solubility and should exhibit a high viscosity. A high viscosity solvent results in smaller bubble size of decompressed CO_2. Larger surface area to volume ratio is, therefore, realized with smaller bubble sizes as compared with larger bubble sizes, thereby resulting in more contact between the analytes and the collection solvent. Higher viscosity also makes the bubbles move slower, which increases the contact time of the analytes with the collection solvent (*30*). Acetophenone is soluble in most organic solvents and *N,N*-dimethylaniline is soluble in alcohol and chloroform (*43*). Chloroform is a relatively viscous solvent; therefore it was believed to probably be the best starting point to find an appropriate collection solvent for these analytes. On the contrary, recovery of these analytes was surprisingly poor in chloroform (81% and 79% recovery respectively with RSDs over 12%). Methanol, on the other hand, proved to be a better collection solvent. Acetophenone was trapped with an efficiency of 94% and *N,N*-dimethylaniline at 86%. Perc has the highest viscosity of any of the solvents studied, but conversely it was the collection solvent with the overall lowest recoveries for all of the analytes studied.

Viscosity appears, therefore, to not be uniquely critical to obtaining high recoveries. In fact, there was no correlation between any of the solvent physical properties considered (e.g. boiling points, density, viscosity, surface tension, and Hildebrand solubility parameter) and analyte recovery. **Table IX** lists the solvent properties of the liquid collection solvents studied. Besides the collection solvent physical properties (boiling point, density, viscosity, surface tension) listed in **Table IX**, the actual analyte solubility in the collection solvent should be considered for efficient trapping. If an analyte is not solubile in or has a low solubility in a solvent, then trapping could be problematic. Unfortunately, there are no literature data for solubilities of acetophenone, *N,N*-dimethylaniline, naphthalene, decanoic acid, 2-naphthol, and C_{24} in acetone, acetonitrile, carbon tetrachloride, chloroform, cyclohexane, methylene chloride, hexane, methanol, or Perc.

Referring to **Table X**, it can be seen that the recovery results of acetophenone fell into two distinct groups. Acetone, acetonitrile, carbon tetrachloride, cyclohexane, hexane, and methanol yielded recoveries averaging 92% with RSDs of 3.6% and below. A second group consisted of the chlorinated solvents chloroform, methylene chloride, and Perc, with an averaged recovery of 80%. *N,N*-dimethylaniline recovery results also seemed to split into two groups. Once again, chloroform, methylene chloride, and Perc gave the lowest recoveries; 79% for chloroform and methylene chloride and 72% for Perc. The other six single component solvents averaged a recovery of 88% with the majority of the RSD's below

TABLE IX

SOLVENT PROPERTIES*

SOLVENT	BOILING POINT (°C)	DENSITY (g/mL)	VISCOSITY (centipose)
ACETONE	56	0.792	0.378
ACETONITRILE	82	0.783	0.420
CARBON TETRACHLORIDE	77	1.585	1.232
CHLOROFORM	61	1.485	0.665
CYCLOHEXANE	81	0.779	1.02
METHYLENE CHLORIDE	40	1.335	0.449
HEXANE	69	0.659	0.393
METHANOL	65	0.792	0.754
PERC	121	1.625	1.844

SOLVENT	SURFACE TENSION** (dynes/cm @ 20 °C)	SOLUBILITY# $(cal/cm^3)^{1/2}$
ACETONE	26.21	9.9
ACETONITRILE	29.30	11.9
CARBON TETRACHLORIDE	26.95	8.6
CHLOROFORM	27.14	9.3
CYCLOHEXANE	25.50	8.2
METHYLENE CHLORIDE	26.52	9.7
HEXANE	18.43	7.3
METHANOL	22.60	14.5
PERC	31.74	9.3

* Physical properties of the solvents taken from reference #47: CRC Handbook of Chemistry and Physics

** Methylene chloride and Perc at 15 °C and cyclohexane at 17 °C

Hildebrand solubility strength

TABLE X
ANALYTE RECOVERY Vs. COLLECTION SOLVENT*

ANALYTE	ACETONE	ACETONITRILE	CARBON TETRACHLORIDE
Acetophenone	91% (3.6)	93% (3.2)	93% (1.0)
N,N-Dimethylaniline	88% (3.8)	87% (2.8)	91% (2.2)
Naphthalene	91% (3.8)	94% (2.8)	93% (1.1)
Decanoic acid	99% (14)	78% (10)	88% (4.8)
2-Naphthol	93% (2.8)	91% (4.0)	95% (3.9)
n-Tetracosane	96% (2.5)	90% (3.9)	94% (3.9)
# of Determinations	n = 8	n = 7	n = 8

ANALYTE	CHLOROFORM	CYCLOHEXANE	METHYLENE CHLORIDE
Acetophenone	81% (12)	95% (1.2)	80% (6.1)
N,N-Dimethylaniline	79% (16)	89% (1.6)	79% (5.1)
Naphthalene	87% (6.7)	95% (1.2)	83% (5.0)
Decanoic acid	88% (18)	84% (8.3)	108% (3.8)
2-Naphthol	93% (4.2)	93% (2.6)	95% (2.5)
n-Tetracosane	95% (1.5)	93% (3.3)	97% (2.4)
# of Determinations	n = 8	n = 8	n = 7

ANALYTE	HEXANE	METHANOL	PERC
Acetophenone	93% (2.8)	94% (1.1)	77% (0.7)
N,N-Dimethylaniline	89% (5.7)	86% (1.6)	72% (1.8)
Naphthalene	93% (4.0)	96% (1.0)	77% (1.0)
Decanoic acid	82% (41)	66% (13)	54% (8.4)
2-Naphthol	88% (9.6)	88% (5.1)	73% (2.9)
n-Tetracosane	90% (8.4)	93% (5.0)	76% (2.1)
# of Determinations	n = 7	n = 7	n = 7

* Numbers in parenthesis are RSDs

3.8%. Perc was also the worst collection solvent studied when naphthalene was the analyte, with a recovery of 77%. Methylene chloride also showed a low recovery at 83%. Chloroform had the next lowest recovery at 87%. All other solvents had recoveries over 91% and RSD's between 4.0 and 1.1%. 2-Naphthol and C_{24} recoveries were very similar in behavior. Excluding Perc, 2-naphthol averaged 92% for the eight single component solvents studied, while C_{24} averaged 94% recovery. Perc had the lowest recovery at 73% for 2-naphthol and 76% for C_{24}.

Decanoic acid had the highest RSDs and the lowest recoveries of any of the analytes studied, in the pure solvents. The high RSDs are believed to be due, in part, to problems in the analysis of the compound. The problem of analyzing acids on nonpolar chromatographic columns is well known (*35*). A more polar GC column was not used for two reasons. It was believed that a polar GC column would show adverse affects on the peak shapes of naphthalene, C_{24} and the internal standard pyrene. With the maximum column temperature of 300 ^{o}C used in the analysis, the polar columns available would also be degraded rapidly, therefore, the 5% phenylmethylsiloxane column was used. If the RSD of the ratio of peak area of decanoic acid / peak area of pyrene (I.S.), varied over the analysis time by greater than 10%, then three injections of pure solvent were made and the samples were then rerun. Decanoic acid recoveries for the single component solvents varied greatly from a high of 108% for dichloromethane to a low of 54% when Perc was employed as the collection solvent. The lowest RSD obtained was 3.8% when methylene chloride was the collection solvent and the highest RSD was obtained with hexane at a value of 41%.

Since no single component collection solvent trapped all analytes at 90% (with RSD's of 5 or below) multicomponent collection solvents were devised and investigated. **Table XI** shows the recoveries and RSD for the multicomponent collection solvents. Initially a mixed collection solvent of 7.5 mL methanol and 7.5 mL methylene chloride was studied. This collection solvent, however, did not meet the goals of our study, since both acetophenone and *N,N*-dimethylaniline had recoveries below 90% (88% and 87% respectively). The RSD's for 2-naphthol and C_{24} were reasonable at 3.0% and 2.4% but the RSD's for the other analytes were from 5.1% to 14%. A second collection solvent consisting of 7.5 mL chloroform and 7.5 mL hexane was evaluated. By combining hexane and chloroform together as a collection solvent, it was hoped that hexane would trap the lighter weight components effectively; while, chloroform would trap the heavier molecular weight analytes. For this combined collection solvent, acetophenone had the lowest recovery at 92% and 2-naphthol had the highest recovery at 98%. The RSD's for the analytes were all below 4% except for decanoic acid that had an RSD of 9.3%.

Liquid trapping effectiveness with the polarity test mix using methanol modified fluids will be discussed in the next chapter. With this in mind, a collection solvent employing chloroform-hexane-methanol was investigated. If methanol modified CO_2 is used, methanol will probably be retained in the collection solvent during the extraction. Higher methanol modifier content in the extraction fluid will result in more methanol in the liquid trap after the extraction run is completed. When a collection solvent of 7 mL chloroform, 7 mL hexane and 1 mL methanol was used, the recoveries of all analytes were 90% or higher. The RSD's fell in the range between 4.2% on the high side for acetophenone to a low of 2.7% for C_{24}. All of these values are in the range of the goal that was set for our investigation. A multicomponent solvent system consisting of 5 mL chloroform, 5 mL hexane, and 5 mL methanol was also studied with similar results. These results afford us confidence that quantitative trapping via a mixed solvent with polar modified extractant fluids will be favorable for a wide polarity range of analytes.

TABLE XI

ANALYTE RECOVERY Vs. MULTICOMPONENT COLLECTION SOLVENTS*

Analyte	Solvent 10[a]	Solvent 11[b]
Acetophenone	88% (7.1)	92% (3.0)
N,N-Dimethylaniline	86% (5.2)	93% (2.6)
Napthalene	90% (5.1)	93% (2.8)
Decanoic acid	93% (14)	97% (9.3)
2-Naphthol	96% (3.0)	98% (4.0)
n-Tetracosane	96% (2.4)	95% (2.7)
# of Determinations	n = 8	n = 8
Analyte	**Solvent 12[a]**	**Solvent 13[b]**
Acetophenone	90% (4.2)	93% (1.7)
N,N-Dimethylaniline	90% (3.1)	95% (1.7)
Napthalene	92% (3.2)	95% (0.9)
Decanoic acid	92% (3.1)	100% (5.1)
2-Naphthol	96% (2.8)	96% (2.2)
n-Tetracosane	94% (2.7)	96% (2.2)
# of Determinations	n = 5	n = 8

*Numbers in parenthesis are RSDs.

[a] solvent 10 = 7.5 mL methanol, 7.5 mL methylene chloride:
[b] solvent 11 = 7.5 mL chloroform, 7.5 mL hexane:
[c] solvent 12 = 7 mL chloroform, 7 mL hexane, 1 mL methanol:
[d] solvent 13 = 5 mL chloroform, 5 mL hexane, 5 mL methanol:

CHAPTER 3

LIQUID COLLECTION EFFICIENCIES AFTER EXTRACTION WITH MODIFIED CARBON DIOXIDE

INTRODUCTION:

Pure carbon dioxide may not have the "strength" to extract the analytes of interest from the matrix. This situation can arise from two factors: the analyte of interest may not be soluble in pure CO_2 or the analyte may be strongly bound to the matrix and pure CO_2 is incapable of disrupting the analyte-matrix interaction. To overcome these problems, carbon dioxide modified with organic solvents has been used. The modifier may displace the analyte from the matrix and bind to the active matrix site or the modifier may add a polar constituent to the extraction fluid and cause the analyte of interest to become soluble in the modified extraction fluid.

MODIFIED FLUID COLLECTION OPTIMIZATION:

While there have been several papers dedicated to trapping studies (*25 - 39*) for unmodified CO_2 extracts, there are relatively few papers describing collection studies after modified CO_2 extractions (*36 - 38*). All of these papers describe trapping with solid phase deposition after extraction and liquid trapping has not been investigated.

Mulcahey in her studies used a Hewlett Packard 7680A extractor and a sample loop to introduce the analytes to the trap (*36*). Acetophenone, *N,N*-dimethylaniline, decanoic acid, 2-naphthol, and C_{24} were studied. A

50 μL sample loop was used to introduce 50 μg of each analyte into the CO_2 stream via a standard solution of 1 mg/mL in methylene chloride. ODS and stainless steel traps were studied under conditions of 1, 2, 4, and 8% (wt/wt) methanol modified CO_2. This corresponded to 1.4, 2.8, 5.5, and 11 mole percent methanol modified CO_2. The traps were evaluated at temperatures from 5 to 80 °C. With an ODS trap, only 2-naphthol showed over 85% recovery at all trap temperatures and all values of methanol modified CO_2 (1, 2, 4, and 8%). Acetophenone and *N,N*-dimethylaniline showed excellent recoveries with trap temperatures at 20 °C for 1 and 2% methanol modified CO_2. At trap temperatures of 30 °C and above, recoveries dropped off steeply. Trapping of decanoic acid was nearly quantitative with 1 and 4% methanol modified CO_2, but not with 2 or 8% (recoveries averaged from 75% with 2% methanol modified CO_2 to 30% with 8% methanol modified CO_2). C_{24} trapping was 90% or better with 1 and 2% methanol modified CO_2, at all trap temperatures. Trapping C_{24} with 4 or 8% methanol modified CO_2 was much more problematic. Recoveries ranged from 10 to 60% with 4% methanol modified CO_2, while recoveries were from 0 to 20% with 8% methanol modified CO_2.

With the stainless steel trap, acetophenone and *N,N*-dimethylaniline were difficult to trap. With 1% methanol modified CO_2, only at 5 °C trap temperature was acetophenone and *N,N*-dimethylaniline recovered (61 and 46% respectively). Decanoic acid showed recoveries ranging from 33 to 72%, which increased with increasing trap temperature. 2-Naphthol and C_{24} were only quantitatively trapped at 50 °C and above, with 1%

methanol modified CO_2. Only acetophenone and *N,N*-dimethylaniline were studied with 2 and 4% methanol modified CO_2 with the stainless steel trap. Recoveries at these conditions were near zero.

Since a single solid phase trap cannot trap quantitatively all of the analytes in the polarity mix, even via a sample loop, at any given temperature, with methanol modified CO_2, the goal of our study was to evaluate the use of liquid trapping for quantitative analyte recovery of the polarity mix. CO_2 modified with acetonitrile, methanol, or toluene at 1, 4, and 8 mole percent was studied with liquid trapping consisting of 15 mL chloroform, 15 mL hexane, 15 mL methanol, or 15 mL of a mixed collection solvent consisting of equal parts chloroform-hexane-methanol.

EXPERIMENTAL:

Extractions were performed on a multi-vessel Dionex SFE-723 supercritical fluid extractor (Dionex Corporation, Sunnyvale, CA). Carbon dioxide (SFE/SFC grade) with helium headspace was obtained from Air Products and Chemicals (Allentown, PA). Modified fluids were introduced into the system by the Dionex SFE-723 modifier module. Acetonitrile (ACN), methanol (MeOH), and toluene were explored as modifiers. HPLC grade acetonitrile was obtained from Mallinckrodt (Paris, KY). Both ACS grade toluene and HPLC grade methanol were obtained from EM Science (Gibbstown, NJ)

Approximately 5.6 grams of Ottawa Cement Testing Sand was placed in a 3.5 mL Keystone Scientific extraction vessel. A spiking solution of acetophenone, *N,N*-dimethylaniline, naphthalene, 2-naphthol, and *n*-tetracosane (C_{24}) was prepared in methylene chloride. A solution of the polarity test mix, approximately 7 mg/mL per component (7000 ppm), was then spiked onto the sand (100 µL spike volume) to yield 700 µg of each component.

All extractions were performed at the same reduced temperature (1.12) and the same reduced pressure. The total extraction time was 30 minutes, 10 minutes at a reduced pressure of 2.4 and 20 minutes at a reduced pressure of 4.67. The fixed restrictors, rated at 250 mL/min decompressed CO_2 flow, were heated to 125 °C. The extracts were collected in 15 mL of the various solvents (chloroform, hexane, methanol, and 1:1:1 mix of chloroform-hexane-methanol), each of which was thermostatted to 5 °C via peltier cooling chips in the Dionex-723. All collection solvents (chloroform, hexane, methanol) were from Fisher Scientific and were HPLC grade or better.

EXTRACT ANALYSIS:

Extract analysis was performed as outlined in **Chapter 2**. Statistical analysis of the data consisted of *ANOVA* and *Tukey* pairwise tests, see **Appendix II**. Oneway *ANOVA*s were run on each analyte individually to see if there were any differences in collection efficiencies between collection solvents for each individual modifier (acetonitrile, methanol, or toluene) at each individual level (0, 1, 4, or 8 mole %). *Tukey* pairwise multiple comparison tests, at the 95% confidence level, were run to determine where differences in the collection solvents occurred. Oneway *ANOVA*s were also run on each individual analyte to see if there were any differences in collection efficiencies for each collection solvent between modifier levels of 0,1, 4, and 8% (acetonitrile, methanol, and toluene). *Tukey* pairwise multiple comparison tests, at the 95% confidence level, were also run to determine where the differences in the collection efficiencies occurred. All statistical calculations were run on the student edition of Minitab® release 8 (Minitab, State College, PA) on a Macintosh SE computer (Apple Computer, Cupertino, CA).

RESULTS AND DISCUSSION:

The Dionex SFE-723 mixes modifier into the liquid CO_2 stream on-line via a mixing tee. The mixing tee is held at 175 atmospheres to insure proper mixing of modifier and CO_2 before it flows to the extractor oven where it becomes supercritical, and through the extraction vessel containing the sample. The modifier percent is accomplished by a computer controlled valve which opens and closes to release the appropriate amount of modifier for the given conditions of temperature, pressure, flow rate, and mole percent modifier chosen. **Table XII** lists the critical points of the modifiers

TABLE XII

MODIFIER CRITICAL PARAMETERS*#

MODIFIER	Tc (°C)	Pc (atm)
ACETONITRILE	274.7	47.7
METHANOL	240	78.5
TOLUENE	320.8	41.6

* CO_2, Tc = 31.3 °C, Pc = 72.9 atm

Values obtained from reference #47: CRC Handbook of Chemistry and Physics.

chosen for study. As can be seen, the critical pressures of the modifiers are very close to pure carbon dioxide, while the critical temperatures are much higher. It is not surprising then that the pressures needed to achieve the same reduced pressure for the modified CO_2 compared to pure CO_2 are not considerably different. There was, however, more variation in the temperatures required to achieve the same reduced temperatures.

Reduced pressure is defined as:

$$Pr = P / Pc$$

where Pc is the critical pressure, P is the extraction pressure, and Pr is the reduced pressure. The reduced temperature is similarly defined as:

$$Tr = T / Tc$$

where Tc is the critical temperature, T is the extraction temperature, and Tr is the reduced temperature.

All extractions were run under the same reduced parameters to ensure that all fluid mixtures were supercritical. **Table XIII** lists the actual run conditions chosen. Critical parameters of the mixed CO_2 modifier systems were calculated using a SF-Solver computer program obtained from ISCO. All extractions were run at a reduced temperature of 1.12 and reduced pressures of 2.4 for step 1 and 4.67 for step 2. Trap temperature and restrictor temperature were held constant during all extractions. Acetonitrile was not investigated at 8 mole percent in CO_2 because at that level CO_2 and acetonitrile are no longer completely miscible and a two layer fluid is predicted to exist (*44*).

TABLE XIII

MODIFIER EXTRACTION PARAMETERS

Fluid#	Tc (°C)*	Pc (atm)*	Extraction Temp. (°C)	Extraction Pressure (atm) Step 1	Extraction Pressure (atm) Step 2
100% CO_2	31.3	72.9	35	175	340
1% ACN in CO_2	33.7	72.8	38	175	340
4% ACN in CO_2	41.6	72.2	47	173	337
1% MeOH in CO_2	33.1	72.9	37	175	340
4% MeOH in CO_2	39.3	73.4	44	176	343
8% MeOH in CO_2	47.5	74.4	53	179	348
1% Toluene in CO_2	34.7	72.4	39	174	338
4% Toluene in CO_2	45.3	71.8	51	172	335
8% Toluene in CO_2	59.2	70.9	66	170	331

Molar modifier percents

* Values obtained using ISCO SF-Solver software (ISCO corporation, Lincoln NE)

TABLE XIV

ANALYTE RECOVERY WITH ACETONITRILE MODIFIED CO_2

	1% Acetonitrile Modified CO_2*			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	79% (3)	92% (6)	96% (2)	74% (5)
N,N-Dimethylaniline	75% (4)	89% (6)	92% (1)	71% (3)
Naphthalene	85% (2)	92% (6)	96% (2)	75% (3)
2-Naphthol	84% (5)	90% (8)	91% (3)	73% (3)
Tetracosane	85% (7)	91% (7)	91% (4)	75% (2)
# of determinations	n = 4	n = 4	n = 3	n = 4

	4% Acetonitrile Modified CO_2			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	90% (1)	97% (2)	72% (1)	71% (2)
N,N-Dimethylaniline	89% (2)	96% (2)	72% (0.5)	71% (2)
Naphthalene	90% (2)	95% (4)	72% (1)	72% (2)
2-Naphthol	93% (6)	96% (5)	64% (2)	68% (4)
Tetracosane	92% (3)	96% (2)	76% (1)	66% (3)
# of determinations	n = 4	n = 3	n = 4	n = 4

* Numbers in parenthesis are RSDs.

TABLE XIV lists the recoveries of the analytes when acetonitrile was investigated as the modifier. Since there are unequal numbers of determinations for the analytes in each solvent, a twoway *ANOVA* could not be run. The data were, however, analyzed by performing a oneway *ANOVA* at 1% acetonitrile modified CO_2 and at 4% acetonitrile modified CO_2 to look at the recovery differences in the four collection solvents. A second set of *ANOVAs* was also run on each individual trapping solvent to see what effects different mole percents of modifier had on the collection efficiencies of the analytes in each individual solvent.

Looking at 1 mole percent acetonitrile modified CO_2 a trend can be seen. Although, 2-naphthol had statistically the same recovery with chloroform, hexane, or methanol (*i.e.* 84, 90 and 91% respectively) as the collection solvent, all other analytes had recoveries that split into two groups (*e.g.* higher recoveries in hexane and methanol, and lower recoveries in chloroform and the mixed solvent). The poor recoveries of all analytes in the mixed solvent are surprising since with pure CO_2, the mixed solvent was clearly superior. With 1% acetonitrile modified CO_2, the mixed solvent gave statistically similar recovery results compared to chloroform.

When 4 mole percent acetonitrile modified CO_2 was investigated as the extraction fluid, once again the recoveries of the analytes fell into two distinct groups. What is surprising in this case is that, now methanol and the mixed collection solvent showed far worse recoveries (approximately 20% worse) than when chloroform and hexane were the collection solvent.

In addition to comparing the four collection solvents at 1 and 4% acetonitrile modified CO_2, each collection solvent was looked at separately, for each individual analyte, across the spectrum of 0, 1, and 4% acetonitrile modified CO_2. With chloroform as the collection solvent, the recoveries of 2-naphthol and C_{24} were worse at 1% acetonitrile modified CO_2, but recoveries were statistically similar when pure CO_2 and 4% acetonitrile modified CO_2 were compared. The recoveries of all analytes were unaffected by extraction fluid composition when hexane was employed as the collection solvent.

Methanol showed statistically similiar recoveries for all analytes between pure CO_2 and 1% acetonitrile modified CO_2, except for *N,N*-dimethylaniline which had a better recovery with 1% acetonitrile modified CO_2. For all analytes, methanol collection of 4% acetonitrile modified CO_2 had the worst recovery of analytes compared to 0 and 1% acetonitrile modified.

With pure CO_2 the mixed collection had quantitative recovery of all analytes, whereas recoveries of all analytes were statistically worse when modified CO_2 was employed. The recoveries of acetophenone and *N,N*-dimethylaniline were similar for 1 and 4% acetonitrile modified CO_2, but for all other analytes, the recoveries dropped statistically as the modifier content was raised form 0 to 1 to 4%.

Table XV shows the collection efficiencies when methanol modified CO_2 was employed. Looking at 1 mole percent methanol modified CO_2,

TABLE XV

ANALYTE RECOVERY WITH METHANOL MODIFIED CO_2

	1% Methanol Modified CO_2*			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	79% (5)	100% (2)	97% (1)	78% (3)
N,N-Dimethylaniline	80% (8)	100% (2)	98% (0.5)	81% (2)
Naphthalene	85% (8)	99% (3)	99% (1)	83% (2)
2-Naphthol	87% (11)	107% (2)	90% (4)	83% (3)
Tetracosane	88% (12)	94% (2)	88% (6)	84% (1)
# of determinations	n = 3	n = 4	n = 4	n = 3

	4% Methanol Modified CO_2			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	51% (17)	95% (3)	94% (4)	80% (4)
N,N-Dimethylaniline	51% (15)	95% (4)	96% (3)	79% (4)
Naphthalene	55% (17)	94% (5)	96% (3)	81% (4)
2-Naphthol	63% (14)	98% (7)	93% (6)	82% (5)
Tetracosane	66% (15)	93% (5)	93% (3)	83% (4)
# of determinations	n = 3	n = 4	n = 4	n = 4

	8% Methanol Modified CO_2			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	90% (9)	91% (6)	93% (2)	83% (1)
N,N-Dimethylaniline	92% (7)	92% (6)	96% (2)	84% (1)
Naphthalene	92% (7)	91% (6)	96% (2)	85% (1)
2-Naphthol	105% (3)	95% (7)	84% (9)	75% (2)
Tetracosane	100% (1)	85% (6)	88% (12)	80% (2)
# of determinations	n = 3	n = 3	n = 2	n = 2

* Numbers in parenthesis are RSDs.

once again, hexane and methanol were statistically superior to chloroform and the mixed solvent for all analytes

When 4 mole percent methanol modified CO_2 was investigated, a slightly different trend was discovered. Hexane and methanol, once again gave equally good recoveries for all analytes and both were superior to chloroform or the mixed collection solvent. The mixed collection solvent, in this case, had analyte recoveries that were statistically better than chloroform.

At 8 mole percent methanol modified CO_2, the recoveries are quantitative for all single component collection solvents with acetophenone, *N,N*-dimethylaniline, and naphthalene. The recoveries of 2-naphthol while quantitative with chloroform and hexane, decrease on going to methanol and the mixed collection solvent. For C_{24}, the mixed collection solvent showed the worst recoveries for the analytes, while chloroform exhibited excellent recoveries.

Once again a comparison was made for each individual collection solvent to note any trends in collection efficiency when switching from 0 up to 8% modifier, in this case methanol. When chloroform was employed as the collection solvent, the recoveries of all analytes were statistically equal for 0, 1, and 8 mole percent methanol modified CO_2 extractions, but 4 mole percent MeOH modified CO_2 extractions gave lower recoveries. With hexane as the collection solvent, the general trend that is seen is that any extraction fluid composition (0,1,4, or 8% methanol modified CO_2) gave outstanding recovery of all analytes. With methanol as the collection solvent, only the recovery of *N,N*-dimethylaniline improved when switching from pure CO_2 to methanol modified CO_2. For all other analytes, the recoveries were statistically the same for each extraction fluid studied. Once again the mixed collection solvent was statistically worse with methanol modified CO_2 as compared to pure CO_2. Recoveries of analytes were statistically equal, although poor, with 1, 4 or 8% methanol modified CO_2 when collected in the mixed collection solvent.

Table XVI shows the collection efficiencies when toluene modified CO_2 was employed. Looking at 1 mole percent toluene modified CO_2, hexane and methanol are again the best collection solvents studied for these analytes. For all analytes studied, the mixed collection solvent was statistically the worst. At 4 mole percent toluene modified CO_2, methanol seems to be the best collection solvent outright when trapping acetophenone, *N,N*-dimethylaniline, and naphthalene. For 2-naphthol and C_{24}, all three neat collection solvents had statistically similar recoveries. When 8 mole percent toluene modified CO_2 was investigated, chloroform, hexane, and methanol gave statistically similar recoveries for all analytes. The recoveries of all analytes dropped when collected in the mixed collection solvent. At 8 mole percent toluene modified CO_2, the recoveries of *N,N*-dimethylaniline, 2-naphthol, and C_{24} range from 64 to 88%. These poor collection efficiencies may reflect the notion that these analytes are not effectively extracted off the sand matrix in the time allotted.

TABLE XVI

ANALYTE RECOVERY WITH TOLUENE MODIFIED CO_2

	1% Toluene Modified CO_2*			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	81% (6)	96% (1)	96% (1)	70% (2)
N,N-Dimethylaniline	75% (6)	89% (1)	88% (1)	66% (2)
Naphthalene	86% (3)	96% (2)	97% (1)	71% (2)
2-Naphthol	83% (13)	87% (14)	96% (6)	70% (8)
Tetracosane	88% (7)	89% (6)	96% (1)	73% (4)
# of determinations	n = 3	n = 3	n = 3	n = 4

	4% Toluene Modified CO_2			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	85% (5)	97% (0.4)	115% (3)	87% (5)
N,N-Dimethylaniline	80% (6)	89% (0.6)	107% (2)	82% (5)
Naphthalene	87% (5)	96% (0.6)	117% (2)	89% (5)
2-Naphthol	80% (6)	87% (3)	89% (7)	79% (7)
Tetracosane	81% (11)	78% (4)	87% (7)	80% (12)
# of determinations	n = 4	n = 4	n = 4	n = 4

	8% Toluene Modified CO_2			
SOLVENT	$CHCl_3$	Hexane	MeOH	555 MIX
Acetophenone	89% (3)	96% (11)	97% (4)	72% (1)
N,N-Dimethylaniline	84% (3)	83% (9)	81% (1)	66% (1)
Naphthalene	90% (3)	92% (9)	94% (3)	73% (1)
2-Naphthol	86% (4)	88% (14)	79% (1)	65% (3)
Tetracosane	84% (6)	78% (9)	82% (12)	64% (2)
# of determinations	n = 3	n = 4	n = 3	n = 3

* Numbers in parenthesis are RSDs.

Finally, when comparing the results for each collection solvent idividually, several trends can be seen. When chloroform was the collection solvent, recoveries of acetophenone, *N,N*-dimethylaniline, and naphthalene were the same with each level of toluene modified extraction fluid studied. The recovery of 2-naphthol declined at 4% toluene modified CO_2 as compared to pure CO_2. Recovery of C_{24} dropped with both 4 and 8 mole percent toluene modified CO_2 as compared to pure CO_2. When hexane was studied, recoveries of all analytes were statistically similar under all conditions studied. Methanol showed the maximum recovery of analytes when 4 mole percent toluene modified CO_2 was used when studying acetophenone, *N,N*-dimethylaniline, and naphthalene. Recoveries with 0, 1, and 8 mole percent toluene modified CO_2 were lower for these analytes. Recovery of 2-naphthol and C_{24} declined when 8% was used.

As was stated above, the mixed collection solvent was an excellent trapping solvent for these analytes when pure CO_2 was used, but it was the worst collection solvent when acetonitrile or methanol modified CO_2 were employed. This trend continues with toluene modified CO_2. Recoveries of all analytes dropped when using modified CO_2 as compared to pure CO_2. Recoveries at 4% toluene modified CO_2 were improved over 1 and 8 percent, but were not as good as 0%.

When using organic modifiers to augment the solvating power of CO_2, it is possible that the modifier will get trapped in the collection vial. *Mulcahey* has theorized that methanol actually coats solid phase traps at certain trap temperatures (*36*). **Table XVII** displays how much modifier was actually used in the 30 minute extraction. The amount of modifier used was calculated by the following formulas:

Step 1:(Gas Flow Rate) X (1/500) X (Time) X (CO_2 Density) = Mass CO_2 (1)

Step 2:(Gas Flow Rate) X (1/500) X (Time) X (CO_2 Density) = Mass CO_2 (2)

Total Mass CO_2 = (Mass CO_2 Step 1) + (Mass CO_2 Step 2) (3)

Mass Modifier = Mole % Modifier X (MW Modifier / MW CO_2) X (Mass CO_2) X (1/100) (4)

Volume Modifier = (Mass Modifier) / (Density of Modifier) (5)

Step 1 is the lower pressure extraction which was run for 10 minutes and step 2 is the higher pressure run which was for 20 minutes. The Dionex measures decompressed CO_2 flow, this flow rate is divided by 500 to get to liquid CO_2 flow. To convert mole percent modifier to weight percent, multiply the mole percent by the ratio of molecular weight of the modifier over the molecular weight of CO_2. As can be seen from the above data, using toluene modified CO_2, 2 to 3 mL of toluene could have been trapped in the liquid trap. High mole percents of toluene modified CO_2 showed the worst recoveries of 2-naphthol and C_{24} across all of the collection solvents. This could be due to the high level of toluene introduced into the trap.

From these data, it can be seen that hexane and methanol trap these analytes well when modified (acetonitrile, methanol, or toluene) CO_2 is

TABLE XVII

VOLUME MODIFIER USED

FLUID COMPOSITION	VOLUME MODIFIER USED
1 Mole % Acetonitrile	0.3 mL
4 Mole % Acetonitrile	0.8 mL
1 Mole % Methanol	0.2 mL
4 Mole % Methanol	0.6 mL
8 Mole % Methanol	1.1 mL
1 Mole % Toluene	0.5 mL
4 Mole % Toluene	1.9 mL
8 Mole % Toluene	2.8 mL

used. Chloroform, which was not a good trapping solvent for the more volatile components in pure CO_2, was not a good trapping solvent for modified CO_2 either. For the mixed collection solvent, in pure CO_2, it trapped these analytes quantitatively. But, with the perturbation of adding modifiers to the CO_2, recoveries were affected severely. Since chloroform recoveries were not quantitative, the "10 mL" of hexane and methanol in the mixed solvent may not have been enough to effectively trap the analytes.

Generally, in a real world application, a class of compounds are the analytes of interest (e.g. PAH's, PCB's, or sulfur containing pesticides). In these cases, trapping could be easier since the analytes have very similar physical properties and their polarity range is small. The test mix studied here may be a worst case scenario in which the analytes are spread over a wide polarity range. Liquid trapping has proven to be better for trapping these analytes (acetophenone, *N,N*-dimethylaniline, naphthalene, 2-naphthol, and tetracosane) than solid phase trapping with pure CO_2 and modified CO_2.

SUMMARY:

Table XX is an overall review of analyte liquid trapping with pure and modified CO_2. From **Table XX**, several trends can be readily seen. The

TABLE XX*
ANALYTE RECOVERY Vs. MODIFIER AND COLLECTION SOLVENT

ACETONITRILE MODIFIED CO_2

	Chloroform			Hexane			Methanol			555 Mix		
	0%	1%	4%	0%	1%	4%	0%	1%	4%	0%	1%	4%
Ace			X	X	X	X	X	X		X		
Dma			X	X	X	X	86	X		X		
Nap	87	85	X	X	X	X	X	X		X		
2-N	X		X	88	X	X	88	X		X		
C_{24}	X	85	X	X	X	X	X	X		X		

METHANOL MODIFIED CO_2

	Chloroform				Hexane				Methanol				555 Mix			
	0	1	4	8	0	1	4	8	0	1	4	8	0	1	4	8
Ace				X	X	X	X	X	X	X	X	X	X			
Dma				X	X	X	X	X	86	X	X	X	X			
Nap	87	85		X	X	X	X	X	X	X	X	X	X			85
2-N	X	87		X	88	X	X	X	88	X	X	84	X			
C_{24}	X	88		X	X	X	X	85	X	88	X	88	X			

TOLUENE MODIFIED CO_2

	Chloroform				Hexane				Methanol				555 Mix			
	0	1	4	8	0	1	4	8	0	1	4	8	0	1	4	8
Ace			85	X	X	X	X	X	X	X	X	X	X		87	
Dma					X	X	X		86	88	X		X			
Nap	87	86	87	X	X	X	X	X	X	X	X	X	X		X	
2-N	X			86	88	87	87	88	88	X	X		X			
C_{24}	X	88			X	X			X	X	87		X			

* X denote recoveries of 89% or greater. Recoveries of 85 to 88% are listed also in the table. Recoveries of 84% or below are not listed in the table.
Ace = acetophenone: Dma = *N,N*-dimethylaniline: Nap = naphthalene: 2-N = 2-naphthol: C_{24} = *n*-tetracosane:

mixed collection solvent was only acceptable when pure CO_2 was employed. When modified CO_2 was used, regardless of modifier identity or amount, recoveries were poor. Chloroform was an acceptable collection solvent for these analytes only when 4% acetonitrile or 8% methanol modified CO_2 was employed, for all other experiments, chloroform was a poor collection solvent. Methanol as a collection solvent had bad recoveries with 4% acetonitrile and 8% toluene modified CO_2, in all other cases, methanol was an excellent collection solvent. Hexane was perhaps the best overall collection solvent studied for these analytes under these conditions. Recoveries were good for all conditions except 8% toluene modified CO_2. It is interesting to note that hexane and methanol have the lowest surface tension (18.4 and 22.6 dynes/cm @ 20 °C respectively) of the collection solvents studied, and were the best collection solvents studied under these extraction conditions.

CONCLUSION:

From a literature review and our studies, collection efficiencies for trapping analytes in a liquid after SFE could be affected by the following:

1) Fluid type (CO_2, NH_3, N_2O, etc.)

2) Modifier type (MeOH, ACN, Toluene, etc.)

3) Modifier concentration (1, 2, 4%, etc.)

4) Time of extraction

5) Fluid flow rate

6) Restrictor type (linear, frit, variable etc.)

7) Restrictor temperature

8) Liquid Trap

8A) Collection solvent (hexane, methylene chloride, etc.)

8B) Collection solvent volume (1, 5, 10 mL, etc.)

8C) Collection solvent temperature

In our studies only CO_2 was investigated as an extraction solvent, because it effectively removed the analytes of interest from the sand. The Dionex 723 supercritical fluid extractor employs linear restrictors. With this set-up, flow rate cannot be independently separated from the pressure used for extraction. In our studies, only restrictors rated at 250 mL/min decompressed flow (30 μm i.d.) were used. Only linear restrictors could be employed with this instrument. In this study, restrictor temperature was studied and a restrictor temperature of 125 to 175 °C was found to be optimal for 100% CO_2. The same conditions were employed for the modifier work. Lower restrictor temperatures resulted in restrictor plugging and higher restrictor temperatures resulted in reduced recoveries. The Dionex 723 employs a liquid collection system to trap analytes after extraction. All collection solvents were thermostatted to 5 °C to improve recoveries. The optimum amount of collection solvent present was found to be 15 mL. The type of collection solvent was varied and it was discovered that no one single component collection solvent efficiently trapped all of the analytes, when extracted with 100% CO_2. A mixed collection solvent consisting of hexane, chloroform, and methanol was determined to be the best collection solvent for this test mixture of analytes.

When modified fluids were studied (1 and 4 mole percent acetonitrile in CO_2 , and 1, 4, and 8 mole percents of methanol or toluene in CO_2), it was discovered that hexane or methanol were excellent trapping solvents for this trap design and these analytes. Modifier identity did play a part in trapping efficiency. For example, trapping when 8 mole percent methanol modified CO_2 was used was easier than trapping with 8 mole percent toluene modified CO_2.

FUTURE WORK:

Future work will center around the use of an ISCO extraction unit, where the restrictor is placed directly into the collection solvent. Future work may also center around the study of alternative extraction fluids, i.e. ammonia, nitrous oxide, and sulfur hexafluoride. Furter studies may be conducted with other collection solvents, besides the nine pure solvents listed. An attempt to re-optimize the extraction conditions to yield good results with chloroform and the mixed collection solvent when modified CO_2 is employed would be very beneficial.

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APPENDIX I

SOLID PHASE INSERT EVALUATION

INTRODUCTION

For off-line trapping of extracted analytes, currently solid phase trapping and liquid trapping are being employed. In an effort to maximize the utility of the Dionex-723 SFE extractor, which normally employs liquid trapping, solid phase inserts were developed. Instead of the unobstructed glass transfer tube shown in **Figure 3** on page 17, a solid phase tube was developed to retrofit the collection vial. With this tube, an indentation was made in the glass transfer tube to hold a layer of C_{18} bonded silica placed between an upper and lower layer of cotton. It was hoped that the analytes would get trapped in the C_{18} layer and be rinsed off with a few milliliters of solvent, instead of solely trapping in 15 mL of solvent. This would improve the trapping ability of the instrument for volatile components and for trace analysis work.

EXPERIMENTAL

The same experimental procedure that was outline in Chapter 3 was followed. When pure CO_2 was investigated, five trap designs were studied. The five traps consisted of; 1) a collection vial with no glass transfer tube and no collection solvent; 2) a collection vial with the old glass transfer tube but no collection solvent, 3) 15 mL of methanol in a collection vial with the old glass transfer tube; 4) a solid phase insert with no collection solvent; and 5) a solid phase insert along with 5 mL of methanol in the collection vial. The only modified CO_2 studied was methanol modified CO_2 at 1, 4, and 8%. With methanol modified CO_2, only three traps were investigated. Traps #3 (15 mL of methanol and the old glass transfer tube), #4 (the solid phase insert with no collection solvent), and #5 (the solid phase insert with 5 mL of methanol collection solvent). Data analysis of the extracts was performed on Minitab® as previously stated.

RESULTS AND DISCUSSION

Tables XIX, XX, XXI, XXII are the raw data for each vial run in these experiments. **Table XXIII** is the analyte recovery for all experiments. When pure CO_2 was studied with the various trap configurations, 15 mL of methanol with the old glass transfer tube and the solid phase insert with 5 mL of methanol in the collection vial, statistically gave much better recoveries for acetophenone, *N,N*-dimethylaniline, and naphthalene compared to the solid phase insert with no collection solvent, or a collection vial with no glass transfer tube, or a collection vial with the old glass transfer tube and no collection solvent. On the other hand for 2-naphthol and C_{24}, all recoveries were statistically equal, for all trap configurations. These latter two analytes are thought to precipitate out of the decompressed CO_2 stream and coat the inner glass tube. As evidence for this idea, when no tube was employed, recoveries of these two analytes were still good, RSD's were high, because the analytes just coated the inside of the collection vial, **Table XXIII**.

With 1% methanol modified CO_2, three traps were investigated, 15 mL methanol with the old glass transfer tube, a solid phase insert, and the

TABLE XIX
SOLID PHASE INSERT RAW DATA - 100% CO_2

Vial #	1	2	3	4
Collection	**Septum Only**	**Septum Only**	**Septum Only**	**Septum Only**
Modifier %	**0% MeOH**	**0% MeOH**	**0% MeOH**	**0% MeOH**
Oven Temperature	35 °C	35 °C	35 °C	35 °C
Flow @ 150 atm	---------------	---------------	200 mL/min	140 mL/min
Flow @ 340 atm	190 mL/min	220 mL/min	420 mL/min	340 mL/min
Total Flow	4.0 L	4.7 L	10.4 L	8.6 L
Notes				
Recovery (%)				
Acetophenone	51.96	47.77	3.84	20.24
N,N-Dimethylaniline	36.21	31.82	2.91	11.15
Naphthalene	54.61	53.80	26.29	37.94
2-Naphthol	88.04	88.86	82.23	91.68
Tetracosane	91.15	91.95	82.23	88.48

Vial #	1	2	3	4
Collection	**Old Tube(no solv)**	**Old Tube(no solv)**	**Old Tube(no solv)**	**Old Tube(no solv)**
Modifier %	**0% MeOH**	**0% MeOH**	**0% MeOH**	**0% MeOH**
Oven Temperature	35 °C	35 °C	35 °C	35 °C
Flow @ 150 atm	130 mL/min	130 mL/min	210 mL/min	---------
Flow @ 340 atm	270 mL/min	330 mL/min	490 mL/min	290 mL/min
Total Flow	6.9 L	7.7 L	11.6 L	5.6 L
Notes				
Recovery (%)				
Acetophenone	6.78	15.75	20.93	34.43
N,N-Dimethylaniline	3.71	9.47	13.85	21.84
Naphthalene	39.43	51.25	41.68	53.00
2-Naphthol	101.63	92.77	91.33	108.96
Tetracosane	95.66	95.06	92.54	103.04

Vial #	1	2	3	4
Collection	**Solid Phase Insert**	**Solid Phase Insert**	**Solid Phase Insert**	**Solid Phase Insert**
Modifier %	**0% MeOH**	**0% MeOH**	**0% MeOH**	**0% MeOH**
Oven Temperature	35 °C	35 °C	35 °C	35 °C
Flow @ 150 atm	---------------	---------------	180 mL/min	160 mL/min
Flow @ 340 atm	190 mL/min	220 mL/min	340 mL/min	320 mL/min
Total Flow	3.9 L	4.5 L	8.3 L	7.7 L
Notes				
Recovery (%)				
Acetophenone	57.10	29.01	17.97	16.08
N,N-Dimethylaniline	29.09	20.95	13.78	90.80
Naphthalene	80.00	65.47	49.40	36.06
2-Naphthol	94.77	95.50	79.71	56.47
Tetracosane	96.24	91.02	93.08	72.33

Vial #	1	2	3	4
Collection	**Solid Phase Insert + 5 mL MeOH**	**Solid Phase Insert + 5 mL MeOH**	**Solid Phase Insert + 5 mL MeOH**	**Solid Phase Insert + 5 mL MeOH**
Modifier %	**0% MeOH**	**0% MeOH**	**0% MeOH**	**0% MeOH**
Oven Temperature	35 °C	35 °C	35 °C	35 °C
Flow @ 150 atm	130 mL/min	130 mL/min	210 mL/min	--------
Flow @ 340 atm	270 mL/min	340 mL/min	500 mL/min	---------
Total Flow	6.5 L	7.7 L	11.8 L	0
Notes				**Rest. Plug**
Recovery (%)				
Acetophenone	89.47	85.85	85.68	0
N,N-Dimethylaniline	82.50	79.98	80.82	0
Naphthalene	89.88	87.30	87.13	0
2-Naphthol	82.04	94.81	93.50	0
Tetracosane	82.87	96.13	97.04	0

Vial #	1	2	3	4
Collection	**Glass Tube + 15 mL MeOH**	**Glass Tube + 15 mL MeOH**	**Glass Tube + 15 mL MeOH**	**Glass Tube + 15 mL MeOH**
Modifier %	**0% MeOH**	**0% MeOH**	**0% MeOH**	**0% MeOH**
Oven Temperature	35 °C	35 °C	35 °C	35 °C
Flow @ 150 atm	250 mL/min	160 mL/min	120 mL/min	370 mL/min
Flow @ 340 atm	480 mL/min	430 mL/min	330 mL/min	780 mL/min
Total Flow	13.6 L	10.6 L	7.3 L	18 L
Notes	**Bad Septum**			
Recovery (%)				
Acetophenone	3.06	93.11	94.57	93.60
N,N-Dimethylaniline	2.95	85.17	86.10	86.98
Naphthalene	3.68	94.03	95.59	95.18
2-Naphthol	3.83	90.56	91.29	81.30
Tetracosane	9.31	93.72	91.19	85.04

Vial #	5	6	7	8
Collection	**Glass Tube + 15 mL MeOH**	**Glass Tube + 15 mL MeOH**	**Glass Tube + 15 mL MeOH**	**Glass Tube + 15 mL MeOH**
Modifier %	**0% MeOH**	**0% MeOH**	**0% MeOH**	**0% MeOH**
Oven Temperature	35 °C	35 °C	35 °C	35 °C
Flow @ 150 atm	100 mL/min	160 mL/min	160 mL/min	200 mL/min
Flow @ 340 atm	170 mL/min	400 mL/min	330 mL/min	460 mL/min
Total Flow	3.2 L	9.1 L	7.6 L	10.6 L
Notes				
Recovery (%)				
Acetophenone	93.72	92.59	92.33	95.11
N,N-Dimethylaniline	85.78	86.11	84.55	88.73
Naphthalene	95.81	96.14	95.71	97.34
2-Naphthol	94.02	83.72	86.24	89.90
Tetracosane	99.13	91.09	92.66	97.44

TABLE XX
SOLID PHASE INSERT RAW DATA - 1% MeOH CO_2

Vial #	1	2	3	4
Collection	Solid Phase Insert	Solid Phase Insert	Solid Phase Insert	Solid Phase Insert
Modifier %	1% MeOH	1% MeOH	1% MeOH	1% MeOH
Oven Temperature	37 °C	37 °C	37 °C	37 °C
Flow @ 175 atm	100 mL/min	130 mL/min	230 mL/min	200 mL/min
Flow @ 340 atm	200 mL/min	250 mL/min	370 mL/min	340 mL/min
Total Flow	4.1L	6.0 L	9.6 L	8.6 L
Notes			Tube Out	
Recovery (%)				
Acetophenone	87.97	75.44	0	32.66
N,N-Dimethylaniline	58.09	57.55	0	8.52
Naphthalene	82.59	80.13	13.11	37.21
2-Naphthol	91.00	97.34	64.06	96.72
Tetracosane	86.35	90.53	85.65	85.57

Vial #	1	2	3	4
Collection	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH
Modifier %	1% MeOH	1% MeOH	1% MeOH	1% MeOH
Oven Temperature	37 °C	37 °C	37 °C	37 °C
Flow @ 175 atm	160 mL/min	170 mL/min	270 mL/min	290 mL/min
Flow @ 340 atm	310 mL/min	340 mL/min	480 mL/min	520 mL/min
Total Flow	7.3 L	8.1 L	12.0 L	13.0 L
Notes	Tube Out	Tube Out		
Recovery (%)				
Acetophenone	66.49	20.57	93.91	97.35
N,N-Dimethylaniline	65.24	18.33	92.11	95.53
Naphthalene	66.15	35.76	94.13	97.05
2-Naphthol	92.05	86.25	95.59	97.89
Tetracosane	85.92	92.31	93.23	92.70

Vial #	1	2	3	4
Collection	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH
Modifier %	1% MeOH	1% MeOH	1% MeOH	1% MeOH
Oven Temperature	37 °C	37 °C	37 °C	37 °C
Flow @ 175 atm	160 mL/min	150 mL/min	240 mL/min	270 mL/min
Flow @ 340 atm	320 mL/min	330 mL/min	490 mL/min	510 mL/min
Total Flow	7.6 L	7.6 L	11.5 L	12.4 L
Notes			Tube Out	
Recovery (%)				
Acetophenone	96.93	97.69	97.47	95.38
N,N-Dimethylaniline	97.66	98.28	97.51	97.06
Naphthalene	98.26	99.42	98.51	97.87
2-Naphthol	91.58	91.26	91.12	84.02
Tetracosane	86.32	93.60	92.13	81.18

TABLE XXI
SOLID PHASE INSERT RAW DATA - 4% MeOH CO_2

Vial #	1	2	3	4
Collection	Solid Phase Insert	Solid Phase Insert	Solid Phase Insert	Solid Phase Insert
Modifier %	4% MeOH	4% MeOH	4% MeOH	4% MeOH
Oven Temperature	44 °C	44 °C	44 °C	44 °C
Flow @ 176 atm	130 mL/min	140 mL/min	230 mL/min	250 mL/min
Flow @ 343 atm	290 mL/min	300 mL/min	430 mL/min	500 mL/min
Total Flow	6.8 L	7.1 L	10.6 L	12.2 L
Notes	Tube Out		Tube Out	
Recovery (%)				
Acetophenone	14.43	88.92	17.57	88.21
N,N-Dimethylaniline	4.69	32.16	8.42	82.77
Naphthalene	34.27	85.32	20.59	85.89
2-Naphthol	90.11	98.00	94.16	96.69
Tetracosane	72.23	101.08	95.44	88.51

Vial #	1	2	3	4
Collection	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH
Modifier %	4% MeOH	4% MeOH	4% MeOH	4% MeOH
Oven Temperature	44 °C	44 °C	44 °C	44 °C
Flow @ 176 atm	100 mL/min	120 mL/min	200 mL/min	160 mL/min
Flow @ 343 atm	210 mL/min	250 mL/min	360 mL/min	370 mL/min
Total Flow	4.1 L	5.9 L	8.5 L	8.7 L
Notes				
Recovery (%)				
Acetophenone	96.01	95.86	78.77	38.67
N,N-Dimethylaniline	92.90	93.49	75.45	35.89
Naphthalene	95.05	95.24	78.20	39.67
2-Naphthol	94.91	98.26	79.42	89.86
Tetracosane	93.81	101.58	77.26	96.92

Vial #	1	2	3	4
Collection	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH
Modifier %	4% MeOH	4% MeOH	4% MeOH	4% MeOH
Oven Temperature	44 °C	44 °C	44 °C	44 °C
Flow @ 176 atm	100 mL/min	110 mL/min	210 mL/min	190 mL/min
Flow @ 343 atm	210 mL/min	240 mL/min	320 mL/min	350 mL/min
Total Flow	4.9 L	5.5 L	8.2 L	8.5 L
Notes				
Recovery (%)				
Acetophenone	90.21	99.36	92.72	91.80
N,N-Dimethylaniline	97.15	99.02	93.55	94.24
Naphthalene	96.82	99.62	93.78	94.01
2-Naphthol	88.27	100.55	90.54	93.37
Tetracosane	90.98	96.87	90.37	94.96

TABLE XXII
SOLID PHASE INSERT RAW DATA - 8% MeOH CO_2

Vial #	1	2	3	4
Collection	Solid Phase Insert	Solid Phase Insert	Solid Phase Insert	Solid Phase Insert
Modifier %	8% MeOH	8% MeOH	8% MeOH	8% MeOH
Oven Temperature	53 °C	53 °C	53 °C	53 °C
Flow @ 180 atm	160 mL/min	210 mL/min	160 mL/min	0 mL/min
Flow @ 350atm	320 mL/min	360 mL/min	270 mL/min	0 mL/min
Total Flow	7.9 L	9.0 L	7.0 L	0.1 L
Notes				Rest. Plug
Recovery (%)				
Acetophenone	83.06	83.31	84.75	10.60
N,N-Dimethylaniline	75.00	76.62	76.16	10.64
Naphthalene	80.63	80.42	81.08	10.59
2-Naphthol	79.80	99.85	101.05	8.30
Tetracosane	80.36	15.23	34.43	8.96

Vial #	1	2	3	4
Collection	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH	Solid Phase Insert + 5 mL MeOH
Modifier %	8% MeOH	8% MeOH	8% MeOH	8% MeOH
Oven Temperature	53 °C	53 °C	53 °C	53 °C
Flow @ 180 atm	0 mL/min	110 mL/min	190 mL/min	210 mL/min
Flow @ 350atm	0 mL/min	210 mL/min	380 mL/min	390 mL/min
Total Flow	0 L	4.6 L	9.0 L	9.5 L
Notes	Rest. Plug			Tube Out
Recovery (%)				
Acetophenone	0	101.36	94.10	93.85
N,N-Dimethylaniline	0	100.02	93.37	96.40
Naphthalene	0	100.70	93.38	95.78
2-Naphthol	0	97.90	93.07	95.20
Tetracosane	0	73.54	77.08	63.50

Vial #	1	2	3	4
Collection	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH	Glass Tube + 15 mL MeOH
Modifier %	8% MeOH	8% MeOH	8% MeOH	8% MeOH
Oven Temperature	53 °C	53 °C	53 °C	53 °C
Flow @ 180 atm	120 mL/min	210 mL/min	180 mL/min	0 mL/min
Flow @ 350atm	310 mL/min	370 mL/min	300 mL/min	0 mL/min
Total Flow	7.7 L	9.2 L	7.2 L	0.1 L
Notes		Tube Out		Rest. Plug
Recovery (%)				
Acetophenone	91.86	42.88	94.83	64.66
N,N-Dimethylaniline	94.53	43.49	97.89	59.03
Naphthalene	94.91	45.03	97.96	67.49
2-Naphthol	78.73	87.43	89.90	89.86
Tetracosane	80.03	92.57	95.43	90.71

TABLE XXIII
ANALYTE RECOVERY WITH SOLID PHASE TUBE INSERT

Pure CO_2*

	Septum Only#	0 mL Solvent##
Acetophenone	31% (74)	19% (59)
N,N-Dimethylaniline	21% (78)	12% (63)
Naphthalene	43% (32)	46% (15)
2-Naphthol	88% (5)	99% (8)
n-Tetracosane	88% (5)	97% (5)
# of Determinations	n = 4	n = 4

	Glass Tube + 15 mL MeOH	Solid Phase Insert	Solid Phase Insert + 5 mL MeOH
Acetophenone	94% (1)	30% (30)	87% (2)
N,N-Dimethylaniline	86% (2)	39% (91)	81% (2)
Naphthalene	96% (1)	58% (33)	88% (2)
2-Naphthol	88% (5)	82% (22)	90% (8)
n-Tetracosane	93% (5)	88% (12)	92% (9)
# of Determinations	n = 7	n = 4	n = 3

1% Methanol Modified CO_2

	Glass Tube + 15 mL MeOH	Solid Phase Insert	Solid Phase Insert + 5 mL MeOH
Acetophenone	97% (1)	65% (44)	96% (3)
N,N-Dimethylaniline	98% (1)	41% (69)	94% (3)
Naphthalene	99% (1)	67% (38)	96% (2)
2-Naphthol	90% (4)	95% (4)	96% (2)
n-Tetracosane	88% (7)	88% (3)	93% (1)
# of Determinations	n = 4	n = 3	n = 2

4% Methanol Modified CO_2

	Glass Tube + 15 mL MeOH	Solid Phase Insert	Solid Phase Insert + 5 mL MeOH
Acetophenone	94% (4)	89% (1)	90% (11)
N,N-Dimethylaniline	96% (3)	57% (62)	87% (12)
Naphthalene	96% (3)	86% (1)	90% (11)
2-Naphthol	93% (6)	97% (1)	91% (11)
n-Tetracosane	93% (3)	95% (9)	91% (14)
# of Determinations	n = 4	n = 2	n = 3

8% Methanol Modified CO_2

	Glass Tube + 15 mL MeOH	Solid Phase Insert	Solid Phase Insert + 5 mL MeOH
Acetophenone	93% (2)	84% (1)	96% (4)
N,N-Dimethylaniline	96% (3)	76% (1)	97% (4)
Naphthalene	96% (2)	81% (1)	97% (3)
2-Naphthol	84% (10)	94% (13)	95% (3)
n-Tetracosane	88% (12)	44% (77)	71% (10)
# of Determinations	n = 3	n = 3	n = 2

* Numbers in parenthesis are RSD's.
#Inner glass tube not employed, no collection solvent employed in an empty collection vial.
Inner glass tube employed, but no collection solvent employed in an empty collection vial.

solid phase insert + 5 mL methanol. Only *N,N*-dimethylaniline showed a statistical difference between traps, with the solid phase insert, with no collection solvent present, having the worst recovery. The solid phase insert had extremely high RSD's for acetophenone, *N,N*-dimethylaniline, and naphthalene. Under these conditions of extremely high RSD's, statistically, the samples can only be said to come from the same population. The solid phase insert, without any collection solvent, is not recommended for trapping these analytes under these conditions.

With 4% methanol modified CO_2, all analytes were trapped equally well, statistically, with any one of the traps employed. *N,N*-Dimethylaniline had such a high RSD for the solid phase insert trap, with no collection solvent, that statistically, it could only be said that the recovery was equal to the other two traps. The RSD's for the solid phase trap with 5 mL methanol were all high, 11 to 14%.

When 8% methanol modified CO_2 was investigated, the recoveries of acetophenone, *N,N*-dimethylaniline, and naphthalene were statistically equal with 15 mL methanol, with the old glass transfer tube, and the trap consisting of the solid phase insert with 5 mL of methanol, and the recoveries with the plain solid phase insert, with no collection solvent, were worse. Recoveries of 2-naphthol and C_{24} were equal across the board.

The use of the solid phase trap, with or without liquid collection solvent in the collection vial, does not improve recoveries of the analytes to any extent. The extra trouble of rinsing the solid phase insert and the considerable problem of the solid phase inserts popping out of the septa, during extraction, discourages their use for these analytes under these conditions. The precision of repeated measurements with the solid phase insert is poor, as denoted by the extremely large RSD's seen. When 15 mL of methanol with the old glass transfer tube is employed, the precision of the repeated measurements are quite good, RSD's are usually between 1 and 7%. *F-tests* were run to check the precision of the various traps investigated, *F-tests* are described in Appendix II. With pure CO_2 as the extraction fluid, the precision of the traps for acetophenone, *N,N*-dimethylaniline, and naphthalene fell into two groups, 15 mL of methanol with the old glass transfer tube and the solid phase insert tube with 5 mL of methanol had much greater precision than the traps consisting of either no glass transfer tube and no collection solvent, or the trap consisting of the old glass transfer tube with no collection solvent, or the trap consisting of the solid phase insert with no collection solvent. 2-Naphthol and C_{24} precision for the five traps were equal, except for 2-naphthol with the solid phase insert and no collection solvent had poorer precision than the other four traps. When 1% methanol modified CO_2 was investigated, the precision of the solid phase insert with no collection solvent trap was much poorer than the other two traps for acetophenone, *N,N*-dimethylaniline, and naphthalene. 2-Naphthol and C_{24} had the same precision for all three traps. At 4% methanol modified CO_2, the solid phase insert with 5 mL of methanol had the poorest precision for all analytes, except for *N,N*-dimethylaniline which had the poorest precision when the solid phase insert with no trapping solvent was employed. At 8% methanol modified CO_2, the precision for all analytes was equal for all three traps, except for C_{24}

where the solid phase insert with no collection solvent had the worst precision.

APPENDIX II

STATISTICS

Analysis of Variance (ANOVA)
Tukey Pairwise Comparison
F-TEST

ANOVA and *Tukey* calculations were performed to determine if statistical difference existed between conditions tested. All calculations were run on Minitab® release #8 on an Apple Macintosh SE.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Test
Between Sample	t-1	SSB	s_B^2 = SSB/(t-1)	s_B^2 / s_W^2
Within Sample	n_T-t	SSW	s_W^2 = SSW/(n_T-t)	
Total	n_T-1	TSS		

Null Hypothesis

H_0: $\mu 1 = \mu 2 = \mu 3$: All population means are the same.

Alternative Hypothesis

H_1: $\mu 1 \neq \mu 2 \neq \mu 3$: At least one of the population means is different from the rest.

n_T: Total sample size: $n_T = \Sigma n_i$

t : # of conditions

SSB: Between sample sum of squares: SSB $= \Sigma n(y_i - y_{ave})^2$

SSW: Within sample sum of squares: SSW = TSS - SSB

TSS: Total sum of squares: TSS $= \Sigma\Sigma(y_{ij} - y_{ave})^2$

y_{ij}: The jth sample observation selected from population i. For example, y_{13} denotes the third sample observation from population one.

y: The sum of all sample observations: $y = \Sigma y_i$

y_i: The sum of the sample measurements obtained from population i.

y_{avei}: The average of the ni sample observations from population i: $y_{avei} = y_i / n_i$

y_{ave}: the average of all sample observations: $y_{ave} = y/n_T$

n_i: The number of sample observations for population i.

Mean Square: Sum of squares divided by its degrees of freedom.

S_B^2: mean square between samples

S_W^2: mean square within samples.

From these equations, the sources of variation for a given data set are determined. Each variation is ratioed with the residual mean square and the resulting values are compared to *F-test* table values for the proper degrees of freedom at a 95% confidence level. The Null hypothesis (H_O) is accepted if $F_{calc} \leq F_{table}$ or rejected if $F_{calc} > F_{table}$.

Tukey pairwise comparison tests are based on the following calculations. Two population means μ_i and μ_j are declared different if:

$$|y_{ave\,i} - y_{ave\,j}| \geq W_{ij}$$

where

$$Wij = q_{\alpha}(t,v) \;\; X \;\; \{(s_W{}^2 / 2) \;\; X \; (1 / n_i + 1 / n_j)\}$$

$s_W{}^2$ is the mean square within samples based on v degrees of freedom, $q\alpha$ (t,v) is the upper-tail critical value of the studentized range for comparing t different populations, and n is the number of observations in each sample (*i* or *j*). $q\alpha(t,v)$ values are provided in statistical tables (ref # 41, page A26 - A27). Minitab® computes a confidence interval to test for differences between the means of two populations. A confidence interval can be constructed where:

$$(y_{ave\,i} - y_{ave\,j}) \pm W_{ij}$$

When this range contains zero, the two means are statistically equal, when the range is either always greater than zero or always less than zero, the two means are not statistically equal at the 95% range. Below is a typical Minitab® printout of the data. This example is for comparisons of C_{24} between three restrictor temperatures (125, 175, and 250 °C) with chloroform as the collection solvent. As can be seen the value of $q\alpha(t,v)$ is

3.73. F_{calc} = 14.73 and F_{table} is 3.81, therefore the Null hypothesis is rejected ($\mu1 = \mu2 = \mu3$: All population means are the same) and the Alternative hypothesis is accepted ($\mu1 \neq \mu2 \neq \mu3$: At least one of the population means is different from the rest). By computing the *Tukey* pairwise comparison test, it can be seen that $\mu_{125} = \mu_{175}$, and that $\mu_{125} \neq \mu_{250}$ and that $\mu_{175} \neq \mu_{250}$. Therefore, it can be statistically said that at the 95% confidence level, the recovery of C_{24} at a restrictor temperature of 250 °C was worse than the recovery at 125 or 175 °C. Also, the recovery of C_{24} at 125 and 175 °C restrictor temperatures are equal, they are from the same population.

```
MTB > Oneway 'C24' 'Rest';
SUBC>   Tukey 5.

ANALYSIS OF VARIANCE ON C24
SOURCE     DF        SS         MS         F        p
Rest        2     909.4      454.7     14.73    0.000
ERROR      13     401.4       30.9
TOTAL      15    1310.8
                                    INDIVIDUAL 95 PCT CI'S FOR MEAN
                                    BASED ON POOLED STDEV
 LEVEL      N      MEAN      STDEV  --------+---------+---------+--------
   125      8     95.23       1.44                    (---*---)
   175      4     96.07       1.33                  (-----*-----)
   250      4     78.11      11.28  (-----*-----)
                                    --------+---------+---------+--------
POOLED STDEV =     5.56                    80        90       100

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0205

Critical value = 3.73

Intervals for (column level mean) - (row level mean)

               125        175

   175      -9.818
             8.131

   250       8.137      7.592
            26.086     28.318


MTB >
```

An *F-test* will determine if the precision between two data sets are statistically different. An *F-test* is performed by the following calculations:

H_0: $S_1^2 = S_2^2$: The variance (standard deviation squared) of population 1 is equal to the variance of population 2.

H_1: $S_1^2 > S_2^2$ or $S_1^2 \neq S_2^2$: The variance of population 1 is greater than or not equal to the variance of population 2.

F: $F = S_1^2 / S_2^2$

Accept H_0 if $F_{calc.} < F_{table}$ for $a = \alpha$, df1 = n1-1, df2 = n2-1. Reject H_0 if $F_{calc.} > F_{table}$ for $a = \alpha$, df1 = n1-1, df2 = n2-1.

α: Confidence level. For a one-tailed test, $S_1^2 > S_2^2$, $\alpha = 0.05$ (95% confidence level). For a two-tailed test, $S_1^2 \neq S_2^2$, $\alpha = 0.025$ (95% confidence level).

df: Degrees of freedom: n-1.

n: # of determinations.

F_{table} can be found in statistical tables (ref #41, pages A6 - A19).

Vita

Peter G. Thompson was born on January 4, 1967 in Kingston, New York. He received his Bachelor of Science degree in Chemistry from Rochester Institute of Technology in May of 1990. In addition to his undergraduate education, he completed cooperative education positions with McCann Manufacturing, Philips Display Component Company, and IBM. He began his graduate studies in Analytical Chemistry at Virginia Tech in September of 1990 under the guidance of Dr. Larry T. Taylor and received his Master of Science degree in Analytical Chemistry in July of 1994. While at Virginia Tech, Peter held a cooperative education position with British Petroleum in the summer of 1991.

Peter G. Thompson