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I am submitting herewith a thesis written by Kristi Jill Anderson entitled "Supercritical Fluid Extraction of Benz(*a*)anthracene from Coal Fly Ash Using Modified Carbon Dioxide and Chlorodifluoromethane". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

E.L. Wehry, Major Professor

We have read this thesis
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Dean of The Graduate School

SUPERCRITICAL FLUID EXTRACTION OF BENZ(*a*)ANTHRACENE FROM COAL FLY ASH USING MODIFIED CARBON DIOXIDE AND CHLORODIFLUOROMETHANE

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ABSTRACT

Benz(*a*)anthracene (BaA) was deposited from the vapor phase onto the surface of a carbonaceous fraction of coal fly ash for extraction efficiency studies. Organic modifiers in conjunction with supercritical fluid extraction with CO_2 were studied to attempt to improve the extraction recovery of BaA from the fly ash matrix. The efficiency of supercritical fluid extraction (SFE) of BaA from the ash using methanol-, toluene-, and dichloromethane-modified CO_2, as well as pure CO_2, was investigated. Modified SFE was performed both in the static (non-flowing) mode and the dynamic (continuous flow) mode to learn if either technique improved the recovery of BaA from the fly ash matrix. Comparisons were made to ultrasonic extraction in toluene to determine if SFE is the best technique for extraction of PAH from fly ash. Toluene-modified CO_2 offered the highest extraction efficiency of the modified CO_2 systems studied and gave recoveries comparable to ultrasonic extraction.

Additionally, chlorodifluoromethane ($CHClF_2$) was investigated as a replacement for pure CO_2 to see if improved recovery of BaA could be achieved. $CHClF_2$ was able to greatly improve the recovery of BaA as compared with SFE using pure CO_2 and gave slightly higher recoveries than both ultrasonic extraction and toluene-modified SFE. The use of toluene-modified $CHClF_2$ was also investigated and proved to be the best extraction medium for the removal of BaA from coal fly ash.

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CHAPTER 1

INTRODUCTION

I. Polycyclic Aromatic Hydrocarbons: Environmental Effects and Analytical Extraction from Adsorbent Surfaces

A. Environmental Effects of Polycyclic Aromatic Hydrocarbons and Coal Fly Ash

Polycyclic aromatic hydrocarbons (PAH) occur in the environment primarily as the products of the combustion of organic matter. The major sources of combustion that produce PAH are automobiles, buses, and trucks; residential furnaces; coke production plants; and coal-fired power plants (1). After release into the atmosphere (in the vapor phase), PAH can adsorb on many environmental surfaces, including air particulate matter, soil and sediment samples, and fly ash (2). Coal fly ash is one adsorbent of particular interest due to the widespread use of fossil fuels as an energy source. The coal fly ash released into the atmosphere is formed as a by-product of the combustion of coal and serves as a highly adsorptive sample matrix for PAH (3). The ash is a heterogeneous mixture that often contains particles of various sizes and chemical compositions (4). The ability to quantify the amount of PAH present in the atmosphere adsorbed on the surface of coal fly ash is important in determining possible environmental hazards associated with PAH.

B. The Need for Analytical Extraction of Environmental Solids

Since the determination many years ago that polycyclic aromatic hydrocarbons (PAH) may be carcinogenic, mutagenic, or both, the need for determination of these compounds in the environment has become important. However, many of the

environmental solids on which the PAH are deposited cannot be analyzed directly without severe interferences. This is due in part to the heterogeneous nature of the solids and the inability to obtain a representative sample for analysis. It is also due to the lack of highly sensitive quantitative methods for the determination of organic compounds adsorbed on solid surfaces. In order to quantify the PAH content of a solid, it then becomes necessary to extract the PAH from the sample matrix into a more readily analyzed matrix (e.g., a liquid solvent). The ability to extract and recover PAH from environmental solid matrices is often the crucial step in the quantitative determination of PAH (5).

The degree to which the PAH is adsorbed on the solid is highly matrix-dependent. Coal fly ash is considered a highly sorptive matrix due to the high carbon content of some ashes. The carbonaceous particles in some ashes may cause irreversible adsorption of PAH. Additionally, it has been shown that PAH are not adsorbed uniformly on the surface of the ash (3). These factors must be taken into consideration and have been known to pose particular problems when attempting to quantitatively extract PAH from coal fly ash.

C. Common Methods for Extraction of PAH

Several of the methods used for the extraction of PAH from adsorbent surfaces have been in place for many years. Traditional liquid solvent extractions are the most common and have been performed since the early 1900s. Of the liquid solvent extractions, Soxhlet extraction was for many years the customary method for the determination of PAH on solid samples. Soxhlet extractions are currently used

by the National Institute of Standards and Technology (NIST) as a standard method for the determination of PAH content in environmental samples (6). These extractions take anywhere from six hours to two days to complete and can utilize large amounts of organic solvents such as benzene and methylene chloride. Ultrasonic solvent extraction is another routine method of liquid extraction. It relies on ultrasonic agitation to increase solvent contact with the matrix to displace the molecules adsorbed on the surface. Ultrasonic extraction can be accomplished in a matter of several minutes to one hour. Liquid extractions using ultrasonics are fast replacing conventional Soxhlet extractions due to greater speed and efficiency (4).

More recently, the need for efficient extraction of PAH from solid samples without the generation of large amounts of organic waste has led to the need for more environmentally-conscious, energy-efficient extraction methods. The use of supercritical fluids in extracting PAH from environmental solids has emerged as a viable technique over the past ten years.

II. Supercritical Fluids and Supercritical Fluid Extractions

A. Supercritical Fluids

A substance above its critical temperature and pressure, at which the gas and liquid phases are indistinguishable, is termed a "supercritical fluid". Figure 1 shows the pressure-temperature diagram for a pure compound and its supercritical region. Once a substance reaches this state, it takes on unique properties different from those of a liquid or a gas. Table 1 illustrates how the properties of supercritical fluids

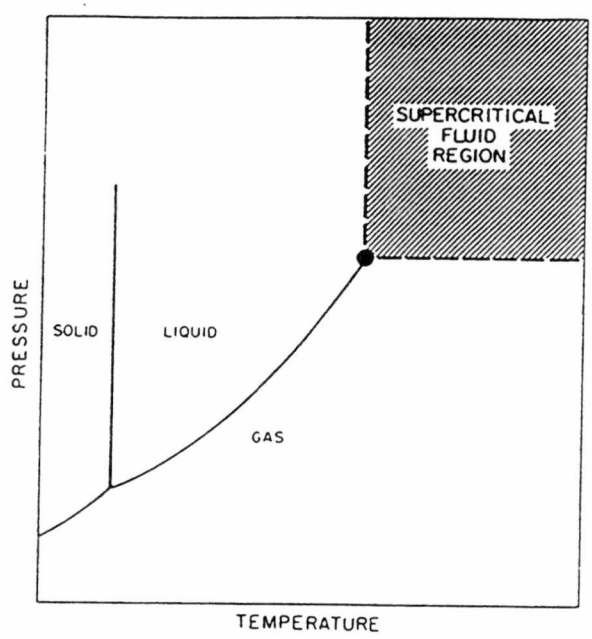

Figure 1. Pressure-temperature diagram for a pure component.
Source: McHugh, M.A.; Krukonis, V.J. *Supercritical Fluid Extraction.* Butterworth-Heinemann: Boston, 1994, p 11.

Table 1. Properties of a typical gas, liquid, and supercritical fluid.
Source: Hoyer, G. *Chemtech.* 1985, 15, 440-448.

	Gas	Supercritical Fluid	Liquid
Density (g/mL)	(0.6-2.0) x 10^{-3}	0.2-0.9	0.6-1.6
Viscosity (cP)	(1-3) x 10^{-2}	(1-9) x 10^{-2}	0.2-3.0
Diffusion coeff. (cm^3/s)	0.1-0.4	(0.2-0.7) x 10^{-3}	(0.2-2.0) x 10^{-5}

compare to those of liquids and gases. The density of a supercritical fluid gives it solvating power close to that of a liquid. With diffusion coefficients larger and viscosities smaller than liquids, supercritical fluids have favorable mass transfer characteristics that are desirable when performing analytical extractions (7).

It has been shown that the solvent strength of a compound in its supercritical state is directly related to the density of the compound (8). The ability to control the solvating power of a supercritical fluid by controlling the pressure and temperature (thus controlling the density) provides supercritical fluids a major advantage over liquids when performing analytical extractions. Table 2 lists critical temperatures and pressures for several compounds. As seen in the table, many compounds have critical conditions that are fairly easy to attain in the laboratory. By far, the most commonly used supercritical fluid has been CO_2. This is likely because of its inertness and low critical temperature. Supercritical CO_2 has also shown a strong solubilizing power for many compounds, both polar and nonpolar.

B. History of Supercritical Fluids and Supercritical Fluid Extraction (SFE)

The ability of a supercritical fluid to dissolve solid materials was first reported by Hannay & Hogarth in 1879 (9). They noted how several inorganic salts could be dissolved in ethanol above its critical temperature (234°C). They also noted that, when the pressure was decreased, the salts were precipitated out of the ethanol. This work sparked the interest of other scientists. In 1896, Villard published a study on supercritical methane, ethylene, carbon dioxide, and nitrous oxide (10). He noted the ability of these compounds to dissolve several solid and liquid hydrocarbons.

Table 2. Critical conditions of representative supercritical fluids. Source: *Handbook of Chemistry and Physics*; Weast, R.,Ed.; CRC Press: Boca Raton, FL, 1989; pp 71-72.

Fluid	T_c (°C)	P_c (atm)
Ammonia	132.5	112.5
CO_2	31.	72.9
$CHClF_2$	96.	49.12
Ethane	32.2	48.2
Ethylene	9.9	50.5
H_2O	374.1	218.3
Methanol	240.	78.5
N_2O	36.5	71.7
Propane	96.8	42.

Some years later, Buchner published data on the solubility of a number of organic compounds in supercritical CO_2 (11). One of the compounds Buchner studied was naphthalene. As a result, naphthalene became the solute of interest in supercritical fluid studies for the next 60 years and was studied extensively by numerous researchers (12-14).

During this period, Francis did the most extensive work. In 1954, he reported the solubility of over 200 compounds in CO_2 at 25°C and 64.6 atm, just below its critical point (15). The study encompassed a number of organic compounds with various functional groups including aromatic and heterocyclic compounds. Although Francis' study was done with liquid CO_2, the results of the study can be extrapolated to estimate the solubility of the compounds in supercritical CO_2. The results of this study were very beneficial in determining the usefulness of SFE for many compounds prior to experimental work.

Over the next few decades and into the early seventies, supercritical fluids were touted as ideal solvents with much promise both in industry and in the laboratory. During this period, two of the more important applications of SFE were the extraction of caffeine from coffee and nicotine from tobacco. However, in spite of several useful applications of SFE, interest in SFE faded during the late seventies to mid-eighties when the initial promises of the capabilities of the new technique failed to materialize. Few papers on SFE were published during this time.

Despite the decline in interest in SFE during the seventies and early eighties, the technique has experienced a revival in the last ten years as environmental concerns have led scientists to seek out more energy-efficient extraction techniques that generate less hazardous waste than conventional extractions with organic solvents. Supercritical fluid extractions may be more cost-efficient on a per extraction basis, require smaller amounts of solvents, use solvents having low toxicities, and are far less time-consuming than typical Soxhlet extractions (7). This

has led to a resurgence of interest in SFE as a promising technique for analytical extractions on a variety of samples.

C. Applications of SFE

As a result of the newfound interest in SFE, the technique has been applied to the extraction of various compounds from many different matrices. Polychlorinated biphenyls (PCB) have been successfully extracted from fish (16), soil samples (17), fly ash, and air particulates (18,19). SFE has also been applied in the extraction of fats from meat (20), flavor compounds from spices (21), and vitamins from plant tissues (22). During these processes, the extract is collected and can be analyzed by a variety of analytical methods including gas chromatography, supercritical fluid chromatography, and ultraviolet spectroscopy. In most cases, however, SFE has routinely been coupled with gas chromatography or supercritical fluid chromatography to separate and analyze the extracted compounds.

PAH have been extracted from several environmental solids including marine sediment, fly ash, air and diesel particulate matter (23), and petroleum waste sludge (24). These extractions have been performed using various supercritical fluids including "modified" fluids in which small amounts (1-10%) of organic solvent are added to the supercritical fluid in an attempt to increase recoveries of PAH. Mauldin reported 68% recovery of pyrene vapor-deposited on coal ash using methanol-modified isobutane (25). Yang and co-workers have reported increased recoveries for high molecular weight PAH from air particulates using CO_2 modified with diethylamine and toluene, as compared with those obtained using 48 hour

Soxhlet extraction. Toluene-modified CO_2 was reported to nearly double the recovery of PAH from diesel soot as compared with pure CO_2 (23). The choice of modifiers for improving recovery of PAH appears to be matrix-dependent. However, the reasons why modifiers are able to improve extraction efficiencies for the various matrices are not clear at this time.

III. Experimental Objectives and Research Outline

A. Study of "Modified" Supercritical CO_2

As previously mentioned, the coal fly ash matrix has been known to pose severe problems when attempting to extract compounds adsorbed on the surface of the fly ash. The purpose of this thesis is to determine if supercritical fluid extraction is superior to ultrasonic extractions for the removal of PAH adsorbed on coal fly ash. Benz[*a*]anthracene (BaA) is used as the representative PAH, and a known amount is deposited from the vapor phase on the ash (26). A carbonaceous coal fly ash sample, known to be very difficult to extract PAHs from, is used as the adsorbent. Supercritical fluid extractions are then performed on samples of the fly ash. The extractions are done using supercritical CO_2 modified with toluene, methanol, and dichloromethane. The extraction efficiencies for the removal of BaA using modified CO_2 are compared with the efficiency of pure CO_2. Traditional liquid extraction using ultrasonics is also performed on the sample for comparison purposes.

B. Comparison of Static vs. Dynamic SFE

Supercritical fluid extractions using modified CO_2 are done in two ways: "dynamic" (i.e., continuous flow) mode and "static" (non-flowing) mode. The dynamic mode of extraction is done by adding the modifier to a pump containing CO_2. The modified supercritical fluid is then pressurized in the pump along with the CO_2 and an extraction cell containing the sample is flushed with the modified CO_2 for approximately 90 minutes. In a static extraction, the modifier is pipetted directly onto the sample in the extraction cell. The cell is then exposed to pressurized CO_2 and held at constant pressure and temperature for about 45 minutes, after which a 45-minute dynamic extraction is performed to collect the extracted PAH. The second objective of this thesis is to determine which mode of modifier addition is more favorable when performing extractions and to determine if either method affects the recovery of BaA from the fly ash.

C. Chlorodifluoromethane vs. CO_2 as a Supercritical Fluid

It has been shown that supercritical fluids, such as N_2O, that have a higher dipole moment than CO_2 can increase the extraction efficiency of higher molecular weight PAH and chlorinated dioxins from both sediment and fly ash (27,28). However, in choosing a supercritical fluid for analytical extraction, one is limited by several factors. Some of the more important considerations include the critical temperature and pressure of the compound; the toxicity and other dangers associated with the use of the compound; and the need for a compound that is in the gaseous state at room temperature conditions to allow for collection of the extract (24). The

use of a pure compound, as opposed to modified fluids, is experimentally easier and may allow for a better understanding of the interactions between the analyte, matrix, and the supercritical fluid. The choice of a compound that meets the requirements and has a significant dipole moment has led to the use of freons as supercritical fluids. Despite the fact that many of the environmentally harmful chlorofluorocarbon (CFC) freons have been banned by the Montreal Protocol, the replacement of these harmful freons with hydrogen-containing freons has made it possible to explore the use of some freons in supercritical fluid extractions.

Freons such as chlorodifluoromethane ($CHClF_2$, Freon 22) have been shown to be much less harmful to the ozone layer and have less global warming potential than their CFC predecessors (29). Chlorodifluoromethane has a dipole moment of 1.4 D, and reasonable critical temperature and pressure values of 96°C and 49 atm, respectively, which make it a plausible supercritical fluid for analytical extractions (30). While not a commonly used analytical extractant, chlorodifluoromethane has been used to extract PAH from diesel particulate matter, oils from spruce needles, and elemental sulfur from bituminous coal. It was shown to yield consistently higher extraction efficiencies than CO_2 alone, often extracting ten times as much analyte as pure CO_2. Chlorodifluoromethane has also been used in the supercritical state to extract polychlorinated biphenyls and polycyclic aromatic hydrocarbons from several environmental matrices such as sediment, petroleum waste sludge,and railroad bed soil with excellent recoveries (24).

The interactions between supercritical chlorodifluoromethane and the various matrix/analyte combinations studied in the past are not clearly understood. Since the fly ash matrix poses particular problems when attempting to quantitatively extract PAH from the surface, it is not known if SFE using chlorodifluoromethane is capable of extracting BaA from the ash more efficiently than pure or modified CO_2. The third objective of this thesis is to determine if chlorodifluoromethane is indeed superior to CO_2 when extracting BaA from carbonaceous fly ash.

CHAPTER 2

EXPERIMENTAL

I. Sample Preparation

A. Coal Stack Ash Fractionation

Samples of "Kaneb" coal ash were obtained from a coal-powered plant in Lakeland, Florida. Coal ash is a nonhomogeneous mixture of many particle types including mineral, ferromagnetic, and carbonaceous particles (31). Because of the nonhomogeneous nature of the ash, it could be separated into fractions according to size, magnetic character, and density of the particles. The ash was previously separated by John Sanders and David Jenkins, graduate students in this research group, using the method outlined by Mauldin (25). The ash was first separated according to particle size using mechanical sieves with 45, 75, 125, and 150 μm mesh size. This separation resulted in five fractions designated *U* (for *unfractionated*) and assigned a number according to particle size. The fractions obtained were labeled as follows: U1 (particle size < 45 μm), U2 (45-74 μm), U3 (75-124 μm), U4 (125-149 μm), and U5 (> 150 μm).

The U3 fraction was then further separated into magnetic and non-magnetic fractions. This was done by passing a bar magnet contained in a 50 mL beaker over portions of the bulk ash. The particles adhering to the outside of the beaker were designated as the magnetic particles and given the label M3 (magnetic fraction, 75-124 μm). The particles left behind were collected and labeled N3 (non-magnetic

fraction, 75-124 μm). The N3 fraction was then further separated.

Due to the difference in particle density of each of the components, the mineral and carbonaceous fractions of the N3 ash could be separated from each other by *elutriation* (i.e., separation on the basis of aerodynamic density). The *elutriator* illustrated in Figure 2 was designed by Sanders (32) and used to further separate the N3 fraction. Small portions (~ 4 g of the N3 ash) were placed on the frit at the base of the elutriator. The device utilized a water-saturated stream of nitrogen that passed through the frit and carried the lighter particles upstream through the elutriator. Because the porous carbonaceous particles had a lower aerodynamic density than the mineral particles, they were carried by the nitrogen stream through the 1 mm orifice and deposited on the base outside the orifice. The nonporous, higher density mineral-enriched particles remained on the frit. The carbonaceous and mineral enriched-particles were then collected and labeled *C3* and *M3*, respectively. The entire separation procedure is summarized in Figure 3.

The C3 ash fraction was chosen for these experiments. The ash was analyzed by Galbraith Laboratories in Knoxville, TN to determine total carbon content of the ash. This was done by combustion followed by gravimetric analysis of carbon as CO_2. The C3 fraction was determined to have a very high bulk carbon content (35.91%). The U3 (unfractionated) ash was determined to have a total carbon composition of 7.42% (25). The coal ash was degassed under a stream of prepurified nitrogen (National Welders Supply, Charlotte, NC) for 24 hours at 250°C as a purification step to remove any organic residue.

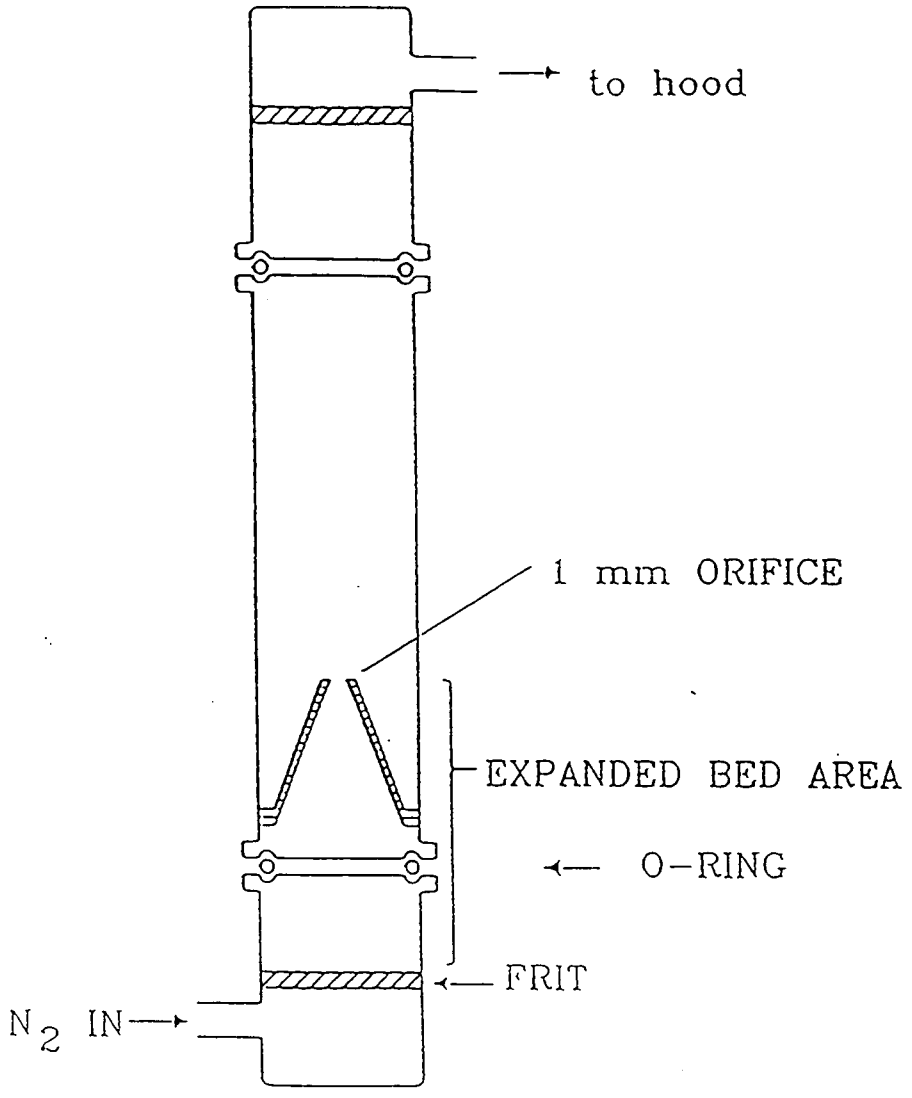

Figure 2. Schematic diagram of *elutriator*.
Source: Sanders, J.K. Ph.D. Dissertation, The University of Tennessee, Knoxville, 1991, p 17.

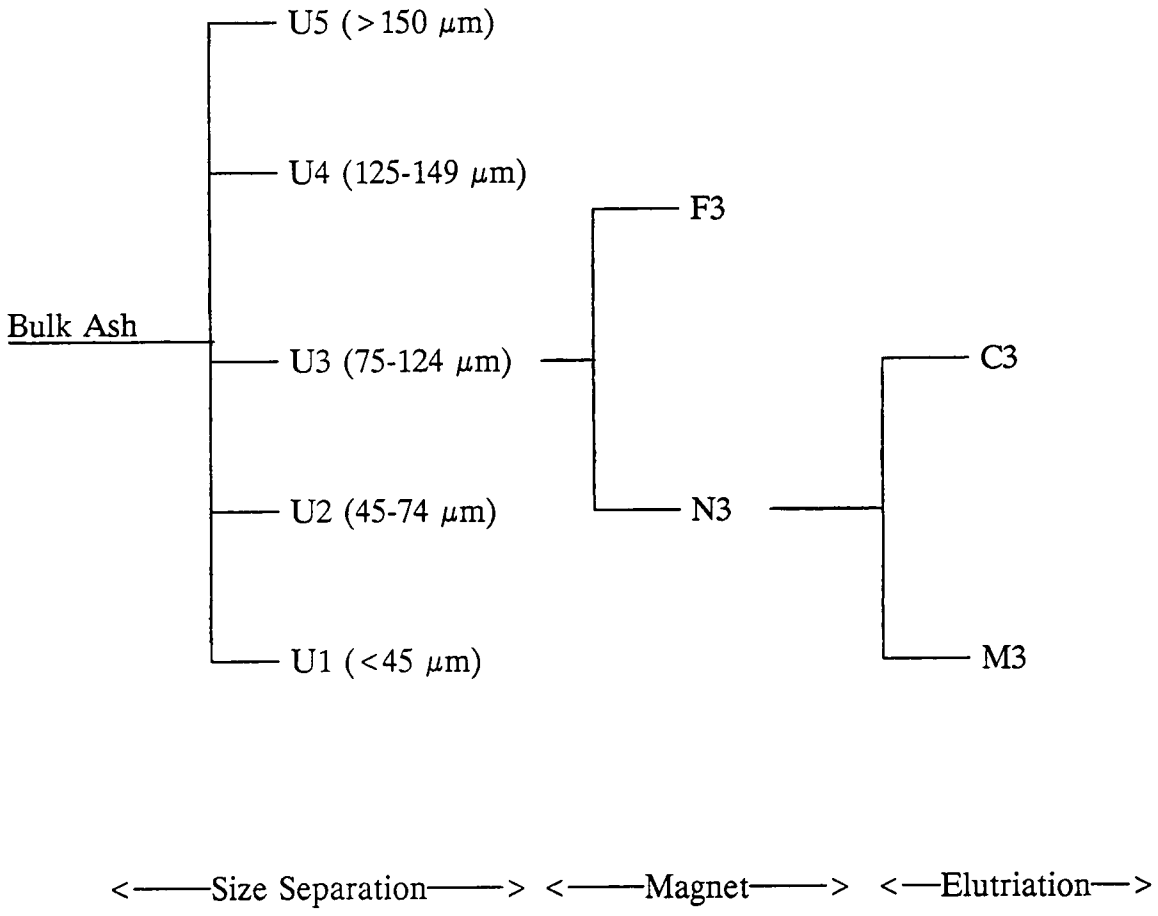

Figure 3. Fractionation scheme for Kaneb coal ash.
Adapted from: Holder, P.S. Ph.D. Dissertation, The University of Tennessee, Knoxville, 1993, p 52.

B. Vapor Deposition of BaA onto Coal Ash

BaA was used as received from Aldrich (99.9% pure). The BaA was deposited from the vapor phase onto the fly ash using a vapor deposition apparatus described by Engelbach, et al. (33) that mimiced the adsorption of PAH in the atmosphere. The apparatus was modified by Mauldin (25). The apparatus shown in Figure 4 was constructed from two Blue M ovens and ⅛" stainless steel tubing. Oven 1 housed a glass diffusion cell that was loaded with the BaA and heated to a temperature below the melting point of the BaA (melting point 157-159°C). The BaA generated in oven 1 was swept by a stream of prepurified nitrogen (National Welders) into oven 2 which housed a glass deposition cell (Figure 5) containing the fly ash sample. The BaA/nitrogen stream entered the deposition cell from the bottom. As the stream exited the deposition cell, it was swept to a flame ionization detector (FID) where the BaA not adsorbed by the ash was detected. The FID (GowMac, model # 40-900) was connected to a chart recorder (Kipp and Zonen BD40) to monitor the signal and obtain a trace such as that shown in Figure 6.

It was necessary to determine the mass flow rate of BaA through the ovens prior to deposition so as to obtain a sample with known surface coverage. This was accomplished by diverting the BaA/nitrogen stream around the sample in oven 2 and into a trap constructed from ⅛" stainless steel tubing in an ice bath. The flow of BaA through the ovens was measured for one hour. The trap was then rinsed with methanol into a 25 mL volumetric flask and quantified by UV-visible spectrophotometry. A mass flow rate of 28.8 μg of BaA per hour was calculated.

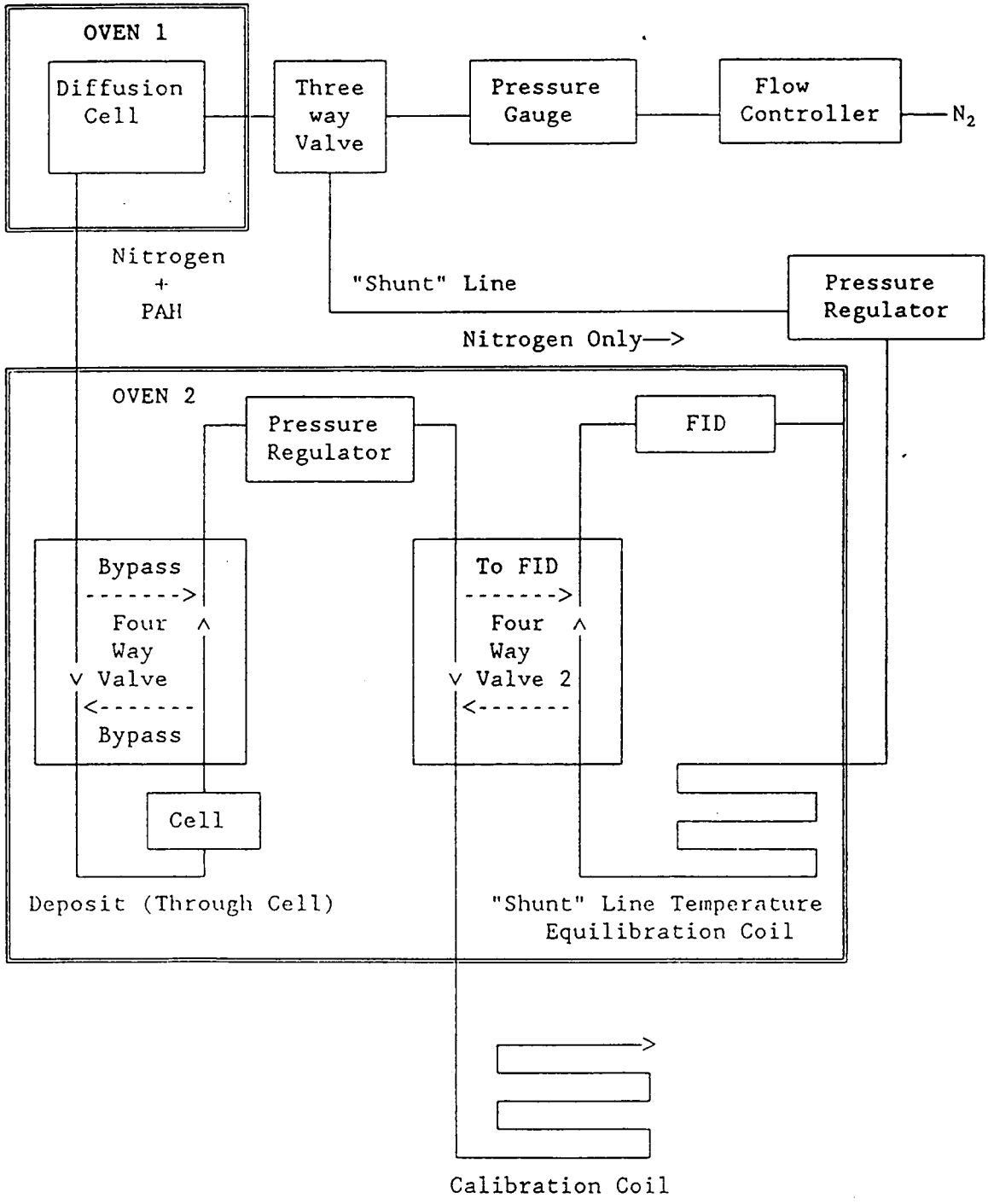

Figure 4. Schematic diagram of vapor deposition apparatus.
Source: Mauldin, R.F. Ph. D. Dissertation, University of Tennessee, Knoxville, 1990, p 41.

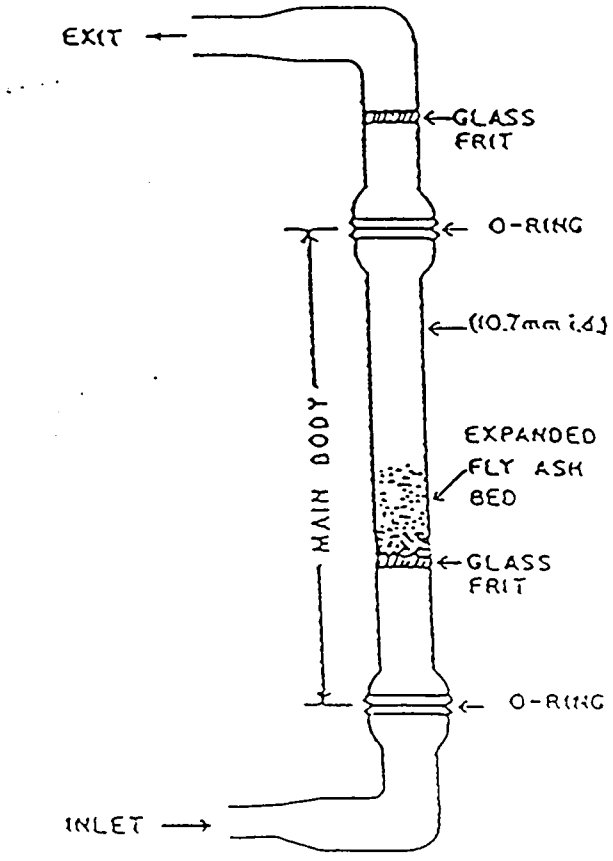

Figure 5. Schematic diagram of primary vapor deposition cell.
Source: Korfmacher, W.A. Ph.D. Dissertation, University of Illinois, Urbana-Champaign,IL,1978, p 46.

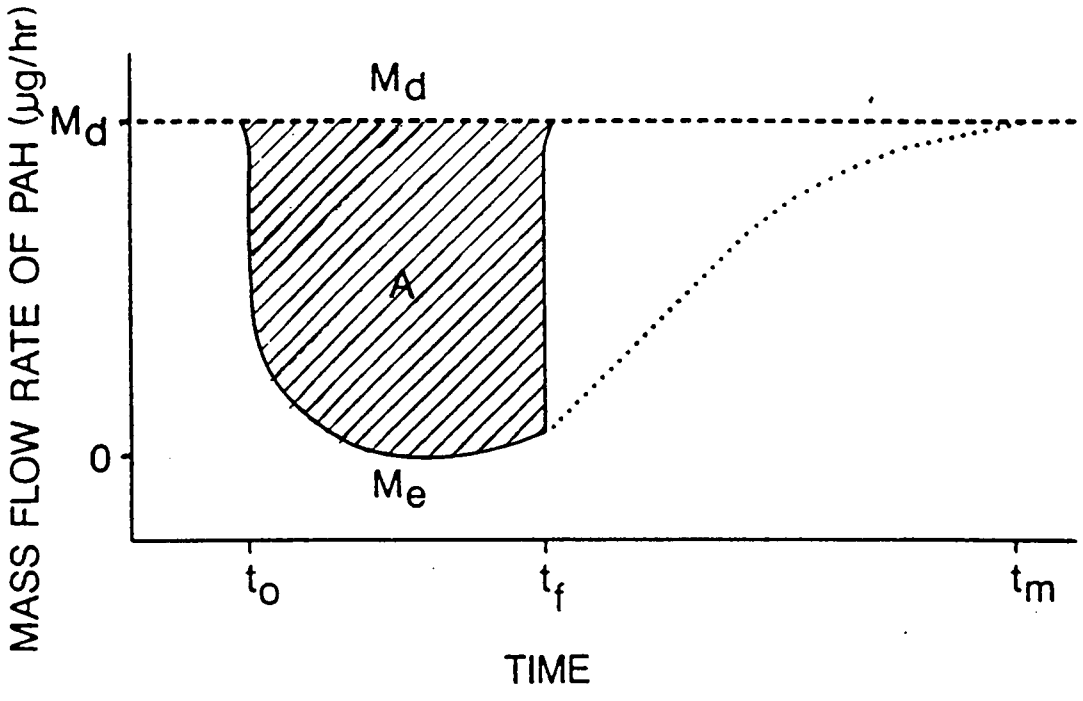

Figure 6. Flame ionization detector plot of mass flow rate of PAH vs. time. M_d represents the mass flow rate of PAH before the PAH enters the deposition cell. M_e represents the mass flow rate of PAH after exiting the cell. *A* is proportional to the total amount of PAH deposited on the fly ash.
Source: Engelbach, R.J.; Garrison A.A.; Wehry, E.L.;Mamantov, G. *Anal. Chem.* **1987**, *59*, 2542.

Using the calculated mass flow rate, the FID response, and the mass of sample, the concentration of BaA on the surface of the sample was calculated as described by Engelbach (33,34). Using 7.38 g of C3 ash, a surface coverage of 83.7 μg of BaA per gram of ash was obtained by a 22.5 hour vapor deposition with oven 1 at 117°C and oven 2 at 148°C.

II. Extraction Methods

A. Ultrasonic Extractions

For ultrasonic extraction of the ash, 130-150 mg samples were weighed into 25 mL volumetric flasks. The flask was filled with toluene and sonicated in a Branson model 1210 sonicator (Branson Ultrasonics, Danbury, CT) for 60 minutes. The solutions were then analyzed for their BaA content by UV absorption spectrometry.

B. Supercritical Fluid Extractions

i. Apparatus and Materials

The SFE apparatus shown in Figure 7 was constructed of stainless steel tubing and Swagelok unions. An Isco model LC-2600 syringe pump (Isco, Lincoln, NE) was used to pressurize the supercritical fluids to 400 atm. The extraction cell that contained the sample consisted of 10 cm of ⅛" stainless steel tubing with Swagelok column end fittings containing 2μm pore diameter stainless steel frits on both ends. The extraction cell was housed in a Blue M oven (model # C-4850-Q). A 20 cm piece of 25 μm internal diameter fused silica tubing (Polymicro Technologies,

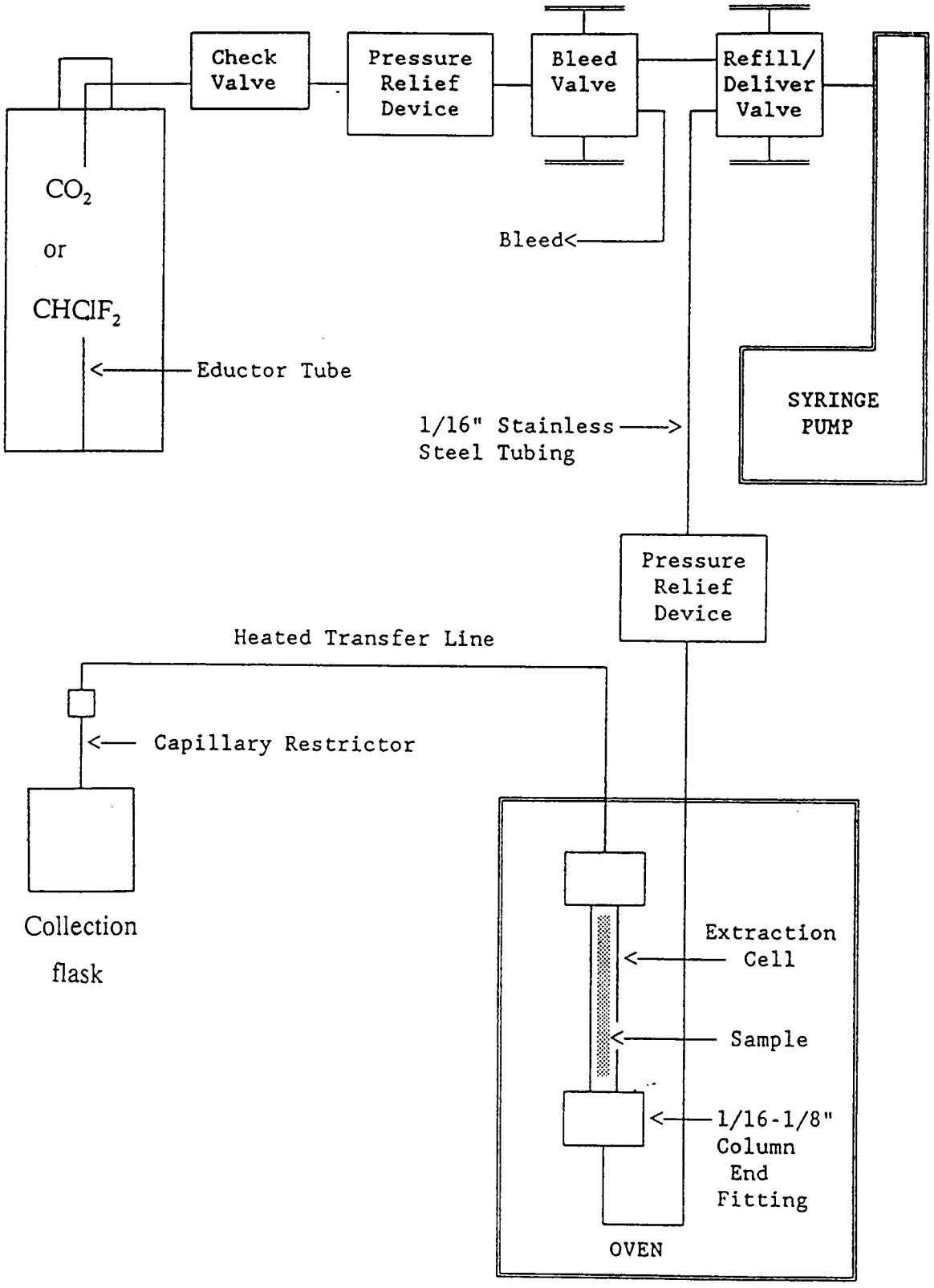

Figure 7. Schematic diagram of supercritical fluid extraction apparatus.

Phoenix, AZ) was contained at the end of the apparatus in order to restrict the flow of fluid out of the system (thus the term "restrictor"). Supercritical fluid chromatography-grade carbon dioxide (Scott Specialty Gases, Plumsteadville, PA) and chlorodifluoromethane (Freon 22®, Aldrich, Milwaukee,WI) were used as extraction fluids.

ii. Procedure

Using the procedure previously described by Mauldin (25), 60-150 mg samples of the C3 fly ash fraction were weighed into the extraction cell. The cell was then placed in the oven and the oven was allowed to equilibrate at a temperature of 150°C for approximately 20 minutes while the pump was filled with fluid. With the deliver valve to the oven closed, the fluid (CO_2 or $CHClF_2$) was drawn into the pump. After the desired amount of fluid was drawn into the pump, all of the valves were closed and the pump pressurized the fluid to 400 atm. Once the pump reached this pressure, the inlet valve to the cell was opened and the cell was flushed with fluid for a period of 90 minutes for the dynamic (i.e., continuous flow) extractions. The extract was collected in solvent (dichloromethane or toluene), and the concentration of BaA in the flask was measured by UV spectrometry.

This procedure had to be altered slightly when using modified supercritical fluids. For modified extractions in the dynamic (flowing) mode, a union on the cylinder-to-pump line was disassembled and 25 mL of modifier was drawn into the pump. The union was then reassembled and 250 mL of CO_2 was drawn into the pump to give a 10% (v/v) modifier concentration. The fluid was then pressurized

and the sample extracted as described above.

Modified extractions performed in the static (non-flowing) mode required that a valve be installed at the exit of the extraction cell to allow for the cell to be pressurized without loss of modifier. A concentration of 10% (v/v) modifier was calculated based on the volume of the extraction cell (0.15 mL). The volume of the cell was only altered slightly (approximately 1%) by the presence of sample. Using a gas chromatography syringe, 15 μL of modifier was pipetted directly onto the sample in the extraction cell. The cell was then loaded into the oven. After the CO_2 in the pump was pressurized, the deliver valve to the cell was opened while the outlet valve to the cell remained closed. The sample was extracted in the static mode for 45 minutes after which the outlet valve was opened and a 45 minute dynamic extraction was performed so that the extract could be collected.

After each 90 minute extraction period, additional SFE was performed on all extractions yielding less than quantitative recoveries. Each sample was exhaustively extracted until no more BaA could be detected. The samples were then transferred to a 10 mL volumetric flask and extracted using ultrasonic extraction in toluene as previously described (p 21) to determine if detectable quantities of BaA remained on the ash after completion of SFE.

III. Quantification of BaA

For collection of the extract, the restrictor was inserted into a 10 mL volumetric flask containing 5-8mL of dichloromethane in an ice bath. For toluene-

modified extractions, toluene was used as the collection solvent, rather than dichloromethane. Off-line collection in solvent and analysis by UV absorption spectrometry was chosen over on-line gas chromatographic analysis (34) because of interferences in quantification of BaA due to impurities in the supercritical fluid when using GC analysis. These unidentified contaminants did not appear to absorb appreciably in the UV spectral region; hence, even if they were trapped in the solvent collection flask, they were assumed not to pose a significant problem in quantification of BaA by UV absorption spectrometry.

In order to assure the efficiency of the collection method, BaA was vapor deposited on silica gel (EM Reagents, Westbury, NY) and extracted using SFE/CO_2 with collection in solvent. Because it is known that SFE using CO_2, or modified CO_2, removes virtually 100% of PAHs deposited on silica (25), the amount of BaA known to have been extracted from the silica could be compared with the amount of BaA detected in the collection solvent.

BaA was quantified by UV absorption spectrometry using a Hewlett Packard model 8452A diode array spectrophotometer. Standard solutions of BaA in toluene or dichloromethane (depending on the solvent used for collection of the extract) were used to generate calibration curves in the form of Beer's law plots (absorbance versus concentration of BaA in μg per mL). It was also necessary to obtain a Beer's law plot for solutions of BaA in methanol in order to quantify BaA when performing collections for mass flow rate determinations with the vapor deposition apparatus.

CHAPTER 3

RESULTS AND DISCUSSION

I. Preliminary Experiments

Figure 8 illustrates the absorption spectrum of BaA in dichloromethane. The absorbance of the most intense peak (at 288 nm in Figure 8) was monitored. The UV absorbances of standard solutions of BaA in dichloromethane, methanol, and toluene were measured and used to generate Beer's law plots (concentration vs. absorbance) for quantitation of BaA. The Beer's law plot for BaA in dichloromethane is shown in Figure 9.

To assure that <100% recoveries obtained by SFE of BaA on fly ash samples were not due to loss of BaA upon collection in solvent, BaA was vapor-deposited on silica gel in the same manner as previously described for the fly ash samples (p. 17). The silica gel samples (coverage = 106.9 μg/g) were then extracted by SFE/CO_2 under the same conditions as the fly ash samples. Recoveries of 104.4 ± 6.0% were obtained, indicating that loss of the extracted BaA with collection in solvent was negligible. Blank extractions were also done on empty extraction cells to assure that any impurities in the SFE system did not interfere with the UV spectra. No impurities were detected in the collection solvent when analyzed by UV absorption spectrometry.

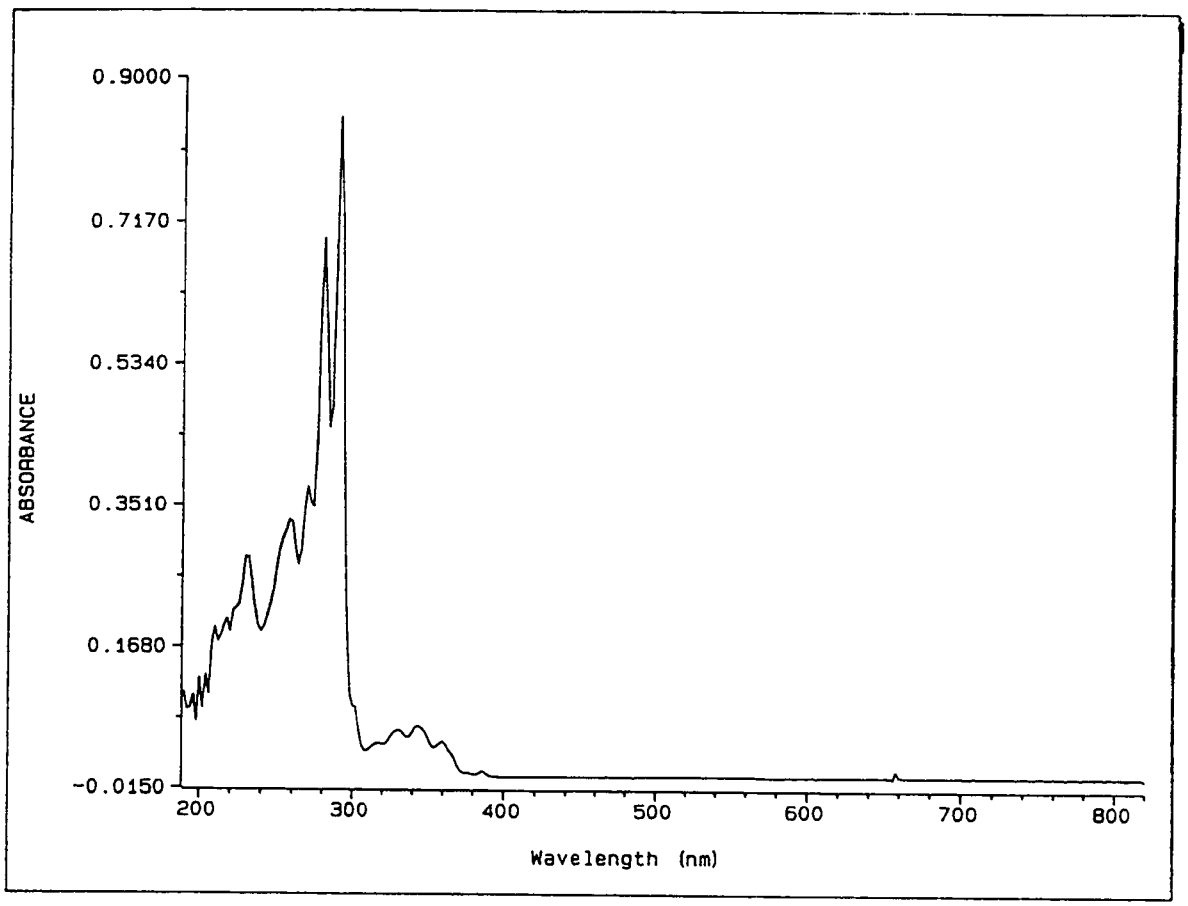

Figure 8. UV absorption spectrum of 2.06 ppm BaA in dichloromethane.

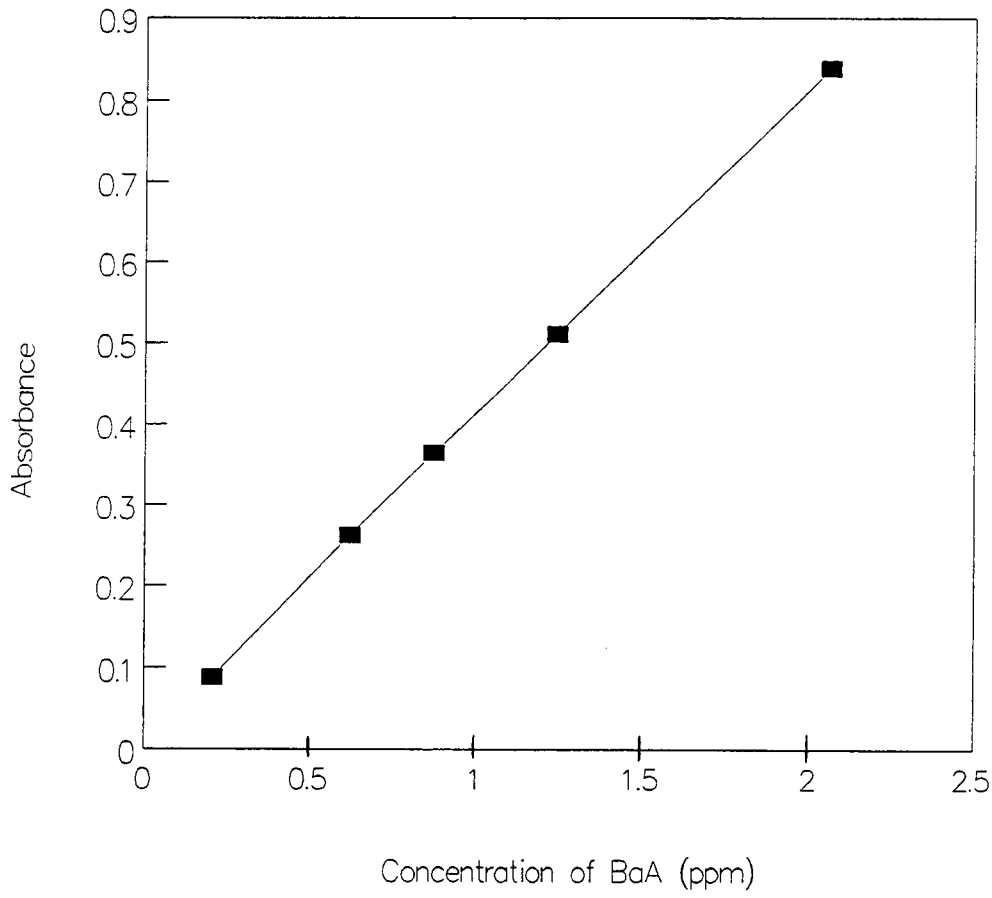

Figure 9. Beer's law plot for BaA in dichloromethane.

II. Extraction Efficiency Using Modified CO_2

Table 3 summarizes the results of extractions performed using pure and modified CO_2 to extract BaA from the C3 ash. Ultrasonic extraction performed on samples of the ash was able to recover 74.2% of adsorbed BaA. Pure CO_2 is not a good extractant for quantitative extraction of BaA from the C3 ash, yielding a recovery of only 49.7%. Subsequent extraction of the ash using pure CO_2 was not able to recover any additional BaA. However, sonication in toluene was able to recover an additional 19.4% of the BaA initially present after SFE/CO_2, indicating that some of the BaA that could not be extracted using pure CO_2 was irreversibly adsorbed to the fly ash.

The use of modifiers increased the extraction efficiency over that obtained using pure CO_2. CO_2 modified with methanol and dichloromethane gave comparable recoveries in the 50-60% range. However, toluene proved to be the best modifier of the three, yielding recoveries comparable to those obtained using ultrasonic extraction of the ash. The percentage of BaA recovered by one extraction using toluene-modified CO_2 was nearly the same as the percentage of BaA recovered by methanol- and dichloromethane-modified CO_2 in two extractions.

It is not likely that improved recoveries with toluene modifier can simply be attributed to the solubility of BaA in toluene, since dichloromethane is also an excellent solvent for PAHs. The manner in which addition of modifiers to CO_2 affects the extractability of PAHs from various solid matrices is not well understood.

Table 3. Comparison of supercritical fluid extraction efficiencies using pure CO_2, modified CO_2, and $CHClF_2$.

Extraction fluid	% recovery of BaA				
	First SFE	Second SFE	Total SFE	Sonication following SFE	Total by all methods
Pure CO_2 (0%)	49.7 ± 5.4	*	49.7 ± 5.4	19.4 ± 4.0	69.1 ± 6.7
CO_2/methanol					
static (10%)	52.7 ± 5.8	9.6 ± 4.8	62.3 ± 7.5	10.6 ± 7.7	72.9 ± 10.8
dynamic (10%)	49.2 ± 6.9	6.5 ± 5.2	55.7 ± 8.6	12.1 ± 5.8	67.8 ± 10.4
CO_2/toluene					
static (10%)	70.2 ± 4.3	*	70.2 ± 4.3	*	70.2 ± 4.3
dynamic (10%)	68.4 ± 8.2	*	68.4 ± 8.2	*	68.4 ± 8.2
CO_2/dichloromethane					
static (10%)	57.9 ± 4.8	13.4 ± 1.6	71.3 ± 5.1	6.5 ± 1.0	77.8 ± 5.2
dynamic (10%)	54.3 ± 6.4	10.1 ± 3.4	64.4 ± 7.2	7.2 ± 5.5	71.6 ± 9.1
$CHClF_2$ (0%)	81.1 ± 3.7	*	81.1 ± 3.7	*	81.1 ± 3.7
$CHClF_2$/toluene					
static (10%)	89.4 ± 4.6	*	89.4 ± 4.6	*	89.4 ± 4.6

* indicates that no BaA could be detected; the absorption peak was below the limit of detection.
All ± values are 95% confidence intervals. Modifier concentration is noted in parentheses.

The ability of the modifier both to solvate the target analyte and to interact with the matrix affects the efficiency of extraction of the analyte.

Others have reported improvements in the recovery of PAH from diesel soot and urban air particulate matter using toluene-modified CO_2 as opposed to pure CO_2 and methanol-modified CO_2 (35). Since both of these matrices have similar characteristics to fly ash (i.e., all are highly carbonaceous matrices produced under high temperatures) toluene may indeed be the modifier of choice for carbonaceous matrices.

III. Static vs. Dynamic SFE

Figure 10 illustrates the differences in recoveries when using the 45 minute static/45 minute dynamic extraction as opposed to a 90 minute dynamic extraction for modified SFE systems. In each case, both methods of modifier addition gave similar recoveries. Static extractions produced consistently higher recoveries but only by a small margin. Since the sample is exposed to the fluid for the same total time in both extraction modes, these results indicate that a continuous flow of fluid is not necessary to achieve adequate recoveries.

Extractions done in the static mode were more precise and reproducible while extractions done in the dynamic mode were more prone to error (as indicated by the error bars in Figure 10). This may be due to inefficient mixing of the modifier and the CO_2 in the pump. Cylinders of modifiers pre-mixed with CO_2 are available commercially but their use has been reported to result in irreproducible modifier

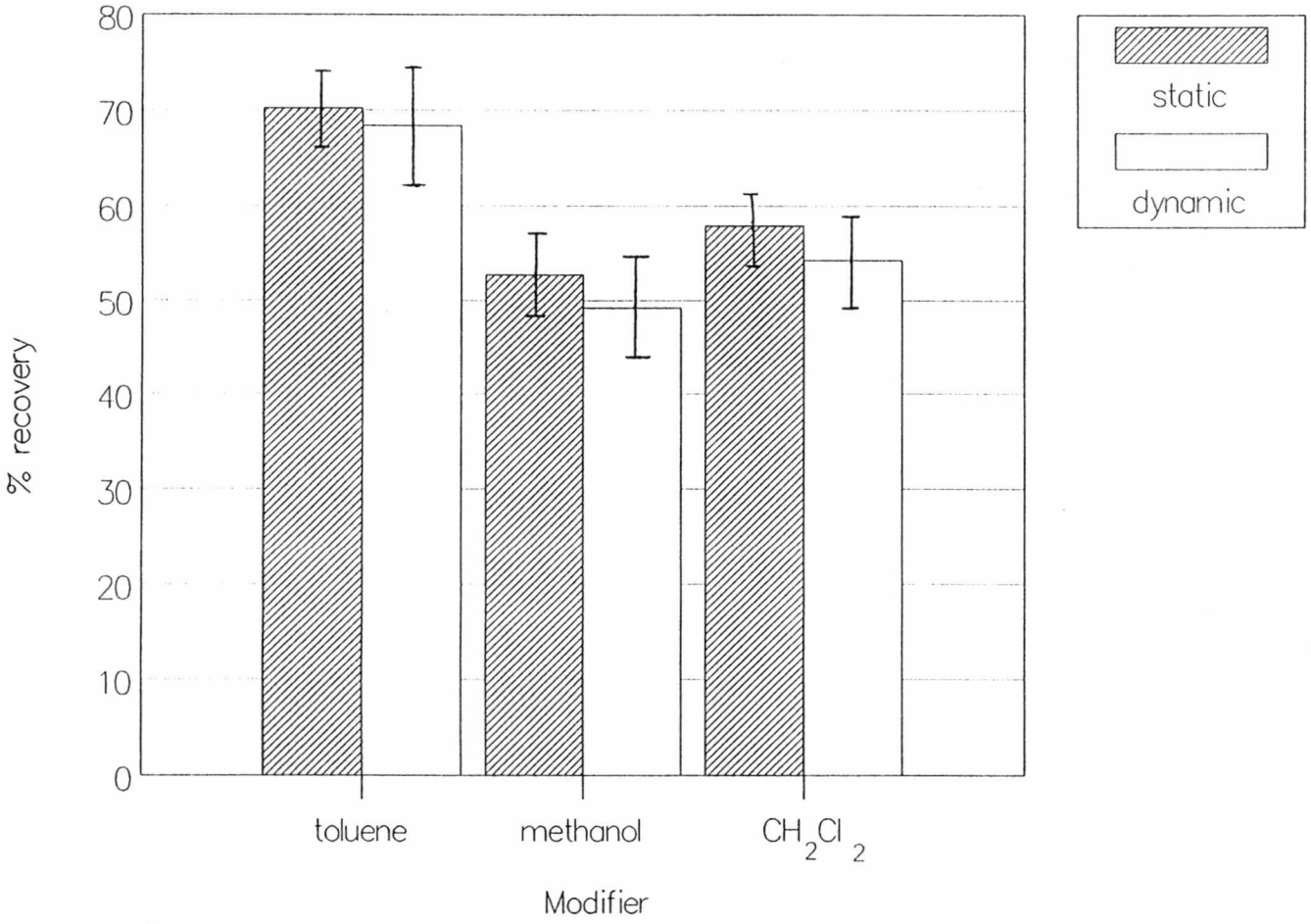

Figure 10. Recoveries of BaA from fly ash using 45 minute static/45 minute dynamic extraction vs. 90 minute dynamic extraction.

concentrations (36), and they are available only with a limited choice of modifiers. Additionally, dual pumping systems are available that would deliver both the modifier and the supercritical fluid simultaneously. However, these systems can be costly in comparison to the single-pump system used in this experiment.

Performing modified SFE in the static mode was much easier in this experiment since it did not require any disassembling of the apparatus. Static extractions also have the advantage of requiring less solvent to perform. Less than one milliliter of modifier was required to perform a set (3-4) of static extractions while dynamic extraction required 20-25 mL of modifier. The results obtained here indicate that a simple addition of modifier directly to the sample is adequate to allow the modifier to enhance the recovery of BaA from the fly ash. This conclusion is consistent with the data reported by Yang, et al. (35).

IV. Extraction Efficiency Using $CHClF_2$

Extractions of the C3 ash with supercritical $CHClF_2$ gave improved recoveries over all of the modified CO_2 systems studied. An example of the UV spectrum of extracted BaA in dichloromethane using SFE/$CHClF_2$ is shown in Figure 11. No apparent change in the spectrum occurred when $CHClF_2$, rather than CO_2, was used as the supercritical fluid. SFE/$CHClF_2$ was able to recover 81.1% of adsorbed BaA in one 90 minute extraction. Further extraction using $CHClF_2$ was not able to recover any additional BaA, indicating that the sample was exhaustively extracted in 90 minutes or less. This increased extraction efficiency is not likely due to the ability

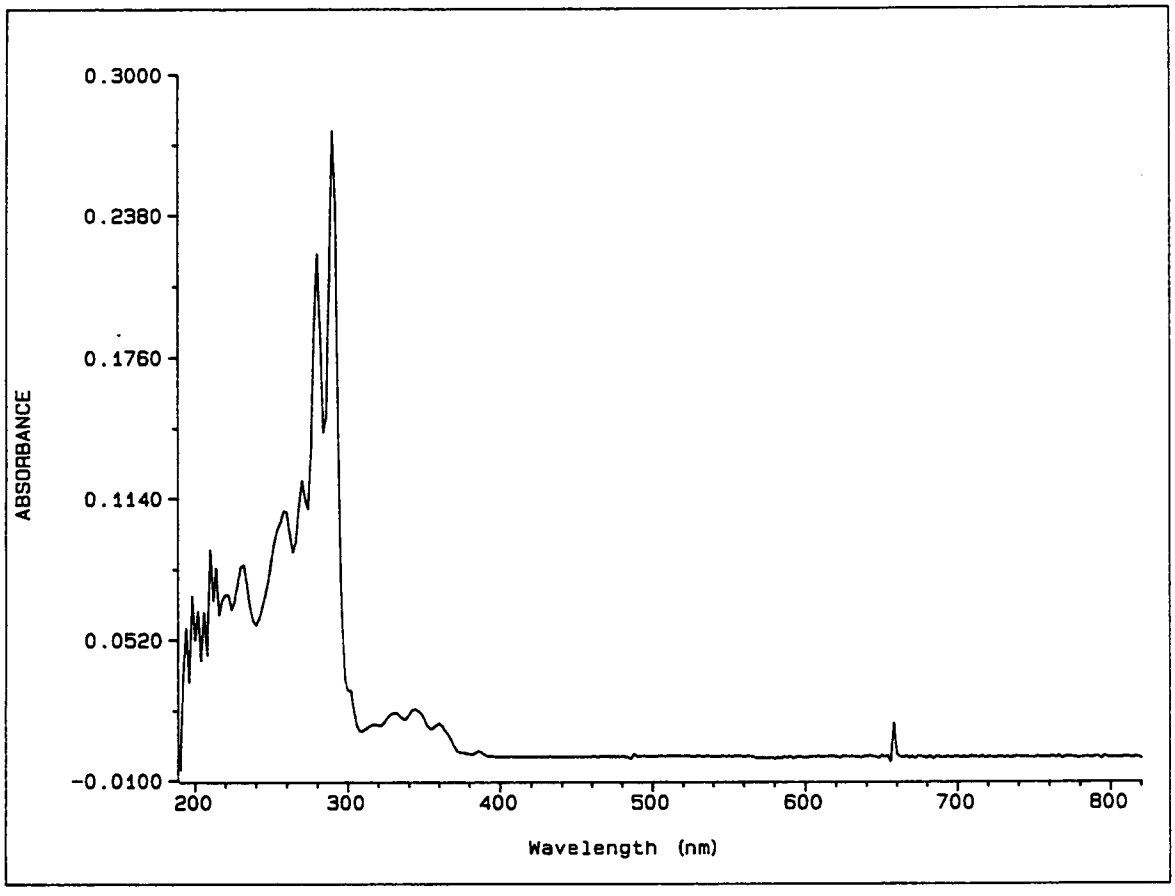

Figure 11. UV absorption spectrum of BaA extracted using SFE/$CHClF_2$ with collection in dichloromethane.

of the supercritical fluid to solvate the BaA, since $CHClF_2$ and CO_2 have comparable solvent strengths at 400 atm (24). Conceivably, the increased extraction efficiency can be attributed to the ability of $CHClF_2$ to interact with the fly ash matrix to release the adsorbed BaA and then compete efficiently with the analyte for active matrix sites to prevent readsorption.

$CHClF_2$ gave even higher recoveries of adsorbed BaA than did toluene-modified CO_2. To see if the use of toluene-modified $CHClF_2$ could further improve the recovery of BaA from fly ash, extractions were done in the static mode on the same sample under identical conditions using 10% toluene as a modifier for $CHClF_2$. The extraction efficiency using toluene-modified $CHClF_2$ was significantly improved, as can be seen in Table 3. The results indicate that toluene may interact with the fly ash matrix in a manner slightly different from $CHClF_2$. However, the combination of toluene and supercritical $CHClF_2$ allows for nearly quantitative recovery of BaA from the carbonaceous fly ash fraction.

Ultrasonic extraction in toluene was performed on the samples after SFE and showed no BaA present when analyzed by UV absorption spectrometry. These results indicate that approximately 10% of the BaA vapor-deposited on the fly ash sample is so strongly adsorbed that none of the extraction methods employed here was able to remove it. However, these results do suggest strongly that toluene-modified $CHClF_2$ is an excellent choice for the extraction of PAHs from carbonaceous adsorbents. It is rather surprising that no other previous investigations into the use of supercritical $CHClF_2$ (24) for extraction of PAHs explored the use of

modifiers to increase extraction efficiencies. This may perhaps be attributed to the fact that others who have studied supercritical $CHClF_2$ have calculated its efficiency in extracting PAHs based on surface coverages determined by Soxhlet extraction performed on the sample. However, in these experiments, the calculations are based on surface coverages obtained when a known amount of PAH was vapor deposited on the fly ash sample.

CHAPTER 4

CONCLUSIONS

The use of organic modifiers in conjunction with CO_2 in SFE can improve the recovery of BaA (and likely other PAH) from coal fly ash. Pure CO_2 alone cannot extract as much BaA as ultrasonic extraction. However, small amounts of organic modifier can increase the extraction efficiency of SFE/CO_2 to compare with that of ultrasonic extraction in toluene. Toluene-modified CO_2 is advantageous over dichloromethane- and methanol-modified CO_2, extracting greater amounts of BaA in only one extraction, whereas the other modified CO_2 systems required second extractions to recover virtually the same amount of adsorbed BaA.

Extractions using modifiers with CO_2 done in the dynamic mode and the static mode offer similar recoveries. However, static extractions are easier to perform, use less organic solvent, and offer better reproducibility than dynamic extractions. Using the static extraction method, it may also be possible to investigate other modifiers in less time than would be needed using the dynamic extraction technique.

The use of pure $CHClF_2$ as a supercritical fluid was found to increase the extraction efficiency to an even greater extent than toluene-modified CO_2. Additionally, the use of 10% toluene modifier in supercritical $CHClF_2$ improved the recovery of BaA to nearly quantitative. Since this was a highly carbonaceous ash fraction, considered to be a highly sorptive matrix that often poses problems when

attempting to extract PAH from the surface, the use of toluene-modified $CHClF_2$ certainly warrants further investigation.

The interactions between the modified supercritical fluid and the matrix/adsorbate system are not well understood at this time. However, in order to recover more of the BaA from the surface of the fly ash, the modifier may alter the fly ash matrix in some way to allow for desorption of the analyte and at the same time occupy active sites on the matrix to prevent readsorption of the analyte. The ability of the modifier to alter the supercritical fluid to increase its ability to solvate the BaA may also contribute to increased recoveries but to a much lesser degree.

The dramatic increase in recovery of BaA from the carbonaceous ash fraction when using supercritical $CHClF_2$ may be attributed to the ability of $CHClF_2$ to somehow affect the surface of the ash to allow for desorption of the BaA. The improved recoveries observed with the addition of toluene modifier to $CHClF_2$ indicate that toluene may be an excellent modifier for SFE regardless of the supercritical fluid. Nevertheless, the toluene-modified $CHClF_2$ system is far superior to any other system previously studied for the removal of PAHs from carbonaceous coal fly ash.

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