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Quantitative supercritical fluid extraction of organics

Mahanama, Kariyawasam Ranaweerage Ranjith, Ph.D.

City University of New York, 1990

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QUANTITATIVE SUPERCRITICAL FLUID EXTRACTION OF ORGANICS

by

Kariyawasam Ranaweerage Ranjith Mahanama

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

1990

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

QUANTITATIVE SUPERCRITICAL FLUID EXTRACTION OF ORGANICS

by

Kariyawasam Ranaweerage Ranjith Mahanama

Adviser: Professor David C. Locke

Off-line supercritical fluid extraction developed specifically for analytical sample preparation and analysis of middle-sized PAHs are described. The analytical SCFE method has been evaluated with emphasis on the efficiency of the extraction and collection steps. Solid adsorbent traps [silica and octadecyl bonded phase] demonstrated the capability of collecting extracted compounds efficiently. Experimental parameters were evaluated to optimize the extraction of middle-sized PAHs and it was found that the efficiency of extraction increases with pressure [density] and temperature. Quantitative extractions were performed at 544 atm, 60°C for 15 minutes. Enhancement of the efficiency of extraction is due to two factors: enhancement due to the greater molecular interactions with the increase of the pressure [density] and enhancement due to the vapor phase composition with the increase of temperature. Solubility of iso-ring PAHs in SCF vary with the size and molecular topology. Peri-condensed pyrene dissolves easily in SCF carbon dioxide compared to analog cata-annelated chrysene and triphenylene. This trend is similar to the variation of melting point with the molecular structure.

Extractions of spiked samples from sorptive Montour fly ash samples were quantitative except for benzo[a]pyrene and acenaphthalene. Extraction of spiked top soil samples demonstrated an easier extraction medium than sorptive fly ash. Nonpolar aliphatic hydrocarbons modifiers enhanced the recovery of PAHs from fly ash. It was found that the enhancement increases with the carbon number of the modifier but the selectivity of the extraction decreases rapidly. SCF extracts were cleaner than liquid extracts and selective HPLC-UVD determinations eliminated extra sample handling and tedious separation techniques.

As demonstrated by quantitative recovery of standard PAHs, SCF carbon dioxide provides a powerful alternative to liquid solvents for the extraction and recovery of PAHs. The extractions are simple, inexpensive and rapid to perform. Four to five extractions can easily be performed within two hours. Use of carbon dioxide as the SCF solvent made solvent disposal problems and toxicological problems of exposure to the solvent insignificant compared to conventional liquids. Extracted materials are not exposed to the light or to excessive heat which reduces the possibility of photo- or thermo- decompositions. Overall this is a much superior method for the extraction and analysis of middle-size PAHs.

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Introduction

Supercritical fluid extraction [SCFE] is a technique that exploits the solvent power of supercritical fluids at temperatures and pressures above the critical point. The alternative term **"dense-gas extraction" [1]** has been used to emphasize the fact that the density of the supercritical phase is the principal factor in the extraction process. From this terminology it is clear that a gas only becomes an efficient solvent at high density. The term **"destraction"** derived from the Latin words **"destillare"** and **"extrahere"**, has been used in Germany **[2]** to acknowledge that the technique is a combination of liquid extraction and distillation. Because SCFE blends the application of solvent effects [chemical differences] and differences in volatility which are the basis of two important separation processes namely distillation and extraction.

Figure 1. **[3]** shows the phase diagram of pressure versus temperature for a pure compound. The lines TA, TB and TC divide the diagram into three regions. These regions represent the range of pressures and temperatures where the three different states of matter can be distinguished. These are gaseous [G], liquid [L] and solid [S] states. On the lines two phases are in equilibrium and at the triple point, T, all the three phases coexist. The line TC, as has been known since the classic experiments of Andrews **[4]**, terminates at the critical point C. Above the critical point, a difference between the gaseous and liquid can no longer be observed and result in the formation of the supercritical region.

The supercritical region is not a fourth state of matter. The border of this region is illustrated by the dashed lines. Crossing one of these dashed lines does not result in a phase change, where crossing a solid line does. A gas can be transformed into a liquid by condensation, which can be

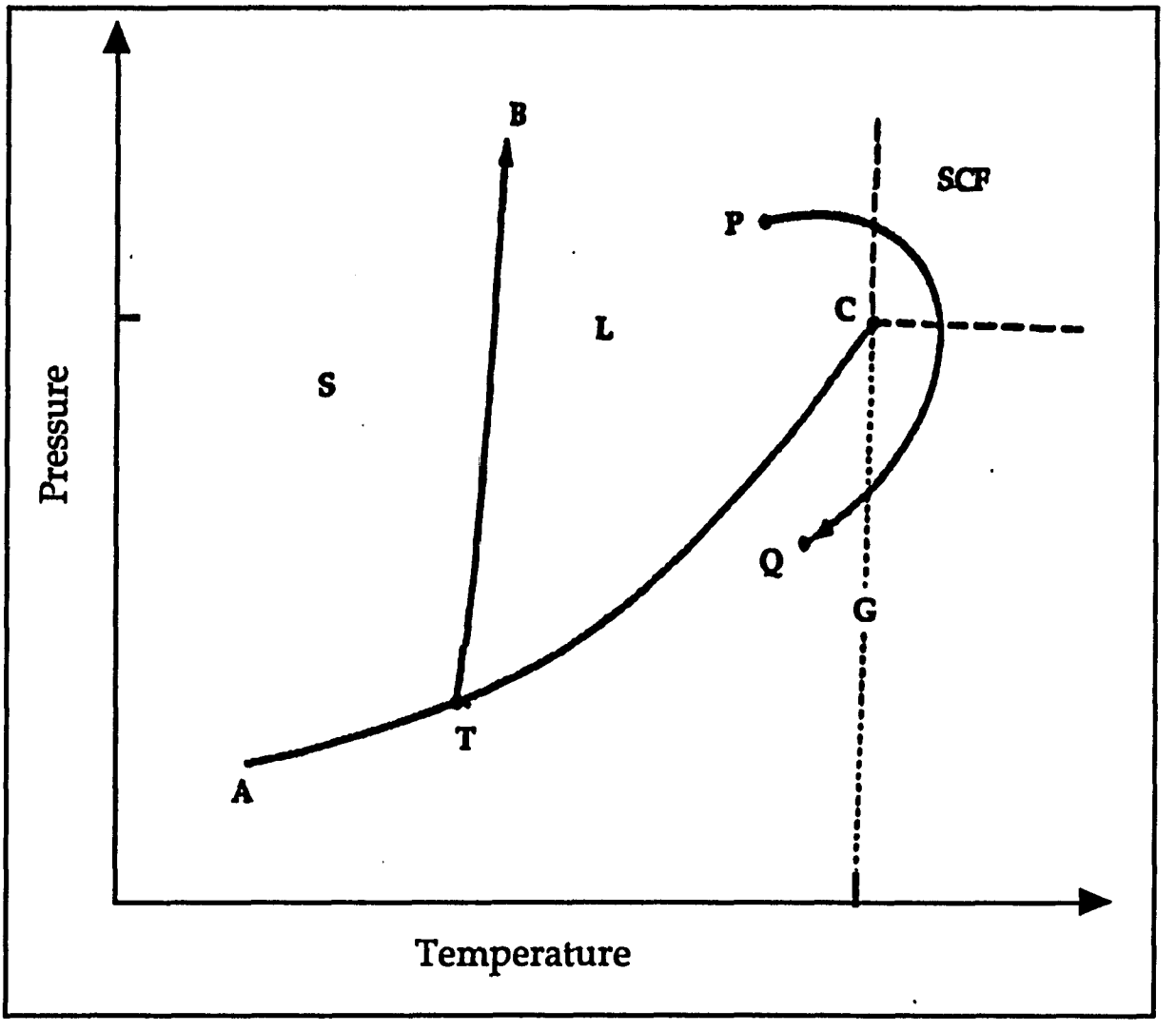


Figure 1. Phase Diagram [from ref. 3]

S: Solid phase
L: Liquid phase
G: Gas phase
SCF: Supercritical Fluid region
T: Triple point
C: Critical point
AT: Sublimation curve
BT: Fusion curve
CT: Vaporization curve
PQ: L to G without a phase change

achieved by increasing the pressure or decreasing the temperature. The opposite process, evaporation, can be achieved by increasing the temperature or decreasing pressure. Both condensation and evaporation are phase changes, during which the physical properties [density, viscosity, diffusivity, etc.] change abruptly. A gas can also be transformed into a liquid in a manner indicated by the arrow in Figure 1. During this process, a phase change will not take place. It has been stated that physical properties of a pure compound show continuous rather than abrupt variations when passing through one of the dashed lines [5].

The special name "supercritical fluid" signifies the behavior of this fluid which has been heated above and compressed beyond its critical temperature and pressure. In fact, in the supercritical region molecules can not stick together [condense] but continue to fly around like independent gas molecules no matter how much pressure is applied. The properties of SCF's depend on the fluid composition, pressure and temperature.

In the supercritical region, it is possible to take advantage of the variety of interesting and useful properties. Table 1. [6] compares certain properties of gases, liquids and supercritical fluids. The compressibility of a supercritical fluid is largest just above the critical temperature and small changes in pressure result in large changes in density of the fluid. The density of a supercritical fluid is typically two to three orders of magnitude greater than that of a gas and of the same order of magnitude of a liquid. Because of the higher compressibility, shorter intermolecular distances can result in higher intermolecular interactions. In the presence of a solute, this type of interaction can result a higher capacity for the solutes.

The viscosity, a measure of the ability of a substance to flow, of a SCF is almost as low as that of a gas and two orders of magnitude lesser

Table 1

Comparison of properties of SCF, gas, and liquid@

	ρ [g/ml]	η [g/cm-sec]	D [cm^2/s]
Gas[a]	$[0.6\text{-}2]\times10^{-3}$	$[1\text{-}3]\times10^{-4}$	0.1-0.4
SCF[b]	0.2-0.5	$[1\text{-}3]\times10^{-4}$	0.7×10^{-3}
SCF[d]	0.4-0.9	$[3\text{-}9]\times10^{-4}$	0.2×10^{-3}
Liquid[e]	0.6-1.6	$[0.2\text{-}3]\times10^{-2}$	$[0.2\text{-}2]\times10^{-5}$

ρ - density, η -viscosity, D - Diffusivity, c-critical

a - at atm,15-30°C

b - properties at Tc & Pc

d - properties at Tc & 4Pc

e - at 15-30°C

@ from ref. 3.

than that of a liquid. This low viscosity leads to faster mass transport which can be facilitated both by pumping and natural convection. The diffusivity of a SCF is three orders of magnitude greater than liquid. The higher diffusivity [or higher diffusion coefficient] of a SCF relative to a liquid imparts excellent powers of penetration into a porous solid structure. Moreover, it can result in shorter interphase equilibration times than with a liquid. The low viscosity and the absence of surface tension in supercritical fluids increases the speed of percolation so the passage of the solvent into the interstices of a porous matrix is enhanced. The properties of gas-like diffusivity and viscosity, zero surface tension and liquid-like density combined with the pressure-dependent solvent powers of a SCF provides the impetus for applying SCF in different separation procedures. Overall it is apparent that a SCF can be used as an excellent medium for an extraction process[6,7,8].

1.1 Extraction

Preferential affinity of a solvent for an analyte in a sample matrix is the basis for an extraction. This affinity is exploited to effect a concentration of the analyte into the solvent and can be used to separate the analyte from the matrix. A good extraction solvent should possess certain properties. The solvent should be able to dissolve the desired analyte better than the other constituents in the matrix. In addition to this selectivity, solvent should demonstrate a high capacity for the analyte. This helps to minimize the volume and time required to extract quantities sufficient for analysis. Extraction should yield quantitative recoveries of the analytes from the sample matrix without degradation of the analyte. In the ideal case, extracted sample should not contain species that interfere with the analysis of the target analytes, and samples should be ready for analysis without further treatment. The ideal solvent should be chemically inert toward any component in the sample matrix and should also be stable under the

extraction conditions.

From an economic perspective, a desirable solvent should not be corrosive to the equipment and should be relatively inexpensive. Another significant consideration is the time required of personnel and equipment to accomplish the extractions. Toxicological factors should be considered regarding exposure to the environment and the ability to dispose of the solvent. In addition to these criteria, one has to consider the convenience of recovering the analyte from the solvent without leaving interfering solvent artifacts.

As mentioned earlier, SCFE is a hybrid of the separation techniques of distillation and extraction. It is interesting to compare these two separation techniques with SCFE.

1.1.1 SCFE vs Conventional Extraction

SCFE may be viewed as an extension of conventional liquid extraction to high temperatures, with some differences. In SCFE, separation based on differences in solvent effects is enhanced by differences in vapor pressure. Fractionations can be done easily by stepwise changes in solvent power in the loading or the release steps, or both, without the use of additional components. To vary the solvent power of liquid solvents, it is necessary to change temperature significantly or to use additional chemical species. For a given solvent and solute, SCFE capacity can vary from low values typical of poor solvents to high values typical of good solvents as temperature and pressure vary. The ability to drop loadings to low levels is important in the selective separation of chemically similar components. As solvent loadings decrease, the ability to discriminate between chemically similar components increases. The residual solvent in the extract can be easily eliminated without distillation in supercritical solvents because they

are gases at ambient conditions. The favorable mass transport properties, supercritical solvents allow a more rapid approach to equilibrium. Hence they can penetrate deeper and more readily into substrates than can liquid solvents. Large differences in densities between phases and the low viscosity of the SCF phase lead to easy phase separations. In SCFE, it is relatively easy to obtain extracts that are free of entrained solids and liquid drops which is a common problem in conventional extraction processes.

1.1.2 SCFE vs Distillation

SCFE can be viewed as an extension of distillation to high pressures but with some major differences. In SCFE, separations are based on the nonideality introduced by high pressures. In distillation, a light phase is formed by vaporizing part of the mixture to be separated; in SCFE, the light phase is usually a new component not present in the original, unseparated mixture. In SCFE, differences in solvent effects can enhance separations based on differences in vapor pressure. SCFE can separate components with similar low vapor pressures, which are susceptible to heat degradation. In distillation, the driving force for fractionation is a temperature gradient across the distillation tower, whereas in SCFE the driving forces can be temperature, pressure, or both.

1.2 Advantages

The advantages of SCFE compared with the other conventional separation methods are listed below.

1. The ability to control the solvent power is the most important advantage of a supercritical fluid. The solvent power of a pure supercritical fluid increases with increasing density. This often allows extraction conditions to be optimized for a target analyte by simply changing the pressure or temperature. In conventional extraction methods, another component has

to be added to the system in order to vary the solvent power of the solvent. Class-selective extractions of particular compound classes are possible by extracting the same sample at two different pressures. Thus, simultaneous fractionation and extraction can save time and labor compared to the partitioning processes accompanied with the conventional extractions .

2. The poor solvent power of SCFs compared to organic liquids towards analytes of very low volatility offers an other interesting advantage. By suitable choice of pressure and temperature a selective extraction can be effected for the analytes of medium to low volatility. The importance of this phenomenon arises because the alternative separation technique, distillation, can not be applied for these compounds.

3. The solvent power of the SCF can be altered by adding a modifier [entrainer] to the SCF. For example, adding a polar modifier to a non-polar SCF allows extraction of polar analytes. Hence entrainers can create a wide range of solvent power for analytes with different polarity. The same advantage can be achieved in Soxhlet extraction but with the restriction of operation only to certain azeotrope conditions. Non-azeotrope conditions result in evaporation of the lower boiling liquid without condensation back into the solvent reservoir. The entrainer in SCFE can facilitate extraction either by selectively interacting with the analytes or by displacing the analytes from an adsorptive matrix.

4. The favorable mass transport properties of SCFS compared to liquids can produce more efficient extractions. Greater penetration power by the SCFs can increase the efficiency of extraction even from highly sorptive matrices where liquid extraction methods often fail. Shorter equilibration times make SCFE 10 - 100 times faster than conventional Soxhlet extraction. Extraction times of SCFE are shorter even than extraction by sonication, and,

moreover, the selectivity of the SCFE is much better than sonication.

5. Low critical temperatures, Table 2, [9] of the some of the useful SCF solvents makes it feasible to perform SCFE at moderate temperatures. Extraction systems can be designed to prevent exposure of sample to light and air. These features makes SCFE applicable to thermally labile, photosensitive and easily oxidizable compounds. These types of problems are very common with the conventional extraction methods. Hence the applicability of the conventional methods towards some analytes are restricted, especially in the food and pharmaceutical industries where many products are thermally labile and can not be separated by distillation.

6. In SCFE, complete separation of the analytes from the fluid can be accomplished by isothermal decompression or isobaric heating depending on the nature of the analyte and the experimental procedure. In liquid extraction processes, the analyte is diluted in a large volume of the solvent during the extraction process. To recover the analytes, solvent has to be distilled out or rotovaporised which is more time-consuming. Moreover, these concentration process can cause loss or degradation of the analytes.

7. Experimental difficulties sometimes encountered in liquid extraction methods such as formation of emulsions and chemical reactions between the matrix and the solvent are not found in SCFE. These problems can lead to loss of some analytes and will not allow quantitative experiments.

8. The use of carcinogenic organic solvents such as halogenated hydrocarbons and benzene are not allowed in the food industry because incomplete solvent recoveries leads to contamination of the product.

Table 2

Critical Temperatures, Pressures, Densities and properties at Supercritical Conditions [T_r=1.02, P_r=2.0]@

Solvent	T_c [°C]	P_c [atm]	ρ_c [g/ml]	ρ_{SFC} [g/ml]
Ethylene	9.2	49.7	0.217	0.365
Xenon	16.6	57.6	1.113	1.893
Freon*	28.9	38.7	0.580	1.010
Carbon Dioxide	31.1	72.9	0.466	0.803
Ethane	32.2	48.2	0.203	0.352
Nitrous Oxide	36.4	71.5	0.452	0.764
Sulfur Hexafluoride	45.5	37.1	0.738	1.315
Propane	96.7	41.9	0.217	0.375
Ammonia	132.4	111.3	0.235	0.358
1-Butene	134.9	36.0	0.221	0.401
n-Butane	152.0	37.5	0.228	0.388
Diethyl ether	193.5	35.9	0.265	0.440
n-Pentane	196.5	33.3	0.237	0.393
n-Hexane	231.6	29.3	0.233	0.388

r - reduced, c - critical, ρ - density

*- Chloro trifluoro methane

@ from ref. 6.

Carbon dioxide, the most common supercritical fluid used in the extraction processes, is highly acceptable in food analysis.

9. Solvent disposal, and the exposure of laboratory personnel, limits the use of some organic solvents in laboratories. These barriers can be avoided by using a biologically safer fluid such as carbon dioxide as the extracting medium. The extracting material can be vented or recycled which obviates the use of large solvent disposal collectors.

10. The high purity and the low cost of the common fluids used make SCFE a much more economically favorable alternative to conventional liquid extraction processes. Also the presence of impurities in organic solvents can produce highly uncertain results, especially in trace analysis. Interestingly, supercritical fluids can be recycled without the need of much purification whereas time-consuming distillation processes have to be used to recover expensive organic solvents.

11. On and off line compatibility of supercritical fluid extraction with other analytical methods expands the versatility of this method. Sample handling can be minimized by coupling SCFE with GC, HPLC or SCFC which could be much more favorable in trace organic analysis. On the other hand, the ability to determine the analytes by off line methods helps to visualize a complete picture of the analyte.

1.3 History and development

The concept of supercritical fluid extraction was first recognized in 1879 by Hannay and Hogarth [10]. They observed the solubility of potassium iodide in supercritical ethanol and showed that the reduction of pressure resulted in the precipitation of the salt from the fluid. They demonstrated

the applicability of this concept to other salts and to low molecular weight hydrocarbons. The next development was the discovery of the effects of supercritical methane in petroleum formation and migration [11]. Meantime it was realized that the solvent power of supercritical fluids may have been involved in geological processes through the influence of water in rock formation [12]. It was also realized that deposits on the blades of steam turbines from water above its critical temperature could be caused by silica dissolving in the steam and then being deposited as the high pressure steam expands [13]. During the development of high-pressure hydrogenation it was observed that lubricating oil dissolved in the compressed gas, which led to diminished lubricating efficiency. In petroleum technology it was found that supercritical solutions could exhibit retrograde behavior, such as the condensation of a vapor phase on isobaric cooling [14,15].

The first proposal for practical application of supercritical extraction was made in 1943 describing a method for deasphalting petroleum oils [16]. In the USSR, Zhuze described a similar scheme based on a pressure-controlled process using supercritical propane. Supercritical methane has been used for fractionation of crude oil, extraction of lanolin from wool grease and ozocerite wax from ores [17].

In the early 1950's Ziegler and Gilbert discovered the "Aufbau" reaction of triethylaluminum with ethylene under pressure at 100°C [18]. On the laboratory scale this experiment was done in an autoclave charged with triethylaluminum and ethylene. To determine the amount of ethylene in the autoclave, it was weighed at different pressures and in one instance it was found that the tube was overfull. For safety this autoclave was vented through a cold trap and it was observed that triethylaluminum condensed in the cold trap. This phenomenon was not understood at that time, and it

was assumed that triethylaluminum was carried into the trap either in the form of droplets or crept up the side of the autoclave. Not much attention was paid to this phenomenon. Subsequently, this reaction drew much attention and is now used on a large scale to prepare long-chain primary alcohols which are used to prepare biodegradable detergents.

In 1962 for the first time, Zosel from the Max Planck Institute investigated the ability of pressurized ethanol to transport high-boiling materials [2]. This was a result of a difference of opinion with a licensee concerning the quality of the products of the "Aufbau" reaction. Under the experimental conditions α-olefins were produced as a by-product. Large quantities of this by-product was observed in the product of the licensee and it was virtually not found under similar conditions by Zosel. This controversy arose from the difference in the experimental procedure. Under the conditions applied by Zosel, the resulting by-product was removed from the reactor by supercritical ethylene. This leads to the separation of the by-product from the main product. Zosel explained this removal could not be associated with the partial pressure of the α-olefins because they have relatively low vapor pressures. This result provided another milestone in supercritical technology; Zosel proved that supercritical fluids could be used to separate some components from a mixture.

During the last two decades, quantitative SCFE has been developed under the supervision of Dr. David C. Locke in Queens College of the CUNY. Rapid extractions are performed using non-flammable, non-hazardous, inexpensive, pure carbon dioxide as the extracting fluid in a home-made extracting system in the absence of light and air at relatively low temperatures. Extractions are performed in a static equilibrium mode

and the extracted analytes are quantitated by means of off-line techniques. During this period of time, Locke's research group demonstrated the capability of this method by extending application from the extraction of vitamins in baby formulas and ready-to-eat cereals, to extraction of potential carcinogenic pollutants in environmental solids [73-80]. This dissertation is also a result of the progress of the development in quantitative analytical SCFE in Locke's research group.

The purpose of this study is to investigate and develop the use of SCFE to extract and recover PAHs from different environmental solids. Since the most important carcinogenic or mutagenic compounds in PAHs are considered to be the middle-sized compounds [81], primary concern of this study is focused on these PAHs [three to five fused rings]. Extractions were performed by the use of a simple and inexpensive home-made extraction system, which can be constructed from commercially available fittings and tubing in a few minutes. Important information pertaining to solute trapping, efficiency of extraction in terms of pressure, temperature, equilibrium time and density; differences in solubility of isomers; and matrix effects were evaluated and are discussed here.

Process Scale Applications

Although the concept of supercritical fluids as solvents has been established for nearly a century, there is a renewed interest in SCFE, intensified due to; increased government scrutiny of stringent pollution-control laws; the search for a wider base for petrochemical feed stocks; and a change in process economics caused by rapidly increasing energy costs. In addition to these factors, increased performance demands on materials, which can not be met by traditional processes, created a strong background for these developments. Technically SCFE works for all the applications listed in Table 3 [19]. Few of these process scale applications are discussed here; detailed discussions are available in reviews [1, 6, 15, 20, 21] and books [8, 22,23].

2.1 Food Industry

It is precisely the safety features of carbon dioxide that make it an attractive solvent for the food and pharmaceutical industries. It is environmentally nonhazardous, nontoxic, nonflammable, noncorrosive, inexpensive, and available in high purity. In the food industry, carbon dioxide is not regarded as a foreign substance or additive unlike organic solvents such as hexane or methylene chloride and it is an inert that does not react with food constituents. In general, SCFE does not leave residues in the product, which can be a problem in conventional processes. Due to these features, the Food and Drug Administration has classified carbon dioxide as Generally Recognized As Safe [GRAS] [24].

2.1.1 Coffee and Tea

Decaffeination of coffee using supercritical carbon dioxide is one of the most developed processes in food technology. The commercial production of decaffeinated coffee was started in Germany in 1978 [2]. In the

Table 3

Applications of Supercritical Fluid Extraction[@]

Natural products and food

- Decaffeination of coffee and tea
- Deodorization of oils and fats
- Extraction
  - nicotine from tobacco
  - vegetable oil and fats from seeds
  - food coloring from plant materials
  - flavors, fragrances, aromas and perfumes
  - hops and spices
  - fruit juices
  - lanolin from wool
  - drugs from plant material
  - oil from potato chips and other snack foods

Processing heavy hydrocarbons

- Deasphalting petroleum fraction
- Recovery and purification of used oils and lubricants
- Coal liquefaction
- Shale, tar sands and lignite extraction
- Processing low-vapor-pressure oils
- Extracting ozokerite from its ore
- Working up heavy petroleum fractions

Polymer processing

- Extract solvent, monomer, oligomer from polymer
- Polymer fractionation

Table 3. [cont'd]

Applications of Supercritical Fluid Extraction [cont'd]

Chemical separations and purifications

- Oxygenated organics from water
- Separation of aromatic and paraffinic hydrocarbons
- Separation of nonpolar from polar compounds
- Aromatic isomer separation
- Isotope separation
- Purification of organometallic compounds

Regeneration

- Activated carbon
- Adsorbents
- Filters
- Catalysts

Chemical reactions

- Waste detoxification in supercritical water
- Carboxylic acid extraction from water

Solids removal from viscous media

Tertiary oil recovery

Potable water from sea water

Chemicals from renewable resources

Comminution via precipitation from supercritical fluids

Deposition of materials in microporous substrates

@ from ref. 19.

commercial process, green coffee beans are soaked with water before the extraction. This water in the coffee beans acts as an entrainer to the non-polar carbon dioxide during the extraction of polar caffeine flavor volatiles. Caffeine loaded carbon dioxide is washed with warm water which recovers the caffeine. The supercritical carbon dioxide is recycled to the extraction chamber. Extracted caffeine can be recovered by distillation. Most interestingly this process extract caffeine selectively without the loss of aroma. Instead of washing, caffeine can be recovered from supercritical carbon dioxide by adsorption onto activated charcoal. By charging the extract vessel with beans and charcoal simultaneously, the extracted caffeine can be selectively diffused into the charcoal. The charcoal can be separated from the beans by sieving. Decaffeination of coffee by SCFE has proven the success of this industrial procedure by lowering the caffeine content to less than 1%. The same concept can be applied to decaffeination of tea.

Extraction with an organic solvent involves different steps. First the flavor of the coffee or tea is removed by extraction with petroleum ether. The deflavorized coffee or tea is moistened and passed through ammonia solution to remove the caffeine salts. The caffeine is then extracted by trichloroethylene or dichloromethane. After the coffee or tea is dried the flavors are restored. The crucial point of this type of extraction is the removal of halogenated organic solvents which are potentially carcinogenic.

2.1.2 Spices

Another important application of SCFE in the food industry is the processing of spices. As a general rule, the best extract should have the aroma, flavor and hot characteristics of the original spice. Extracts with supercritical fluids posses those characteristics. In addition, the resulting

extract has advantages such as better utilization, uniformity, shelf-life and sterility over the original spice [25]. Extraction of piperine from ground black pepper, capsacine from ground red chillies and essential oils from ground nutmeg were patented by Vitzthum [6,8]. In these extractions, the degree of extraction for the main constituents was found to be greater than 97% proving the excellence of SCFE in spice processing.

2.1.3 Hops

Supercritical carbon dioxide is used to extract α-acids from hops, which are used to give beer its characteristic taste [25,26]. Although the yields are similar to those using toxic methylene chloride, the extract's color, composition, and texture are more controllable. Moreover, both the aroma, and the bitter taste constituents can be extracted simultaneously resulting an extract organolipticaly identical to the original hops. Extraction of aroma constituents from black tea [27], cocoa butter and aroma constituents from cocoa beans [28], and nutmeg butter from nutmeg [25] are some of the other process developed on the industrial scale.

2.1.4 Snack Foods

SCFE of oils from food samples is another interesting area which has been explored. Zosel has extracted oil from soybean flakes, corn and bones using propane, ethane, carbon dioxide or nitrous oxide. Several trade journals describe development of supercritical carbon dioxide process for extracting oils from potato chips and other snack foods [29,30]. Nutritional value and shelf life of these snack foods has improved after oil extraction.

2.1.5 Plant & Fish Oils

SCFE has been used to deodorize plant oils such as soybean, palm, peanut, coconut, and sunflower. Using a carbon dioxide / hydrogen mixture, a simultaneous removal of free fatty acids and hydrogenation for

the plant oils has been accomplished by Zosel and others [7, 31,32]. Attempts were made to separate fish oils from free fatty acids and protein residues using SCFs where conventional processing by high-vacuum and molecular distillations can cause degradative reactions at high temperatures. Supercritical ethane is used to separate cod liver oil into 50 fractions, some having molecular weights as high as triglycerides, which are inseparable using conventional distillations [2].

2.2 Natural Products

Attention has been paid to the extraction of natural products from plant materials. Although the physical and chemical plant environment can hamper the extraction, caraway fruits, peppermint leaves, camomile flowers, cannabis, sunflower seeds and sesame seeds gave rise to about 20 different compounds including limonene, menthol and triglycerides [33,34]. Alkaloids are one class of compounds commonly found in natural products. Supercritical carbon dioxide demonstrates poor efficiencies in extracting alkaloids with relatively polar functional groups, such as hydroxyl groups. Supercritical nitrous oxide yields much better results.

2.3 Pharmaceuticals

In pharmaceutical applications, supercritical fluids have the potential to extract drugs from plants, without the side effects of chemical decomposition that can result from extraction using liquid organic solvents [35]. An example is the extraction of camomile using carbon dioxide, which selectively extract bisabolol, its oxides, proazulenes, coumarins, and fragrant components leaving polysaccharides, acids and flavenoids [7]. Extraction of crude opium for codeine, narcotine and papaverine [33,36,37] and of cincohona bark for quinine [33,36] are a few of the other pharmaceutical applications for plants. Selective extraction of mevinolin drug from the fermentation broth is described by King and Larson [38].

2.4 Tobacco

Denicotination of tobacco is a process similar to the decaffeination of coffee. In both of these processes the raffinate is the primary interest and the extract is secondary. Tobacco treated with organic solvents for the removal of nicotine often acquires a rubbery texture which is a disadvantage for further processing. Extraction with supercritical carbon dioxide is a possibility, though it causes some expansion of the tobacco. It can also be used to provide a tobacco aroma which could be used to impregnate a neutral matrix. Extraction on the industrial scale occurs in three steps. In the first stage, the aroma is removed selectively by extraction with the carbon dioxide and is used to impregnate a previous batch from which the nicotine and the aroma is removed. This is done by allowing the supercritical phase to expand into the batch. The de-aromatised tobacco is moistened, and the nicotine removed in an isobaric and isothermal recycling operation involving a selective sorbent. A third stage is carried out to ensure the homogeneous distribution of the aroma in the finished batch by repeated dissolution. The nicotine content in the tobacco can be reduced up to 95% [25] by this process.

2.5 Petroleum Industry

With the increase in energy cost for distillation or liquid solvent extraction, less energy intensive SCFE has become popular in the petroleum industry. In addition to the cost, fractionation of low vapor-pressure oil by the conventional methods exhibit difficulties. High vacuum or molecular distillation methods demonstrate difficulties if there are impurities present with the same volatility. Fairly high solubilities of these oils in organic solvents reduce the selectivity in fractionation with organic solvents. In contrast to these methods, the poor solvent powers of supercritical fluids towards these oils has been used for their fractionation. By controlling the solvent power using pressure and temperature, synthetic and natural oils

such as silicones, fluoroethers, α-olefins and petroleum resins were fractionated more effectively [21].

An alternative fractionation procedure has been attempted which uses a liquid solvent as an entrainer [39]. The function of the entrainer is to increase the solubility of the substrate in the supercritical phase, and to enable product separation to be achieved without reducing the solvent pressure. This is done by choosing an entrainer which becomes partly miscible with the supercritical fluid at a temperature not far above the extraction temperature. The advantages of extractive distillation are thus exploited for the separation of mixtures of slightly volatile compounds.

2.6 Coal Processing

Kerr-McGee utilized supercritical fluids for coal processing in the critical solvent deashing process, in which ash and insolubles are removed from the coal [40]. In the Coal-SCFE process developed by the U.K. National Coal Board [41], supercritical fluid penetrates into the coal and selectively extracts the lighter hydrogen-rich materials which are better suited and require less of the expensive hydrogen for the conversion to premium fuel. The remaining carbonaceous part of the coal can be used for gasification and combustion. Advantage of these two processes are low fluid-oil ratio, easy solvent recovery and flexibility.

2.7 Environmental Control

Supercritical fluid technology has been developed to separate hazardous materials from the environment. These separation processes can be grouped into three categories based on the concentration of the pollutant and the mode of separation, namely, one-step process, two-step process and reactive process [42]. The one-step process is most applicable when the concentration of the material to be removed is high. Here the sample is

directly contacted with supercritical fluid; the sample and the extracted pollutants are separated from the matrix in a single step. Extraction of priority pollutants from soil and ash samples [43] and recovery of alcohols from aqueous samples [44] are two of the most important examples in this group.

In the two step process, an intermediate phase is used to concentrate very dilute pollutants from gas and liquid streams. A properly selected adsorbent or a filter is used to trap the pollutants for a secondary supercritical fluid separation. The most interesting application for the two step process is the augmentation of current methods of waste water treatment that use either activated carbon or synthetic resin adsorbents for the purification of industrial waste streams [45]. In these systems, the solvent is used to regenerate beds of adsorbent that have become saturated with the contaminant, allowing the adsorbent to be recycled. Current methods such as steam stripping and thermal regeneration are energy-intensive and therefore expensive to use. Synthetic resins which are more efficient and selective than activated carbon are temperature sensitive precluding thermal regeneration.

In reactive separation, supercritical fluid simultaneously dissolves the material and serves as a reaction medium for a specific chemical change causing detoxification. Destruction of organics in waste water streams is one of the important examples [46]. Wastes are slurried and then mixed with oxygen and supercritical water. Under the supercritical conditions of water, the nonexistence of hydrogen bonding due to the high temperature produces an organo-like medium, an excellent solvent, which can result in complete miscibility of the fluid with the organics. Under the oxidation conditions, organics are rapidly oxidized to light gases such as carbon dioxide and nitrogen, and halides are precipitated from the very low

dielectric supercritical water. Another important application is the precombustion-desulfurization of high-sulfur coals [47]. Supercritical ethanol has been used as the supercritical solvent which provides an excellent medium for both extraction and removal of the sulfur constituents from coal.

2.8 Polymer Processing

Conventional processing methods of most polymeric materials do not achieve the desired specific product performance. The solvent characteristics of SCF have demonstrated that SCF processing of polymers can be a viable concept in treating such materials. The polymer studies reported to date can be categorized into five general groups: polymer fractionation; high-pressure polyethylene polymerization/fractionation; extraction of low-molecular-weight oligomers; supercritical fluid chromatography analysis of polystyrene; and polymer-organic solvent phase separation [8]. Krukonis suggests [8] reactive monomers, which are used in applications that require high purity can potentially be purified by SCF processing techniques. This will be a big contribution in producing soft lenses, dental polymers, surface coatings and similar materials from varying structure and reactive functionality where distillation processes are difficult due to temperature sensitivity.

2.9 Redistribution of Particle Size via SCF Nucleation

A process concept to utilize the pressure-dependent solvation power of SCFs to comminute materials was reported in 1981 [48]. Industrial, comminution of materials is carried out by grinding or by precipitation from solution, but many chemicals are sensitive to these processes because of temperature effects or because of co-precipitation of impurities from liquid solutions. Supercritical Fluid nucleation offers the potential to tailor particle size and size distribution free of temperature and solvent impurity

limitations. Attractive candidates for comminution by SCF nucleation are heat labile dyes, fine chemicals, pharmaceuticals and intermediates which must be formed in some specific particle size for subsequent processing or use. In the process a material is dissolved in a SCF and subsequently expanded to a pressure which results in the nucleation of a desired particle size and size distribution. Since many complex organic materials can be dissolved in a variety of SCFs, the only technical requirement for application of this process concept, it is expected that comminution by this technique will find applications especially in fine chemicals and pharmaceuticals.

Analytical Applications

The unique properties of supercritical fluids has prompted their use for a variety of applications in the field of analytical chemistry. By far the largest number of applications occur in the field of chromatography, where these compressed gases are employed as highly interactive mobile phases. Its extraction analog, SCFE, the most significant analytical technique to emerge in the 1980's, has generated a considerable interest in various areas of organic analytical chemistry. Following is a review of analytical supercritical fluid extraction.

Historically, the first description of an analytical SCFE was published in 1976 [49], in which Stahl and Schilz introduced a solvent-free micro-analytical system coupled to thin-layer chromatography. However, quantitative and more numerous applications of this method were not reported until recently. Most of the recent analytical investigations focused on samples similar to those already explored in industrial applications such as the determination of the caffeine from coffee [50], the extraction of oils from natural products [51], and the removal of pesticide residues from plant sources [52] or organic pollutants from environmental sorbents, such as Tenax-GC [53,54] polyimide-based resins [55], XAD resins [56], and polyurethane foam [56,57]. Only a limited number of studies have been done on direct extraction of environmental solids such as fly ash [58,59], river sediment [58,60,61], urban dust [56,58,60,62], and diesel exhaust particulates [53].

3.1 Static and Dynamic Extraction

Quantitative analytical supercritical fluid extractions can be performed in two different modes, namely static equilibrium and dynamic, depending on the mode of sample contact with the supercritical fluid. In

the static equilibrium extraction mode, supercritical fluid is confined in a closed volume in which sample is equilibrated with SCF for a period of time known as the equilibration time. After equilibrium is reached, the extract-laden SCF is released and the extracted sample is collected for further analysis. In the dynamic extraction mode, a continuous flow of the supercritical fluid is passed through the bed of the sample at a constant flow rate and the extract is continuously collected. As far as the instrumentation is concerned, the static equilibrium mode employs a valve to create a closed system whereas a flow restrictor such as a capillary tube is used to maintain continuous flow in the dynamic extraction. Actually, most of the static equilibrium mode extractions are semi-continuous at the releasing step, unless the sample is separated within the extraction chamber.

3.2 On-line and Off-line Detection

The extracted analytes are subsequently analyzed by an appropriate instrumental method. This analysis may be off-line or on-line depending on the chosen analytical method. Several examples of on-line SCFE coupled with SCFC [52,63-65], GC [60,62,66-69] or HPLC [70,71] have been reported. The straightforward adaptation to most forms of chromatography offers the luxury of eliminating tedious sample preparation techniques which are often far more time consuming than the actual chromatographic analysis. A single analysis using traditional extraction and fractionation procedures can take days to complete, whereas SCFE-coupled chromatography is often carried out within one hour, with higher efficiencies. The extraction itself is faster and there are no intermediate reconcentration steps in which solutes may be lost, or contaminants introduced. Moreover, maximum sensitivity can be achieved because all the extracted analytes can be quantitatively transferred into the chromatographic column, which is particularly attractive for small sample sizes and for trace analysis where low levels of analytes are present. In addition, the variable solvating power of a SCF

provides the mechanism for the selective extraction of the components of interest from the sample matrix and provides the basis for an automated method where sample preparation and analysis can be instrumentally linked.

3.3 Coupled Techniques

SCFE coupled with chromatography has proved that to be method of choice for the analysis of organic compounds adsorbed onto a solid matrix. Possible applications of coupled SCFE / GC are listed in Table 4. [67].

Thermally stable, low molecular weight compounds are analyzed by SCFE / capillary gas chromatography which provides simpler operation and higher efficiencies than are feasible with SCFE/SCFC or SCFE/HPLC. Moreover, SCFE / capillary GC is amenable to the vast majority of compounds extractable with non-polar fluids such as carbon dioxide. SCFE / SCFC is an important technique for the high resolution analysis of high molecular weight or thermally labile compounds, where SCFE / capillary GC is not suitable. SCFE / HPLC is the least popular combination since nearly all the SCFE / HPLC applications can be performed by SCFE / SCFC with a greater efficiency.

SCFE / GC need not require any modifications to a commercially available GC. The simplest configuration for a dynamic SCFE / capillary GC was introduced by Hawthorne and Miller [53], in which the extraction cell restrictor is inserted directly into the capillary GC column through a standard on-column injector. During the period of extraction, the extracted compounds are deposited onto the GC column using cryogenic focussing. After the extraction is complete, the restrictor is removed from the injector and the GC oven is temperature programmed to elute the analytes. The success of this configuration has been evaluated by observing two factors;

Table 4

Applications of SCFE/GC@

Sample analyzed	Analyte
Coffee beans	Caffeine
Agricultural products	Pesticides
	Organic components
Air particulates	Polychlorinated biphenyls [PCBs]
	Polycyclic aromatic hydrocarbons [PAHs]
River Sediment	PCBs
Coal Tar	PAHs
	Biological Markers
Diesel exhaust particulates	PAHs
	Alkanes
Woodsmoke particulates	Phenolics
Fly ash	PAHs
Tobacco	Nicotine
	Pesticides
Spices, herbs	Flavor components
Treated wood	PAHs
Cigarette ash	Heterocyclic aromatics
Chewing gum	Flavor components
Orange peel	Fragrance components
Sorbent resins	Toxic organics

@ from ref. 67

reproducibility and the shape of the chromatographic peaks. Replicate studies demonstrated good quantitative reproducibillities implying the success of transferring extracted materials without loss. Good chromatographic peaks comparable to standard on-column injections with liquid solvents proved the success of cryogenic focussing. This configuration has been reported to yield good quantitative results for a variety of sample matrices including sediments, airborne particulate matter, sorbent resins and food products [53,57,59,64].

The direct deposition of the extracted analytes inside the GC column makes the on-column SCFE/GC approach unsuitable for some sample types. For example, samples with high fat contents will result in very poor chromatograms because the fat is also extracted and deposited inside the GC column. Not only poor chromatograms, but also reduction of column life time can be observed, which is a common problem in on-column injection of non-fractionated extracts. But the excellent stability of modern capillary column stationary phases avoids the need of choosing samples for SCFE/GC. Even when the column is assaulted with large quantities of nonchromatographable species, performance can be regained by simply trimming several centimeters off the front of the column. Another problem that can be associated with SCFE/GC coupling is the extraction of water from the sample. This extracted water can be transported into the GC column and freeze, resulting in a plugged column. Placing selective sorbents between the extraction cell and the GC column may have potential for removing matrix compounds and water from the extract before deposition in the GC column which eliminates these two major difficulties in coupled SCFE / GC.

A combination of a tandem switching valve and an injection valve has been used to interface SCFE with SCFC [65]. With this design, extraction

can be performed even under static equilibrium conditions. After the extraction is performed, a portion of the extracted material can be introduced onto the column for chromatography. The remainder of the extracted material, concentrated in the supercritical fluid can be used for further injections. This interfacing configuration prevents overloading the analytical column, and by selecting a suitable column and mobile phases SCFE / multi mode chromatographic analysis can be performed.

In contrast to on-line detection methods, off-line detection methods provide a means of concentrating extracted materials before the analysis, which can lower the achievable detection limits. In addition, off-line detection methods are extremely useful in the analysis of unknown analytes, because the extracted analytes can be detected using several methods which can provide a wide spectrum of information about the unknown analyte. Analytical experiments such as solubility studies, where a large quantity of the analyte is being used, are generally performed using off-line methods. The biggest draw back of the off-line methods is the extra sample handling in which incomplete recovery of the extracted materials from the trap or ineffective trapping, dilution or concentration steps before the analysis can produce unreliable results.

3.4 SCF Solvents

As in the industrial applications, carbon dioxide has been the solvent of choice in analytical supercritical extractions. Nearly two third of the analytical scale SCFE have been performed with carbon dioxide. In addition to carbon dioxide, nitrous oxide and non-polar hydrocarbons such as ethylene, ethane and iso-butane have been used for the extraction of organics. Nitrous oxide has been reported to extract PAHs with higher efficiency than carbon dioxide from various matrixes [60]. Although its molecular structure is similar to carbon dioxide, nitrous oxide has a small

dipole moment and weak basic properties [72]. This small molecular difference between carbon dioxide and nitrous oxide has produced dramatically different outcomes in extractions [59-61]. Another significant difference in the solvating properties was reported for supercritical carbon dioxide and iso-butane [56], in which iso-butane yielded higher extraction efficiencies for higher molecular weight PAHs than carbon dioxide.

Most of the solvents available for SCFE are somewhat weak solvents compared to organic solvents. This weakness enhances the selectivity but limits their applicability. For example, supercritical carbon dioxide and nitrous oxide have sufficient polarity to extract relatively non-polar species such as alkanes, polycyclic aromatic hydrocarbons [PAHs] and flavor fragrance compounds, but they may not useful for the rapid extraction of more polar and higher molecular weight analytes. The ability to control the solvent strength and the poor solvent power towards some analytes has been cleverly used for selective fractionations. PAHs and alkanes can be selectively extracted from various sample matrixes by controlling the solvent strength [53]. For example, poor extraction capabilities of carbon dioxide towards polar dioxins and furans has been effectively used to clean up fly ash prior to the extraction of the toxins [59].

3.5 Modifiers

The addition of a small amount of a polar modifier, in order to modify the solvent properties of weak solvents, has been explored. These experiments demonstrated a significant improvement in the efficiency removal of difficultly extractable compounds from various matrixes. The introduction of these polar modifiers can produce a binary system with new critical parameters. Generally, these binary systems do not exhibit a significant increase of the fluid density. But it has been observed that there is an increase of the solvent power in this mixture compared to the pure

fluid itself. In addition, polar modifiers can introduce specific interactions such as H-bonding with the analytes as well as weakening the interactions between the analyte and the matrix. Methanol has been the most studied modifier for the available SCFs.

A comparative study between five different supercritical fluid media: carbon dioxide, nitrous oxide, ethane, carbon dioxide modified with 5% methanol and nitrous oxide modified with 5% methanol demonstrated different efficiencies for the extraction of PAHs from fly ash, river sediment and urban dust SRM 1649 samples [60]. Supercritical carbon dioxide and ethane demonstrated the poorest recoveries of PAHs from these three matrixes whereas nitrous oxide gave moderately higher recoveries from all three systems. Both carbon dioxide and nitrous oxide demonstrate an increase in the efficiency of PAHs extraction with the 5% methanol modifier, but the 5% methanol-modified nitrous oxide yielded the best recoveries. The extraction efficiency of PAHs from a fly ash sample was much lower than from urban dust and river sediment sample. It is clear from all these experiments that the solvent as well as the matrix play a major role in governing the success of the analytical scale experiment. In fact, this is the main difference between the analytical scale and engineering experiments in supercritical fluid technology. The main concern in engineering experiments, such as solubility studies, is how much of the solid is going to dissolve in the fluid. But the success of analytical scale experiment is dependent on both the solubility and the recovery.

Supercritical carbon dioxide has been successfully employed to remove spiked standards and organic pollutants from sorbent traps [53-57]. The process of desorption by supercritical carbon dioxide is far superior to conventional thermal desorption methods. Thermal desorption methods

have their own limitations such as the inability to desorb the most strongly retained compounds at temperatures that do not destroy either the compounds or the sorbent itself. The universality of the supercritical carbon dioxide desorption concept has been demonstrated by extracting four different environmentally significant compounds, representing four different classes,: anthracene [PAHs] hexachlorocyclohexane [chlorinated hydrocarbon], hexachlorobiphenyl [PCB], and parathion [organophosphate pesticide] from a Tenax trap. In the case of hexachlorobiphenyl and parathion, thermal desorption gave only very poor recoveries as compared to supercritical carbon dioxide, which gave quantitative recoveries for all four of the above-mentioned compounds [54]. This can lead to a powerful approach for the recovery of analytes that have been collected on the sorbent resins from air and water samples.

Different adsorbent materials demonstrate different efficiencies towards the desorption process. In a similar study, four different polyimide-based sorbents have been tested in place of Tenax-GC. Again, recoveries using supercritical carbon dioxide were in excess of 90% for all the compounds chosen, although the process of desorption was more difficult as compared to Tenax-GC [55]. SCFE of PAHs from polyurethane foam [PUF] plugs demonstrated relatively easier desorption than from XAD-2 resins with both supercritical carbon dioxide and iso-butane. Moreover the SCFE of the PUF plugs was accomplished with less fluid than was used for the XAD-2 resins, but similar or better extraction efficiencies were reported in both the cases [56].

Theory

Thermodynamic models describing phase equilibria associated with SCF extraction can be separated into two general classes: those describing SCF-liquid equilibria and those describing SCF-solid equilibria. The main difference between these models are that the solid phase is assumed to dissolve no solvent [82,83] and in multi-component systems, no solid solutions are assumed to be formed [84]. These two assumptions simplify the analysis considerably by eliminating the composition dependence of the chemical potential of the solid phase. In the case of equilibria between liquids and SCFs, multicomponent solutions are common and considerable amounts of SCF can dissolve into the liquid phase [85]. This leads to a composition dependence of the chemical potential which must be considered in the analysis. As with all the equilibria, the condition for equilibrium is based on standard thermodynamic principles which equate fugacities for each mixture constituent in all phases. For two phases,', and ",

$$f'_i = f''_i \qquad (1)$$

where i= 1, 2, ... m. f_i is the fugacity component i in a mixture of m components. In the case of SCFE of solids, solid [i = 2] is brought in contact with the SCF and equilibrium is attained, then at equilibrium

$$f_2^s = f_2^{scf} \qquad (2)$$

The fugacity of solid component can be determined in each phase from conveniently chosen constitutive equations. Generally, fugacity of the solid component in the condensed phase is calculated from

$$f_2^s = P_2^{vap} \{ \phi_2^{vap} \exp [V_2^s (P - P_2^{vap}) / RT] \} \qquad (3)$$

where P_2^{vap} is the saturated vapor pressure of the solid at the temperature T. The molar volume, V_2^s, is a function of temperature and pressure, but at conditions remote from critical, the condensed phase may often be regarded as incompressible. The fugacity coefficient, ϕ_2^{vap}, corrects for deviations of the saturated vapor from ideal-gas behavior. Hence, the product, P_2^{vap} ϕ_2^{vap}, accounts for the fugacity of the pure solid at saturated vapor pressure. The exponential term, the Poynting correction, takes into account the fact that the solid is at a pressure P, different from P_2^{vap}. The fugacity coefficient and the Poynting correction are often small and sometimes they are negligible. If the temperature T is such that the P_2^{vap} is low, then ϕ_2^s, is very close to unity. The Poynting correction, which is an exponential function of the pressure and is small at low pressures, may become large at high pressures or at low temperatures.

The fugacity of the solid component in the fluid is more difficult to determined. Since there is no clear distinction between gas phases and liquid phases at elevated pressures, two conventional approaches are utilized to obtained the fugacities of the components in the SCF phase; SCF is treated as a highly compressed gas, or as an expanded liquid.

The most common approach is to treat the fluid as a highly compressed gas and to determined the fugacity, f_2^{cg}, from volumetric properties,

$$f_2^{cg} = y_2 \phi_2 P \qquad (4)$$

where y_2 is the mole fraction of solid in the SCF phase and P is the pressure. The fugacity coefficient ϕ_2 characterizes the non-ideal behavior of the solid component in the gas phase relative to ideal-gas behavior, and can be calculated from an equation of state [EOS] using exact thermodynamic relationships [86]. The results are frequently very sensitive to the interaction energies and size factors used, necessitating the development of improved mixing rules to estimate the mixture size and energy parameters needed in the EOS. Combining equations (2),(3) and (4), solubility of the solid in SCF can be represented by

$$y_2 = \frac{P_2^{vap} \left\{ \phi_2^{vap} \exp \left[V_2^s (P - P_2^{vap}) / RT \right] \right\}}{P \phi_2} \qquad (5)$$

The validity of this equation relies on two reasonable assumptions, i.e. the solid phase is pure and the molar volume of the solid is fixed.

By assuming ideal gas behavior, solubility of the solid component in the gas phase can be calculated from Dalton's Law [87]

$$y_2^{ideal} = P_2^{vap} / P \qquad (6)$$

The ratio of the non-ideal to ideal solubility of the solid is defined as the enhancement factor, E, which is a dimensionless measure of the SCF solvent power.

$$E = y_2 / y_2^{ideal} \qquad (7)$$

By substituting equations (5) and (6) into equation (7), an expression can be derived to estimate the enhancement factor for the solubility of a solid in the SCF phase.

$$E = [\phi_2^{vap} / \phi_2] \exp [V_2^s (P - P_2^{vap}) / RT] \qquad (8)$$

High enhancement factors are common in supercritical systems. Since the contribution of ϕ_2^{vap} and the Poynting correction are relatively small, the primary contribution to the enhancement factor is through the fugacity coefficient ϕ_2. There are many empirical EOS's and new ones continue to appear which can be used to estimate the fugacity coefficient of different types of solutes in SCF mixtures. These equations contain empirically determined constants which are derived from mixture rules which state how these constants are dependent on the mixture composition.

A theoretically significant EOS is the virial equation in which virial coefficients can be related to the intermolecular potentials. The virial equation can readily be extended to mixtures. Whereas for any pure component the virial coefficients depend only on the temperature and on the intermolecular potential for the component, for a mixture they depend also on the interaction potentials between molecules of those different components which comprise the mixture. The fundamental advantage of the virial equation is that it directly relates fugacities in the mixtures to intermolecular forces. The practical disadvantage of the virial equation follows from insufficient understanding of the molecular forces. As a result the virial equation is applicable only to those mixtures whose components are non-polar or weakly polar. At moderate pressures, below approximately one-half the critical density of the fluid component, ϕ_2 can be calculated

from a truncated virial equation of state [88-90]. At higher pressures, i. e. higher densities of the SCF, the utility of the virial equation is limited by a lack of knowledge of higher order coefficients [82].

At high densities, an essentially empirical EOS must be used to relate the fugacity coefficient to the pressure, temperature and the fluid phase composition. Most of the cubic EOS's are derived from perturbation theory with certain assumptions. In perturbation theory, the properties of the fluid mixture are related to those of a simpler reference fluid whose EOS and other properties are accurately known. Pure fluids, treated as mixture of hard spheres or mixture of non-spherical hard bodies, have been used as the references in these perturbations which is dependent on the type of solute. The van der Waals EOS was derived by assuming that the integral of the perturbing intermolecular potential for a pair of molecules is a constant which is called the mean field approximation [91]. The Soave-Redlich-Kwong EOS [92] and the Peng-Robinson EOS [93] are obtained by introducing a temperature and density into the perturbing intermolecular potential. Use of the Carnahan-Starling repulsive term [94], instead of the van der Waals version, was based on the derivation of the Carnahan-Starling-van der Waals equation [95] and augmented van der Walls equation [96]. Another perturbation method that has been applied to SCF is the perturbed hard-chain theory [97] and its variations [98-102]. This model addresses the asymmetry of the size of the molecules, taking into consideration the ability of the solvent to interact with only part of the solute.

A different approach has been the use of lattice gas models or those including scale laws [103] which are nonanalytic. The lattice gas models are based on the idea of distribution of molecules over the sites in a three-dimentional lattice. These approaches address the fact that behavior in

the immediate vicinity of the solution critical point is non-classical and can not be described correctly by a classical EOS or its modifications. Introduction of the so-called universal critical exponent can be used to describe the thermodynamic properties in terms of the distance from the critical point. Hence, lattice gas models can be used to impose the correct asymptotic behavior at the critical point. Although this approach is useful in the complete understanding of the critical region, there is not much significance in this approach in terms of SCFE because nearly all the SCFE processes are operated away from the critical region.

An alternative approach is to treat the SCF as an expanded liquid [104] and obtain the fugacity, f_2^{el}, of the solid component in the fluid phase from solution theories,

$$f_2^{el} = y_2 \gamma_2 f_2^0 \qquad (9)$$

where f_2^0 is the fugacity of solid component in a specified standard state. The activity coefficient γ_2 characterizes the non-ideal solution behavior of the solid component relative to the chosen standard state. Therefore the solubility of a solid in the SCF phase can be calculated from combining the equations (3) and (9) into (2) as

$$y_2 = \frac{P_2^{vap} \{ \phi_2^{vap} \exp [V_2^s (P - P_2^{vap}) / RT] \}}{\gamma_2 f_2^0} \qquad (10)$$

When the standard-state fugacity is specified as the fugacity of the pure liquid at the system temperature and pressure, γ_2 characterizes

deviations from Raoult's law behavior for the solid component. The activity coefficient can be evaluated at a fixed reference pressure and at constant temperature at which it is a function of composition only. The best reference pressure is the critical pressure P_c. At this pressure, the solubility of the solid component is negligible and the activity coefficient is essentially the activity coefficient at infinite dilution, $\gamma_2^{\infty}[P_c]$, which is constant at a fixed temperature. For the limited solubility range under consideration, it is a good approximation to use both this infinite dilution activity coefficient and the partial molar volume at infinite dilution. Since the SCF mixture is highly compressible in the critical region, the partial molar volume at infinite dilution has to be evaluated from an EOS. The infinite dilution activity coefficient is a characteristic parameter for the binary mixture and therefore is obtained from mixture data.

4.1 Data Correlations

4.1.1 Enhancement vs Density

Johnston and Eckert [95] reported an empirical correlation between the log enhancement factor and the density. Later, Schmitt and Reid [105] noted that the plots of log enhancement versus the pure solvent density, instead of the mixture density, can also be used to correlate the solubility results. Interestingly, these plots showed fine splitting of the solubility isotherms which formed parallel lines corresponding to the various system temperatures. Furthermore, they suggested that the solubility isotherms can be made to collapse into a single generalized line, by proposing the empirical model

$$\log E = \alpha \rho_r + \beta + \sigma [T-T_{ref}] \qquad (11)$$

where α and β represents the slope and y-intercept of the reference temperature, σ the isotherm spacing constant, and T and T_{ref} are the system and reference temperature, respectively.

4.1.2 Concentration vs Density

Chrastil [106] derived a relationship relating the solubility of a solute [g/l] to the density [g/l] of the supercritical solvent based on the assumption that a molecule of the solute associates with a fixed number of solvent molecules at a given temperature and this solvato complex is in equilibrium with its surroundings. From equilibrium considerations and the approximation of the Clausius-Clapeyron equation, the following equation was derived:

$$\ln C = k \ln \rho + \Delta H/RT + q - k \ln M_1 + \ln[M_2 + kM_1] \qquad (12)$$

where k is the association constant, ΔH ($= \Delta H_{sol} + \Delta H_{vap}$) represents the total heat of the reaction where ΔH_{sol} is the heat of solvation and ΔH_{vap} is the heat of vaporization, R the universal gas constant, q is a constant and, M_1 and M_2 are the molecular weights of the solvent and solute, respectively. Chrastil suggested that a plot of the log of the solute concentration versus log of the solvent density should result in direct proportionality over a wide range of temperatures and pressures. For a given solute-solvent system equation (12) can be rewritten as

$$C = \rho^k \exp[a/T + b] \qquad (13)$$

This simple three-parameter equation was modified by Adachi and Lu [107] since k is density-dependent. Introduction of two more additional parameters produced a better correlation for a total of 37 different systems. Generally the unmodified equation successfully fits data for non-polar solutes. However, it was found that the slopes of the solubility isotherms decrease with increasing temperature when the solutes are polar [108,109]. This indicates that at high temperatures fewer molecules are involved in the solvato complex.

Recently Kumar and Johnston [110] showed that the solute solubility varies linearly with the solvent density when graphed in either log-log or log-linear co-ordinates. The relationship between the concentration of the solute in the SCF and the fluid density was derived by expressing the fugacity coefficient of the solute in terms of solvent density instead of pressure as is done in the conventional thermodynamic treatment. Interestingly, they were able to relate the slopes of these plots to the isothermal compressibility of the solvent. Furthermore, the partial molar volumes generated from this model were in good agreement with the available experimental data.

4.1.3 Enhancement vs Pressure

A semi-empirical correlation can be derived from equation (8), using the assumption that the fugacity coefficient and the solid molar volume do not depend on the pressure of the system. Under these conditions equation (8) can be rewritten as

$$\ln E = \ln \left[\phi_2^{vap} / \phi_2 \right] + \left[V_2^s (P - P_2^{vap}) / RT \right] \qquad (14)$$

Hence, the plot of log enhancement versus $(P - P_2^{vap})$ should fit a straight line where the slope of the line is a measure of the solid molar volume and

the intercept is a measure of the fugacity coefficient.

Zieger and Eckert [111] developed this correlation using regular solution theory and the van der Waals EOS. Their proposed semi-empirical correlation uses the van der Waals EOS and mixing rule to determine the fugacity coefficient of the solute in the fluid phase in terms of the solubility parameters of the solute and solvent as

$$\ln \phi_2 = \ln[1+\delta_1^2/P] - \varepsilon_2^*\Delta\,[2-\Delta] + V_2^L P/2.3\,RT \qquad (15)$$

where ε_2^* is the dimensionless energy parameter given as

$$\varepsilon_2^* = \delta_2^2\, V_2^L /2.3\,RT \qquad (16)$$

δ_1 and δ_2 are the solvent and solute solubility parameters, Δ [$= \delta_1 / \delta_2$] represents the ratio of the solubility parameter of the solvent to solute, and V_2^L is the molar volume of the solute which has been evaluated by treating the solid as a subcooled liquid and thus extrapolating liquid properties below the melting point. Alternatively such properties can be more readily estimated by atomic and group contribution methods [112].

The Hildebrand solubility parameter is introduced to relate the enhancement of volatility with pressure, temperature and the size and the nature of the solutes. An appreciation of the meaning of the solubility parameter in physical terms is well described by Fedors [112]. In the above treatment, Zieger and Eckert defined the solubility parameter as originally defined by Giddings [113] according to van der Waals theory

$$\delta_1 = a_1^{1/2} \rho_1 \qquad (17)$$

The constant a is the energy parameter in the van der Waals equation. The solubility parameters of the solutes are calculated from knowledge of their thermal properties.

Substituting equation (15) into equation (14) and introducing two empirical temperature-independent parameters η and υ, the final correlation can be derived as

$$\log E = \eta \left[\varepsilon_2^* \; \Delta/y_1 \{2 - \Delta/y_1\} - \log \{1 + \delta_1^2/P\} \right] + \upsilon \qquad (18)$$

where y_1 is the equilibrium mole fraction of the solvent. Zieger and Eckert claimed that the above semi-empirical correlation will produce linear behavior with the collapsing of the solubility isotherms over a wide range of SCF conditions, thereby resulting in a single generalized line. The parameters η and υ represent constants that are characteristic of each solvent and solute respectively.

Correlations based on this equation indicates that solubility data do collapse onto a straight line **[108, 111]**. Moreover, it was found that the binary systems involving the same SCF solvent produced lines of similar slopes implying that η is a function of the SCF only.

Polycyclic Aromatic Hydrocarbons

During recent years, it has become increasingly evident that cancer in man is linked to environmental factors. In particular, attention has been focused on the importance of chemical carcinogens in the environment. The historical evolution of knowledge about chemical carcinogens and environmentally induced carcinogenisis is strongly linked to advances in characterization of polycyclic aromatic hydrocarbons [PAHs]. Until the beginning of this century there existed a natural balance between the production and natural degradation of PAHs, which kept the background concentration low and fixed [114]. However, with increasing industrial development throughout the world, the natural balance has been disturbed and the production and accumulation rates of PAHs are constantly rising. Therefore, the identification and determination of PAHs in environmental samples is an urgent and important analytical problem.

PAHs can be defined as organic compounds containing two or more fused benzene rings which may or may not have substituent groups attached to one or more rings. PAHs have their main sources in fossil or synthetic fuels, and combustion or high-temperature reactions of organic materials. Since these sources are ubiquitous in an industrialized society, there are large numbers of stationary as well as mobile sources of PAHs. The stationary sources include industrial operations, power and heat generation, residential heating, incineration and open fires. The mobile sources include diesel-and gasoline-engine automobiles, trucks, airplanes and sea traffic. In all these processes organic material is burned or strongly heated and will in most cases result in emissions of PAHs. The amount of PAHs released from any process is largely dependent on raw materials and combustion technology. PAHs are associated with particulate matter and often emitted from smoke stacks, and hence subject to considerable aerial

transport. This makes PAHs one of the most widely spread classes of environmental contaminants.

A prerequisite for the control of PAHs in the environment is an understanding of the chemical and physical properties of the PAHs as well as methodologies for analysis. Except for analysis of pure PAHs themselves or PAHs from analytically compatible matrices, or the analysis by rapid screening procedures, which rely upon some unique molecular or spectral properties, most analytical methods for quantifying PAHs require a preliminary extraction step because few sample matrices can be analyzed directly without serious interferences. In addition, a high degree of separation efficiency is necessary. Besides the many different compounds with a wide boiling point range that may be formed during a high-temperatue combustion, there also exist many possibilities for structural isomers of PAHs; the biological effect may differ for isomeric molecules although the chemical and physical properties are very similar. A detailed knowledge of the sample composition is therefore required for estimating the potential hazard of PAHs in the environment. Finally, a high sensitivity of detection is required both for analyzing samples collected over a relatively short period of time and for detecting minor components which may be of biological significance.

As mentioned earlier, analytical procedures are initiated with an extraction step to remove the PAHs from the bulk of the sample matrix. The objective of the extraction procedure is to separate PAHs from the bulk sample matrix in as high a yield as possible with minimal coextraction of other classes of compounds or contaminants, or degradation of the extracted PAHs. This extraction step places the PAHs into an analytically more compatible matrix where the sample can be easily analyzed. With some sample matrices a simple extraction is the only sample preparation

necessary before analysis, whereas others may require extensive fractionation to produce a suitable PAH isolate. The degree of sample handling and workup is a function of both the sample matrix and the analytical method employed for PAH measurement. In either case, the extraction procedure must quantitatively remove PAHs from the sample matrix or the extraction recovery must be known for the PAHs analysis to be accurate and precise. The purpose of the present study is to investigate and develop such a methodology using supercritical fluids which can provide reliable information of the PAHs in the environment.

5.1 Extraction of PAHs from Solid Samples

The Soxhlet extractor is probably the most widely used method for extraction of PAHs from environmental solids. PAHs are soluble in many organic solvents and there have been several recommendations for the best solvent for Soxhlet extraction. Several factors have to be considered in selecting a suitable solvent for the extraction. Aromatic solvents such as benzene and toluene have been regarded as good solvents for the extraction of PAHs, due to similar structure which can enhance the recovery. But benzene is not widely used because of its suspected carcinogenic activity. Cyclohexane which is potentially nonhazardous has been used to extract PAHs instead of benzene. Use of high boiling liquids can degradete thermally unstable molecules in the extraction pot and can lead to loss of volatile analytes during the concentration process. Thus low boiling liquids such as methylene chloride have been extensively used in extraction of low molecular weight and thermally labile PAHs. Use of polar solvents such as methanol will yield an extract containing more unwanted materials and will be less selective.

Sonication of slurries of environmental solids in organic solvents has been the most widely used alternative to Soxhlet extraction for recovery

of PAHs. In this method a high-intensity ultrasonic vibrator is used to produce solvent cavitation around the sample matrix particles which presumably leads to enhanced solvent contact and mixing with the sample. The main advantage of the ultrasonic procedure appears to be in its much more rapid extraction, by a factor of 30-40 times than Soxhlet [115,116]. It also appears to be far more reproducible. Reports claim a 1.3% relative standard deviation for reproducibility in extraction of total air particulate PAHs vs 26% for Soxhlet extraction [115,116].

5.2 Determination of PAHs

5.2.1 Gas Chromatography

Gas Chromatography [GC] has proved to be an exceptional by useful and versatile instrumental tool for analyzing compounds that have a low molecular weight [upto 500] and that can be volatilized without decomposition. In principle, GC is a simpler, more direct method for determination of PAHs than many other methods, provided that a suitable column can be found. The technique of fused silica capillary GC has been brought to a level where excellent reproducibility, high sensitivity and high resolution have been attained [117]. However, there are some problems encountered in the resolution of some isomeric PAHs. Nematic liquid crystal phases have been demonstrated to have potential in achieving separations of some isomeric PAHs [118,119]. But one of the problems with this nematic liquid crystal phase is that it tends to bleed and be rather unstable at elevated temperatures.

The most widely used GC detector for PAHs is the flame ionization detector [FID]. This is a result of its universally accepted characteristics of excellence response linearity, sensitivity and reliability. Lao et. al. [120] have reported response factors for a large number of PAHs using an FID. As

expected, response increases with molecular weight and response factors are similar for most structural isomers. Cantuti et. al. [121] showed that the response of the electron capture detector [ECD] to PAHs was dependent on the structure of the compound, and that the detector could be selective for PAHs in hydrocarbon mixtures. Bjoresth and Eklund [122] measured the ECD/FID response ratios for 29 PAHs and found that many isomers could be differentiated by measurements of the ratios. Grimsrud [123] found that adding oxygen carrier gas greatly enhanced the signal from a constant-current ECD for certain PAHs. This response enhancement was found to be dependent on the structural details of the PAHs. It was suggested that this structure-dependent response enhancement could assist in the identification of resolved PAHs isomers.

The most powerful approach available today for the analysis of complex PAH mixtures is capillary column gas chromatography/mass spectrometry [GC/MS]. The maximum resolution of mixture components before mass spectral analysis is of the utmost importance in providing unambiguous identifications of individual compounds. This is especially true in the case of PAHs because conventional mass spectra of many isomers are identical. The mass spectrometer is therefore unable to provide the correct structure by itself, thus prior separation by high-resolution capillary columns is essential.

5.2.2 High Performance Liquid Chromatography

Since its inception in the early 1970's high performance liquid chromatography [HPLC] has been used for the separation of PAHs. HPLC does not approach the high separation efficiency of capillary gas chromatography, but does offer several advantages for the determination of PAHs. First, HPLC offers a variety of stationary phases capable of providing unique selectivity for the separation of PAHs isomers that are often difficult

to separate by GC. Selectivity in HPLC is achieved because of interactions of the solute with both the stationary phase and the mobile phase rather than with only the stationary phase as in GC. Secondly, ultraviolet [UV] absorption and fluorescence spectroscopy provide extremely sensitive, and more important, selective detection for PAHs in HPLC. Finally, HPLC provides a useful fractionation technique for the isolation of PAHs for subsequent analysis by other chromatographic and spectroscopic techniques. Because of these characteristics, HPLC has been employed extensively for the determination of PAHs.

Reversed-phase HPLC on chemically bonded C_{18} [octadecyl] stationary phases is by far the most popular liquid chromatographic mode for the separation of PAHs, providing unique selectivity for the separation of PAH isomers and particularly alkyl substituted PAHs. In addition, the compatibility of reversed-phase HPLC with gradient elution techniques and the rapid equilibration of these columns to a new mobile phase composition make reversed-phase HPLC a convenient separation technique.

Polar chemically bonded stationary phases used in conjunction with non-polar mobile phases [normal-phase HPLC] have also been employed for the separation of PAHs. Several polar stationary phases are available containing such functional groups as amine, diamine, nitrile, diol, ether and nitro phenyl bonded to the silica particles [124]. In the normal-phase mode on these polar columns, the PAHs separations achieved are similar to those obtained on the classical adsorbents such as silica and alumina. In contrast to reversed-phase HPLC, the presence of an alkyl group on the PAHs has only a slight effect on the retention on the amine phase [125]. This characteristic is often advantageous in pre-fractionation techniques for the analysis of complex mixtures. The use

of normal-phase HPLC on polar bonded phases also eliminates one of the major difficulties encountered with classical adsorbents, i. e. non-reproducible retention owing to small changes in the moisture content of the eluent. Finally, the use of volatile non-polar mobile phases facilitates the concentration of collected fractions by evaporation and also in LC/MS.

5.2.3 Supercritical Fluid Chromatography

Although SCFC is not being evaluated as a separation technique in this study, it is interesting to compare SCFC with the other techniques for the separation of PAHs. PAHs have been analyzed using SCFC almost since the earliest studies of SCFC as an analytical technique. Sie and Rijnder [126,1127] used PAH standards ranging from naphthalene through coronene as model solutes to develop many theoretical aspects of SCFC. These same investigators also demonstrated the first application of SCFC to a real sample containing PAHs, applying SCFC to the analysis of coal and polyphenyl tars [128]. Jentoft and Gouw [129,130] applied SCFC to the separation of standard PAHs as well as the separation of components in a PAH-rich sample from automobile exhaust. The application of small particle diameter packed columns using SCF carbon dioxide at high pressures resulted in fairly rapid SCFC analysis of some selected PAHs in a standard mixture [131]. In addition, the use of modifiers in SCF mobile phase has been studied to determine the effect on retention of PAHs in SCFC [126,129,132]. Moreover, open tubular [capillary] columns provide high resolution SCFC analysis of PAHs [133-135].

GC and HPLC fail to provide completely satisfactory analysis of many complex PAHs samples which extend over a large range of molecular weights. GC provides the high resolution necessary for the complexity of PAH-containing samples, but is restricted in its application by the low

volatility of the high molecular weight PAHs. HPLC provides the solvating power necessary to analyze many of the larger PAHs, but lacks the high resolution needed to deal satisfactorily with the complexity of the PAH samples. SCFC exhibits good solvating ability, comparable to or better than liquids. SCFC also shares with HPLC the ability to control mobile phase selectivity. The mobile phase selectivity in SCFC can be varied by changing either the pressure [136] or density [137] of the SCF or by changing the polarity of the mobile phase [138]. At the same time, diffusivity and viscosity are more favorable for chromatographic efficiency in SCFs than corresponding liquids. Hence, SCFC offers a high resolution chromatographic technique which is capable of analyzing samples with the wide molecular weight ranges common to PAH-containing mixtures.

Capillary SCFC, in particular, offers several advantages in PAHs analysis. The openness of capillary columns eliminates large pressure drops across the analytical column. This allows much longer columns to be used, yielding a greater number of theoretical plates resulting in better resolution. The small pressure drop also allows more sensitive control of density of the SCF. Since the density of SCF determines the solvating ability, density programming in capillary SCF mobile phase provides a powerful technique to extend the molecular weight range of compounds which SCFC can analyze [137]. The sensitive density control which is possible in open-tubular columns make density programming in capillary SCFC extremely useful for PAHs analysis of complex samples. Another advantage of capillary SCFC is the versatility of detectors available. The best detectors available in both HPLC and GC can be used in capillary SCFC [133,134,137] in the absence of modifiers. Capillary SCFC has also been coupled to flame detectors commonly used in GC [135]. Furthermore, due to the small mass flow rates in capillary SCFC, it has proven straight forward to interface a capillary SCFC to a mass spectrometer [139,140].

5.3 PAHs in Fly Ash

Fly ash has been reported [141,142] to be a difficult matrix from which to extract PAHs. It is considered difficult because of the low quantities of PAHs which are present and because of the large number of other organic compounds present in the sample [143]. Low concentrations of PAHs are the result of two factors: first, that PAHs are efficiently destroyed by the high temperatures and excess oxygen used in coal-fired, electric power plants [144]; and second, that the fly ash matrix adsorbs PAHs more strongly than other environmental PAH matrices [141,145]. Other combustion products which contain PAHs are carbon black, diesel exhaust, cigarette smoke, flame-broiled or smoked foods, soot from wood fires and ash from municipal incinerators [146-152].

5.3.1 Extraction of PAHs from Fly Ash Samples

Several methods have been used to extract PAHs from fly ash; these include Soxhlet extraction with organic solvents [145,146,153], sonication of slurries of fly ash in organic solvents [153,154], and liquid extraction at elevated pressures [155,156]. Soxhlet extractions of fly ash have been performed with benzene, toluene, pyridine, cyclohexane, methylene chloride, methanol, acetone, water and mixtures of solvents. Soxhlet extraction of PAHs from fly ash is not quantitative with any of the above solvents [141]. Pyridine, benzene and toluene were found to be the most effective solvents on the basis of control experiments involving spiked fly ash samples [153]. Combinations of benzene and methanol, whether in sequence or as the azeotrope, are also frequently used [146,153]. Junk and Richard [153] spiked fly ash samples with mixtures of PAHs at 100, 250 or 1000 ng/g and compared recoveries from Soxhlet extractions with pyridine to recoveries with benzene. Recoveries of PAHs by Soxhlet extraction with pyridine were higher than recoveries with benzene by 20 percent.

Poor PAH extraction recoveries from highly sorptive matrices have led to some unusual modifications of the Soxhlet procedure. For example a modified Soxhlet method was attempted [157] with a heating tape to allow the use of naphthalene and methyl naphthalene as an extraction solvent in order to improve the extraction recoveries of six- and seven-ring PAHs from lamp black. A single 6 hr Soxhlet run using naphthalene extracted almost twice the amount of benzo [ghi] perylene and coronene from lamp black than did two 20 hr extraction with benzene. However this procedure has the disadvantage that smaller two ring PAHs are not recovered due to their high volatility at these temperature conditions.

Junk and Richard [153] spiked fly ash samples with mixtures of PAHs at concentrations of 100, 250 and 1000 ng/g and compared recoveries from sonication of fly ash slurried with pyridine to recoveries with benzene. Recoveries of PAHs by sonication with pyridine were higher than recoveries with benzene by 60 percent. Recoveries of benzo [a] pyrene from spiked fly ash were reported to range from 7 to 62 percent. Harrison et. al. [154] spiked fly ash samples with ^{14}C-labelled benzo [a] pyrene at a concentration of 6 ng/g, then sonicated slurries of the spiked fly ash in methylene chloride or methylene chloride : toluene [1 : 1] or toluene : methanol [4 : 1]. Extracts were analyzed by liquid scintillation counting and recoveries of less than 4 percent of ^{14}C-labelled benzo [a] pyrene were obtained. Janssen and Kanij [145] spiked fly ash samples with 700 ng/g of ^{14}C-labelled benzo [a] pyrene and sonicated slurries of spiked fly ash with toluene, xylene or 1,2,4 - trimethylbenzene. Extracts were analyzed by liquid scintillation counting of ^{14}C-labelled benzo [a] pyrene. Recoveries of 35% to 48% were reported and there were no significant differences among recoveries due to solvent. Besemer and Kanij [158] spiked fly ash samples with 10,000 ng/g of ^{14}C-labelled benzo [a] pyrene, then sonicated slurries of fly ash with methanol or acetone. Recoveries of 1 to 21 percent were

obtained. Besemer and Kanij also sonicated slurries of spiked fly ash with an aqueous surfactant, analyzed the extract by liquid scintillation counting, and obtained recoveries of ^{14}C-labelled benzo [a] pyrene up to 14 percent.

Griest et. al. [142], using an ultrasonic technique, reported the extraction of ^{14}C-labeled benzo [a] pyrene from fly ash was incomplete and that the unextracted tracer remained on fly ash. In addition they observed that the PAH extraction efficiency from fly ash is a function of the ring system size. They were able to extract phenanthrene and naphthalene efficiently whereas PAHs with more than three-rings showed pronounced decrease in efficiency. Interestingly, a saturated hydrocarbon of molecular weight greater than benzo [a] pyrene demonstrated much more rapid and complete extraction implying that molecular weight is not the only factor which governs the efficiency of extraction. These observations suggest that the association of PAHs with the fly ash surface might involve π complexes between the aromatic compounds and metals on the fly ash surface. These authors concluded upon further study [141] that the association of aromatic species with carbonaceous particulates is the dominant interaction.

The possibility of surface interactions between PAHs and sorptive matrices has also been demonstrated in other liquid extraction methods. The nature of this surface interaction is reflected by the order of solvent efficiency, aromatic solvents being the best followed by polar solvents. This order of solvent strength suggests that the extraction is dominated by aromatic interactions, which are followed in importance by polar interactions. Nonaromatic, nonpolar solvents exhibit little effectiveness in extracting PAHs from sorptive fly ash samples.

Liquid extraction at elevated pressure has been investigated by Mangani et. al. as an alternative to both Soxhlet extraction and sonication

of slurries of fly ash. They spiked fly ash samples with a mixture of PAHs at concentrations from 2 to 57 ng/g fly ash, loaded the spiked fly ash into a 4 mm diameter, stainless steel tube, and extracted PAHs with toluene at 100°C under 2.5 atm N_2 pressure [156]. Extracts were analyzed by capillary GC/MS using selected ion monitoring of molecular ions with a double-focusing mass spectrometer. Recoveries as low as 71 percent for chrysene and as high as 98 percent for fluorene were reported. Recoveries reported for anthracene, fluoranthene, benz [a] anthracene and chrysene by liquid extraction at elevated pressure were higher than recoveries by Soxhlet extraction with toluene by as much as 50 percent. No data were reported for benzo [a] pyrene. Liquid extraction at elevated pressure has been investigated by Soltys et. al. [155] using cyclohexane, methylene chloride and benzene. Fly ash samples were spiked with 60,000 ng/g of benzo [a] pyrene, loaded into a stainless steel extraction cell and extracted by each solvent for up to 33 hours. Recoveries of benzo [a] pyrene were reported to be 2 percent with cyclohexane, 17 percent with methylene chloride and 97 percent with benzene.

5.3.2 Determination of PAHs from Fly Ash

Only a few research groups have determined concentrations of PAHs in fly ash. Greist et. al. [159] used HPLC with UV detection on extracts of fly ash and obtained concentrations of PAHs from 8 to 37 ng/g fly ash, including 18 ng/g for phenanthrene and 35 ng/g for benzo [a] pyrene. They also report, the use of GC/FID on extracts of fly ash and obtained concentrations of PAHs from 0.03 to 0.9 ng/g fly ash including 0.5 ng/g for phenanthrene and 0.03 ng/g for benzo [a] pyrene. Harrison et. al. [154] used GC/FID and obtained concentrations of 16 to 190 ng/g fly ash for PAHs having as many as four aromatic rings. Avery et. al. [160] used GC/FID and obtained concentrations of PAHs in the range of 0.2 to 40 ng/g fly ash. The concentration range for phenanthrene was also 0.2 to 40 ng/g, but benzo

[a] pyrene was not detected. Morselli and Zappoli [161] used GC/FID on extracts of fly ash and obtained concentrations of PAHs from 9 to 69 ng/g fly ash, including 38 ng/g for phenanthrene and 53 ng/g for benzo [a] pyrene. Mangani et. al. [156] used GC/MS and obtained concentrations of 0.4 to 3.0 ng/g fly ash for PAHs having as many as four aromatic rings.

Experimental

6.1 Chemicals and Supplies

The PAH reference compounds were obtained from the following sources: pyrene and fluorene from Eastman organic chemicals [Rochester NY]; benz [a] anthracene, benzo [a] pyrene, chrysene, fluoranthene, 9-fluorenone, 1,4-naphthaquinone, phenanthrene and triphenylene from Aldrich Chemical Company [Milwaukee WI]. HPLC grade solvents methylene chloride, acetonitrile and methanol were purchased from Fisher Scientific [Fair Lawn NJ]. All the chemicals and solvents were used as purchased without further purification or distillation. Silica gel from J. T. Baker [Phillipsburg, NJ], octadecyl bonded phases and XAD-2 resins [polystyrene divinylbenzene copolymer] from Supelco Inc. [Belfonte, PA], Chromosorb W and Tenax-TA (poly-[2,6 diphenyl-p-phenylene oxide]) from Alltech Associates Inc. [Applied Science Labs, Deerfield IL] were washed in a column with a suitable solvent before use. Water distilled from a Mega Pure System MP-12A [Corning NY] was preserved with 5% [by volume] methanol [HPLC grade] for the HPLC mobile phase. Two fly ash samples obtained from Italy (courtsey of Prof. L. Morselli, Universita degli studi Bologna Italy [Bologna and Parma]) and the Montour fly ash sample (courtesy of Dr. M. D. Applequist, Lehigh University Bethlehem, Pennsylvania), collected from an energy plant of the Pennsylvania Power and Light Company, were subjected to this study. Two top soil samples, one collected from Long Island Rail Road [near the Port Jefferson railway station, Long Island New York], and another sample from Kissena Park [Queens, New York] were also utilized in this study.

Stock solutions were prepared by dissolving weighed amounts of the required PAHs in an appropriate volume of methylene chloride [HPLC grade]. Concentrations of the stock solutions prepared for spiking

chromosorb W, fly ash and soil samples are given in Table 5. Appropriate volumetric dilutions with methylene chloride were made to prepare dilute solutions and the spiked levels are given in Tables 6 and 7. Stock solutions for evaluation of traps and optimum extraction conditions were usually prepared at a concentration of 1mg of PAH in 1 ml of methylene chloride.

All the solutions were stored at 4°C in a cold room when not in use. Spiked samples were prepared in a bottle by pipetting a known volume of stock [or diluted] solution containing all the PAHs onto a known weight of the solid matrix. The spiked sample were air dried and stored in closed bottles at room temperature and throughly mixed before SCFE.

6.2 SCFE Apparatus

The basic units of the SCFE apparatus used at the beginning of the study are shown in Figure 2. The bone dry grade carbon dioxide supplied through a single stage tank regulator was filtered through a Tenax trap and an Autoclave Engineers [AE] 5 micron cup type filter. This filtered gas was pressurized by an Aminco [now Newport Scientific, Jessup MD.] motor-driven single-ended diaphragm compressor with a maximum output of 700 atm. The pressure of the system was controlled either by a Circle Seal internally dome-loaded line regulator or from the tank regulator. This was connected to a Bourdon-type pressure gauge [Ashcroft] reading the experimental pressure and to the extraction assembly via a "T" junction. The "T" junction and the extraction train were thermostatted in a Labline Imperial II circulating radiant heat oven.

The extraction train consistsed of two AE valves [inlet and outlet ends of the extraction chamber], two Swagelock reducing unions [3/8"to 1/4"] connecting the 1/4" valve to the 3/8" extraction chamber, 6" long 3/8" diameter stainless steel extraction chamber, 1/4" stainless steel

Table 5

Stock Solutions

Analyte	A [mg/100 ml]	B [mg/100 ml]	C [mg/100 ml]
Acenaphthylene	00.0	17.3	00.0
Benzo [a] Pyrene	16.1	15.1	20.6
Fluoranthene	16.2	15.5	20.6
Fluorene	19.0	17.0	21.1
9 - Fluorenone	00.0	00.0	20.5
1,4 - Naphthaquinone	00.0	00.0	20.2
Phenanthrene	17.7	16.9	20.1
Pyrene	17.2	16.9	23.6
Triphenylene	15.5	16.5	19.3

A - Stock solution used to spike Chromosorb W

B - Stock solution used to spike fly ash

C - Stock solution used to spike soil

Table 6

Spiked Levels in Fly Ash Samples

Analyte	D [μg/g]	E [μg/g]	F [μg/g]	G [μg/g]
Acenaphthylene	0.346	3.45	34.6	345
Benzo [a] Pyrene	0.302	3.02	30.2	302
Fluoranthene	0.310	3.10	31.1	310
Fluorene	0.339	3.39	33.9	339
Phenanthrene	0.338	3.38	33.9	338
Pyrene	0.338	3.38	33.9	338
Triphenylene	0.329	3.29	32.9	329

D - 2.00 ml of the 1000 times diluted stock B in 10.016 g of fly ash

E - 2.00 ml of the 100 times diluted stock B in 10.026 g of fly ash

F - 2.00 ml of the 10 times diluted stock B in 10.006 g of fly ash

G - 2.00 ml of the stock B in 10.023 g of fly ash

Table 7

Spiked Levels in Soil Samples

Analyte	H [µg/g]	I [µg/g]	J [µg/g]	K [µg/g]	L [µg/g]
Benzo [a] Pyrene	0.102	1.03	10.3	103	1030
Fluoranthene	0.102	1.03	10.3	103	1030
Fluorene	0.105	1.06	10.6	106	1060
9-Fluorenone	0.102	1.02	10.2	102	1020
1,4-Naphthaquinone	0.100	1.01	10.1	101	1010
Phenanthrene	0.100	1.00	10.0	100	1000
Pyrene	0.117	1.18	11.8	118.0	1180
Triphenylene	0.096	0.965	9.63	96.4	964

H - 5.00 ml of the 1000 times diluted stock C in 10.006 g of soil

I - 5.00 ml of the 100 times diluted stock C in 10.003 g of soil

J - 5.00 ml of the 10 times diluted stock C in 10.002 g of soil

K - 5.00 ml of the stock C in 10.001 g of soil

L - 5.00 ml of the 10 times concentrated stock C in 10.007 g of soil

connecting tubes and Swagelock 1/4" fittings. The outlet of the extraction assembly was connected to the collector by an "elbow" Swagelock union. All these parts were guaranteed to withstand pressures of at least 700 atm.

During later studies this system was changed to one with a new pump and extraction thermostat as shown in Figure 3. The Tenax trap and the 5 micron cup filter were removed from the system [in the early studies these two parts were assembled to further purify carbon dioxide and subsequently it was found that carbon dioxide is sufficiently pure]. Now, only the extraction chamber is placed in a heating jacket [Scientific Systems Inc., State College PA.] which can be controlled to a maximum of 99°C ±1°C. This arrangement made it easier to perform the extractions at a higher temperature and quicker temperature equilibrium was established. Using this new arrangement was more convenient and the possible leakages were easily identified during the extractions without thermal fluctuations. A larger extraction chamber [12" long and 3/8" diameter stainless steel] was used which could double the sample load per extraction compared to the previous assembly.

6.3 SCFE Procedure

Prior to each extraction, the extraction train was disassembled, cleaned with methylene chloride and dried. Sample was loaded into the extraction chamber and two prewashed glass wool plugs were inserted into each end of the extraction chamber to prevent the movement of sample during the pressurization and depressurization processes. All the parts were assembled and care was taken to prevent possible leaks at high pressures during the extraction. Initially a few ml of carbon dioxide was flushed at low pressure [~7 atm] leaving both the valves open to replace the trapped air in the assembly by carbon dioxide. Then the second valve was closed tightly and the oven temperature brought to the desired experimental

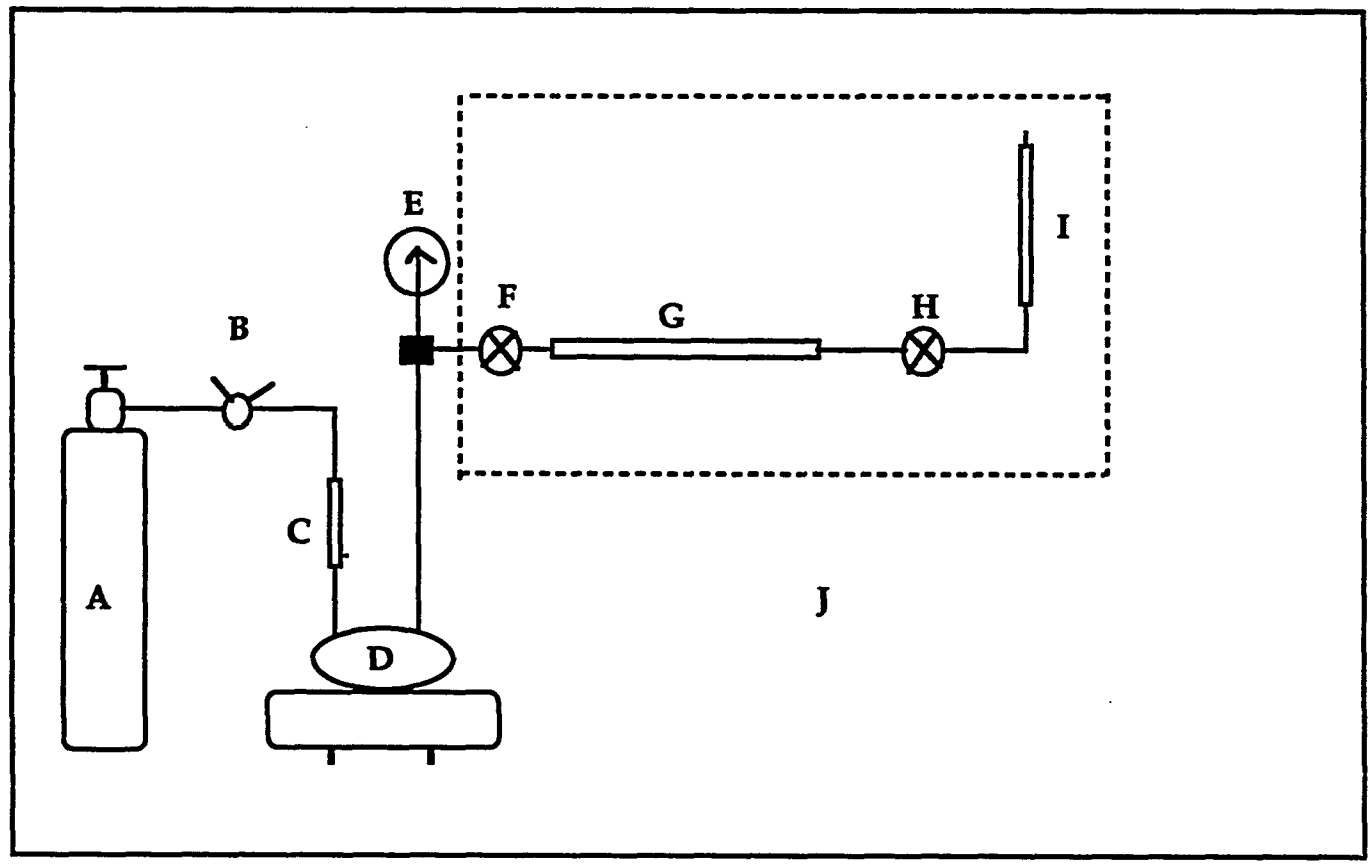


Figure 2. SCFE apparatus [initial set up]

A: Gas tank B: Regulator C: Filter D: Compressor
E: Pressure gauge F: Inlet valve G: Extraction chamber
H: Exit valve I: Trap J: Oven

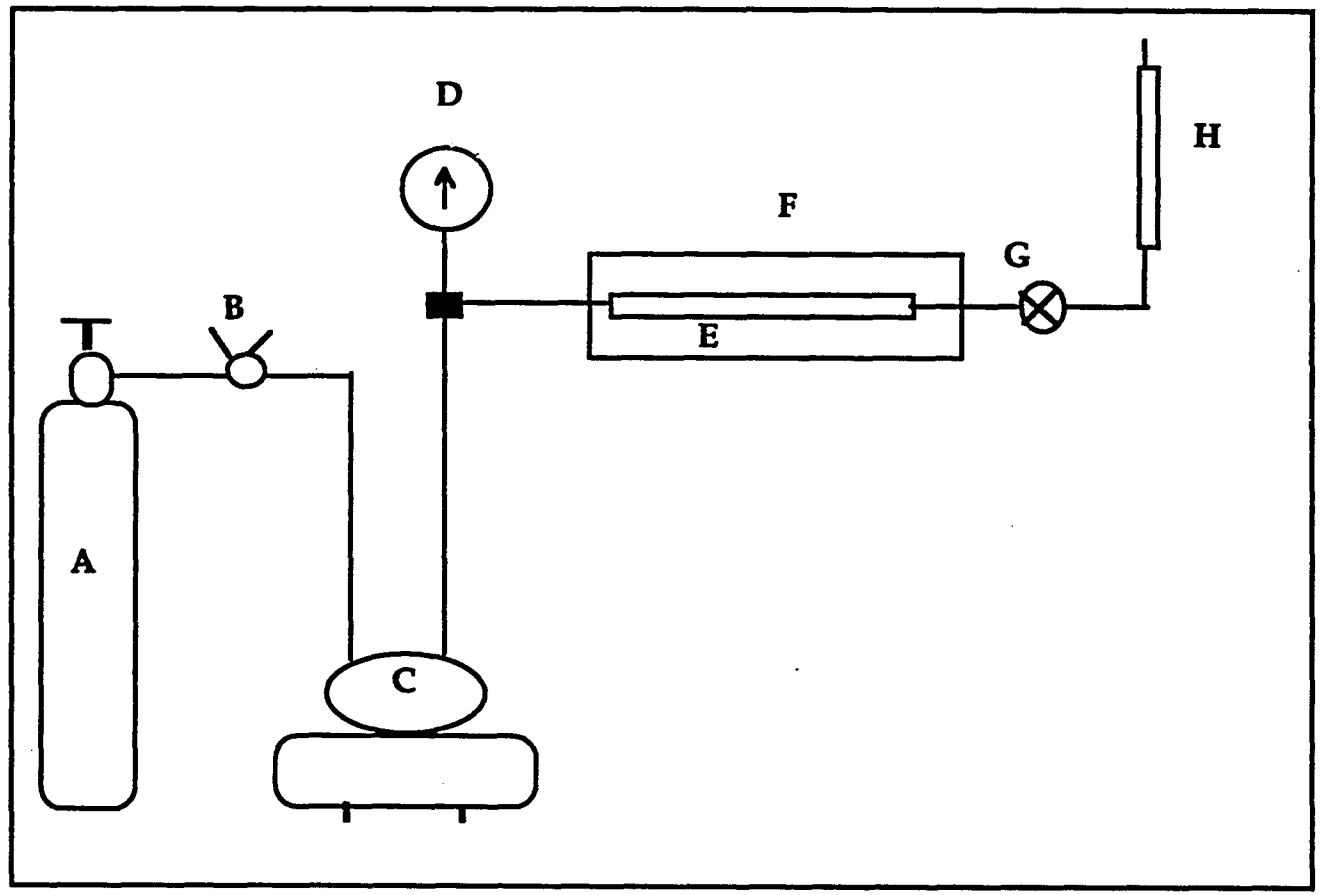


Figure 3. SCFE apparatus [new set up]

A: Gas Tank B: Regulator C: Compressor D: Pressure gauge
E: extraction chamber F: Oven G: Exit valve H: Trap

condition. The system was pressurized to the desired experimental condition and both the temperature and the pressure maintained during the equilibration time. At the conclusion of the equilibration, both the pump and the gas supply were shut off and the second valve slowly opened to bleed out the extract-laden carbon dioxide which was passed through the trap. Once all the carbon dioxide was passed through, the apparatus was disassembled and all the parts past the second valve, including the trap, were washed with 40-50 ml of methylene chloride. The methylene chloride was evaporated from the resultant solution using a Buchi rotary evaporator [Brinkmann Instruments Inc. Westbury NY] to dryness at 40^0C. The residue was dissolved in 1 ml of methylene chloride and quantitated using either GC/FID or HPLC/UV.

6.4 Sonication Studies

Samples were placed in screw capped bottles with the extracting solvent. Each bottle was suspended half-way into water bath of a Branson 72 ultrasonic cleaner [Branson Cleaning Equipment Shelton CT] and was sonicated at full power at room temperature for 15 minutes. The sample was filtered through a prewashed Whatman #1 filter paper, concentrated by rotary evaporation and analyzed. Concentrated samples were filtered through a 5 micron filter assembly to separate particulates before the analysis.

6.5 GC and HPLC Determinations

GC experiments were done using a Hewlett Packard 5880A series Gas Chromatograph equipped with a flame ionization detector [FID]. A temperature program [below] was utilized to separate PAHs on a 30 m x 0.25 mm [id] DB-5 bonded phase [Durabond 5% phenyl - 95% methyl with a 0.25 μm film thickness] fused silica capillary column [J & W Scientific INC.

Folson CA] with helium as the carrier gas. Generally 1 µl of the stock solution or extracted sample solution was introduced into the GC injection port. A split ratio of 200:1 was maintained to prevent overloading the column and to retain good detection limits.

A temperature program with the initial temperature of 150°C for 2 minutes followed by an increment of 10°C/min was utilized to raise the temperature to 250°C in 10 minutes and then maintained 3 minutes at this final temperature with an overall run time of 15 minutes. Effluents were detected by the FID operated at 270°C. Another program was used for the analysis of unknown samples in which an initial 2 minutes at 100°C was followed by an increase of temperature by 8°C/min for 20 minutes to 260°C and then 3 minutes at the final temperature for an overall 25 minutes run time. Compounds were identified by comparision of sample retention times with those of pure standards. Quantitation was accomplished by comparing peak areas of the resolved components with the peak areas resulting from a stock solution of similar concentration.

Most of the extracted materials were separated using C_{18} reversed-phase HPLC. The liquid chromatograph was a Perkin Elmer series 410 LC pump furnished with a C_{18} guard column, 25 cm x 4.6 mm reverse phase C_{18} analytical column [Whatman Partisil 5 ODS-3, Phenomenex, CA] and a Perkin Elmer LC-90 UV absorbance detector. A Perkin Elmer LC-100 laboratory computing integrator was utilized to integrate the peak areas. For identification purposes, a Perkin Elmer LC-235 diode array detector was utilized which was capable of scanning the wavelength region from 195 to 370 nm without resorting to stopped-flow conditions. Nearly all the HPLC experiments were monitored at a wavelength of 254 nm unless specified otherwise. All the solvents were degassed with a flow of helium before the

HPLC determinations and 5% [by volume] methanol [HPLC grade] was added to distilled water as a preservative. Sample was introduced to the analytical column by means of a rotary valve with a 6 µl sample loop. All separations were performed at ambient temperature.

The isocratic mobile phase consisting of 80:20 acetonitrile:water [v:v] was utilized at a flow rate of 1 ml/min for routine analyses. Samples with oxy-PAHs were separated by a linear gradient elution with acetonitrile in water, from 60% to 90%, in 30 minutes with a flow rate of 1 ml/min. For routine quantitative analysis, the diode array detector was by-passed and a fixed wavelength detector was utilized. Peak identifications were based on retention times only. When unknown samples were to be characterized, the diode array detector was employed and both the absorption spectra and the retention times were utilized. For the purpose of quantitation, peak areas were compared to those of standards of similar concentrations. Otherwise a calibration plot constructed for each PAH was used for the quantitation of PAHs at different ranges of concentration.

6.6 Traps

Solid adsorbent traps and cold traps were evaluated for collecting PAHs [phenanthrene, pyrene, chrysene and benzo [a] pyrene] from depressurized carbon dioxide. One ml of a stock solution containing 1 mg each in methylene chloride was spiked into a prewashed or methylene chloride Soxhlet -extracted Whatman #1 filter paper [11 cm diameter], the methylene chloride evaporated, the paper cut into pieces and packed into the extractor. All the extractions were done at 544 atm pressure and 60°C for 15 minutes equilibration time. Solid adsorbent traps consisted of a stainless steel tube [9" long 1/4" diameter and 6" long 1/4" diameter] filled with an adsorbent material [Tenax TA, silica, octadecyl bonded phase or XAD-2 resin]. Adsorbents were supported in the tube by two prewashed

glass wool plugs. One end of the trap was connected to the extraction train by a Swagelock elbow union while the other end was connected to a Tygon tube [2' long 1/4" diameter] through a Swagelock union. The other end of the Tygon tube was dipped into an erlenmyer flask containing 100 ml of a mixture of methylene chloride and methanol [1:1]. Depressurized carbon dioxide was slowly passed through the Tygon tube and bubbled into the solvent mixture. After the depressurization process, the Tygon tube was washed, the washing added to the solvent mixture, which was then concentrated and analyzed. The filter paper, which was used as the sample matrix was sonicated with 15 ml of methylene chloride for 15 minutes. Similarly the extracted eluted adsorbent material was sonicated with 15 ml of methylene chloride for 15 minutes. The sonicated samples were filtered, concentrated and analyzed.

The efficiency of elution from the adsorbent material was evaluated by spiking 1 ml of the stock solution onto a similar quantity of the adsorbent used in the trap. The spiked adsorbent was air dried and eluted with methylene chloride as in the collector. After being washed, the adsorbent was Soxhlet extracted with a mixture of methylene chloride and methanol [1:1] for 24 hours and analyzed.

The configuration of the cold trap is shown in Figure 4. A piece of the Tygon or stainless steal tube was connected to the output of the extraction train and the other end of the tube was dipped into 50 ml of methylene chloride : methanol [1:1] solution [back up trap]. The middle portion of the tube [~9" long] was kept at dry ice temperature. After the extraction, carbon dioxide was allowed to pass through the cold trap and the backup trap.

6.7 Optimum Experimental Conditions for Selected PAHs

Three different parameters were evaluated to optimize the

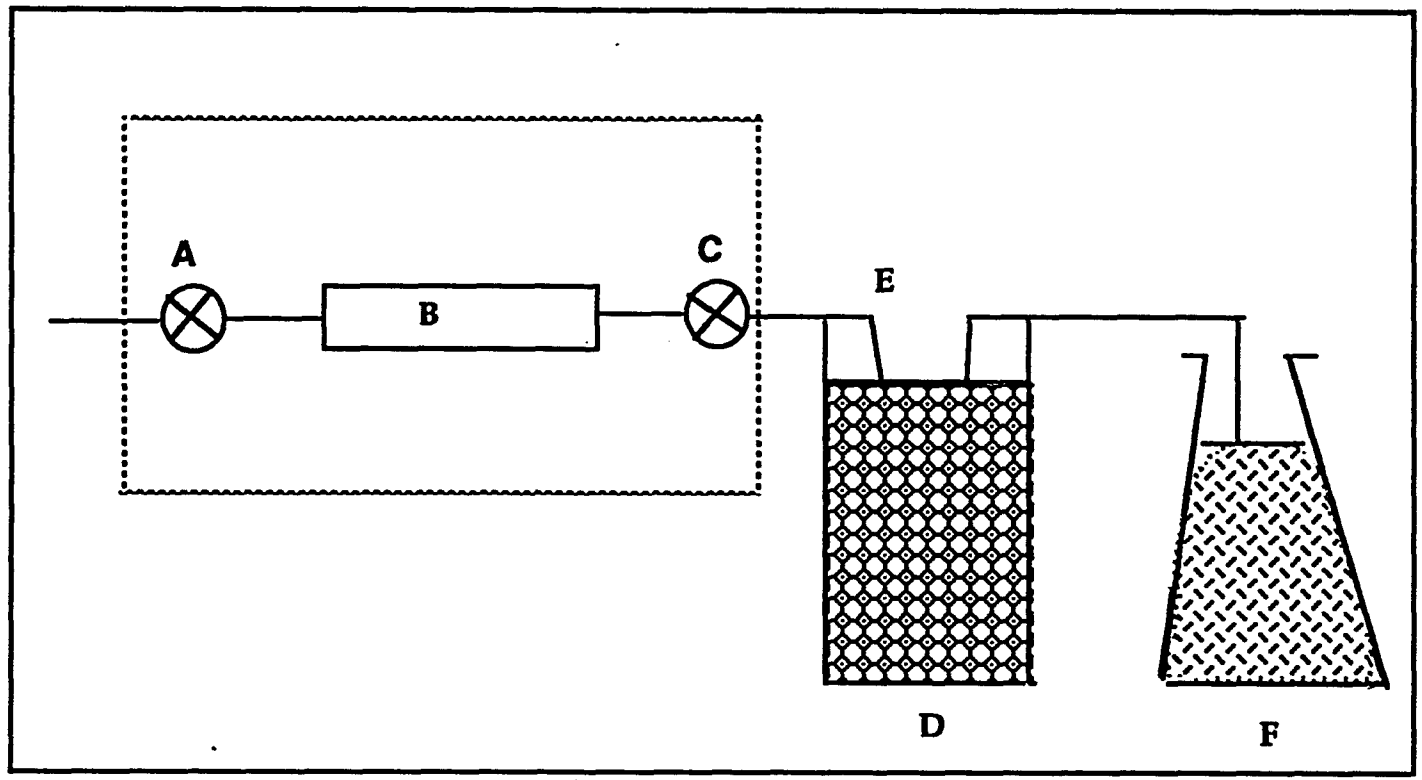


Figure 4. Configuration of the Cold trap

A: Inlet Valve B: Extraction Chamber C: Exit valve
D: Dewer containg dry ice E: Cold trap F: Back up trap

experimental conditions, namely pressure, temperature and equilibration time. Four different equilibration times were studied, 5, 10, 15 and 20 minutes at 408 atm and 60°C. A mixture of four PAHs was used as the stock sample. Spiked filter paper was used as the sample matrix and each experiment was done in triplicate. Fifteen different pressure temperature combinations [pressures ranging from 204-544 atm and temperatures of 45°C, 50°C and 60°C] were studied with 15 minute equilibration times. Each experimental combination was evaluated at least three times.

6.8 Solubility Studies

All the extractions were done in the pressure range of 340-544 atm, at 45°C and 60°C with a 15 minute equilibrium time using a silica trap as the collector. Each compound was extracted at eight different temperature pressure combinations and each trial was done in triplicate. A Tygon tube [2' long 1/4" diameter] was connected to the end of the silica trap and the depressurized carbon dioxide was collected in a volumetric flask by displacing carbon dioxide-saturated water to measure the volume of carbon dioxide used. The extract eluted from the trap was diluted to 500 ml with methylene chloride and analyzed by HPLC/UV at the appropriate maximum absorption wavelength. For pyrene the maximum wavelength was 240 nm; triphenylene, 250 nm; and chrysene, 266 nm. Compounds remaining in the extraction chamber were washed out and diluted to 1000 ml with methylene chloride and analyzed separately to check the mass balance.

6.9 Effect of Density

A series of experiments was designed to evaluate the effect of density on the extraction of PAHs. Density of the SCF was controlled by the experimental pressure and temperature. Each experiment was done in triplicate. The variation of the % recovery was studied as a function of

density at fixed temperature as well as a function of temperature and pressure at fixed density. Fifty ml of the stock solution was spiked into 50 g of prewashed Chromosorb W. The spiked sample was air dried and sonicated for 15 minutes in a closed container in order to prepare a homogeneous mixture. An accurately weighed quantity [~1g] of the spiked sample was used for the extraction.

6.10 Extraction of Fly Ash Samples

Several fly ash samples [Bologna, Parma, Montour] were extracted by SCFE and Soxhlet for the determination of their PAH content. Thirty grams of Montour fly ash was spiked with the 20 ml of the stock solution to study the effect of modifiers in the extraction of the spiked samples. Hexane, dodecane and hexadecane were the modifiers evaluated in this study. A series of dilute solutions were prepared from the stock solution. Two ml of the stock [or diluted] solution was spiked into 10 g of Montour fly ash and the spiked levels of PAHs in fly ash are given in Table 6. Spiked samples were kept in a closed container for four days before the extraction. An accurately weighed quantity [~2 g] of the spiked sample was used for the extraction. All the extractions were done at 612 atm 60^0C for 15 minutes. Each experiment was done in triplicate.

6.11 Extraction of Soil Samples

Soil samples collected from the Long Island Rail Road and Kissena Park were extracted by SCFE and Soxhlet for the determination of their PAH content. The topsoil sample collected from the Kissena Park was sieved through a 80 mesh filter and used for fortifications. A series of diluted solutions were prepared by diluting the stock solution. Five ml of the stock [or diluted] solution was spiked into a 10 g of the Kissena Park top soil and the spiked levels of PAHs in the soil are given in Table 7. An accurately weighed quantity [~2 g] of the spiked soil sample was used in

each extraction and the extractions were done at 612 atm at 60^0C for 15 minutes.

6.12 Evaluation of the Total Organic Content in the Soil Sample

The Walkley-Black method [162] was used to evalate the total organic content in the soil sample. A stock solution of 1.00N potassium dichromate was prepared by dissolving 2.452 g of potassium dichromate in 50 ml of water. Diphenyl amine indicator was prepared by dissolving 0.5 g of diphenyl amine in 20 ml of water and 100 ml of concentrated sulfuric acid. Iron [II] solution was prepared by dissolving 19.61 g of $Fe[NH_4]_2[SO_4]_2.6H_20$ in 80 ml of water and 2 ml of concentrated sulfuric acid, followed by dilution to 100 ml with water. 0.5 g of soil sample, sieved through a 80 mesh size sieve, was oxidized in 10 ml of the stock potassium dichromate solution and 20 ml of concentrated sulfuric acid for 30 minutes. This oxidized sample was diluted to 200 ml with distilled water and 10 ml of 85% phosphoric acid and 0.5 g of sodium fluoride were added before back titration with Iron [II] solution. Thirty drops of the diphenyl amine indicator were added to the solution and the color change form turbid blue to brilliant green was observed at the end point. The same procedure was followed for a blank [without soil] and the % of the organic matter was calculated from

$$\%\,OM = 10\,[1-T/S] \times f \qquad (20)$$

where S is the ml of the ferrous solution needed for the back titration of the blank and T is the ml of ferrous solution needed for the back titration of the soil sample and f is a factor expressed as

$$f = [1.00N] \times [12/1400] \times [1.72/0.77] \times [100/w] \qquad (21)$$

where 1.00N is the concentration of potassium dichromate; w is the weight

of the soil sample.

Results and Discussion

Each reference compound was shown to be of the proper identity by its absorption spectrum. In addition, each reference standard, when injected individually into the HPLC, produced a single peak, thereby suggesting chromatographic purity. Furthermore, the purity index [mathematical value comparing the peak start and peak end] of each individual peak of the reference compound was close to unity. Since reagent grade methylene chloride exhibits the presence of several impurities in concentrated solution [50 ml to 1 ml], HPLC grade methylene chloride was used. High boiling and UV absorbing solvents such as methanol and toluene were avoided in preparing stock solutions and extracts. Fresh stock solution was prepared for each separate set of experiments. This minimized inadvertent errors which can occur in long standing stock solutions such as: adsorption of PAHs onto the wall of the container, photodecomposition of PAHs and evaporation of the solvent. In addition, care was taken to minimize these errors by storing stock solution in dark brown bottles at 4°C in a cold room.

The efficiency of the PAH extraction procedure was evaluated to correlate the analytical measurements for PAH losses and to produce an accurate and precise PAHs determination method. The method of spiking an exemplary sample matrix with unlabeled PAHs was employed to determine the efficiency of extraction. This procedure involved the addition of exactly known quantities of PAHs to the sample matrix which was free of native PAHs. The only uncertainty of this procedure was achieving a uniform, homogeneous spiking. Though the spiked samples were well mixed before the extraction, inhomogenities can be present in the PAH distribution. The advantage of this procedure is that the extraction recoveries can be easily monitored with simple instrumentation. However, the main drawback is that the extraction of each individual sample can not

be monitored. An assumption was made that the PAH extraction recoveries for similar samples were the same. This assumption is questionable because inadverent errors or mistakes in sample handling and subtle differences among the sample matrices of separate samples can lead to unexpected differences in PAH extraction recoveries of apparently identical samples or aliquots of a given sample. The percentage recovery in extraction of spiked PAHs was calculated from the equation

$$\% \text{ recovery} = 100 \times [C_e/C_s] \qquad (22)$$

where C_s denotes the concentration of PAHs spiked into the matrix and C_e is the concentration of PAHs recovered by extraction.

Precision of the results in this off-line SCFE method depends on the chromatographic determination. Both GC/FID and HPLC/UV were used to analyze the extracted compounds. Although retention times were reproducible, peak areas and peak heights of the late eluting signals were diminished after fifty or more injections into the GC. Moreover, separation of PAHs [triphenylene and chrysene] from a mixture was very poor in the GC column. The non-selective flame ionization detector produces great difficulty in quantitative analysis of spiked PAHs from soil and fly ash matrices, but did not cause any trouble with samples from cleaner matrices such as filter paper. Because of these facts, GC determinations were utilized only in comparison studies.

Because of the improvement in sample throughput over GC, reversed-phase HPLC was employed in these analyses. Also, since the electronic spectra of organic molecules vary considerably with changes in symmetry, structural isomers of PAHs were easily distinguished by their absorption spectra. The salient feature of this study is the use of a linear

photo diode array detector to obtain the absorption spectra, which contributed to a more selective determination. Retention times, peak areas and peak heights of the PAHs were found to be highly reproducible and the relative retention times in both isocratic and linear gradient elution are given in Table 8. The HPLC/UV response was found to be linear over a wide concentration range as shown in Figure 5. Correlation coefficients for these plots are between 0.953 and 1.000.

Figures 6. and 7. represent the separation of PAHs extracted from a spiked fly ash matrix and a spiked soil matrix respectively. Peak identifications are given in Table 8. Note that in the spiked fly ash extract chromatogram, Figure 6, there are no peaks due to interfering [non-PAH] compounds. Therefore, additional sample cleanup procedures were not employed. Extracted samples were filtered through a 5 micron filter before injection into the HPLC to prevent the introduction of tiny particulate materials into the analytical column which can reduce the performance and life time of the analytical column. In addition, a guard column was utilized to protect the analytical column.

7.1 Evaluation of Traps

The solubility of solids in supercritical fluids is a very sensitive function of temperature and pressure [density]. Unlike liquids, supercritical fluids are highly compressible and minor temperature or pressure changes lead to large changes in density and therefore the solvent power. Thus the expansion of a supercritical solution produces a substantial solubility decrease creating a supersaturated solution. In our supercritical extraction system, the extraction fluid is expanded to atmospheric pressure after the second valve, thus it will be no longer supercritical and the system will consist of a supersaturated solution of solutes in gaseous carbon dioxide. In fact most of analytes are virtually not soluble in gaseous carbon dioxide,

Table 8

Relative Retention Times

Peak #	Analyte	Isocratic	Linear Gradient
1	Acenaphthalene	1.00	---
2	1,4 - Naphthaquinone	---	1.00
3	9 - Fluorenone	---	1.61
4	Fluorene	1.12	2.23
5	Phenanthrene	1.21	2.42
6	Fluoranthene	1.41	2.86
7	Pyrene	1.52	2.99
8	Triphenylene	1.66	3.32
9	Benzo [a] Pyrene	2.31	4.25

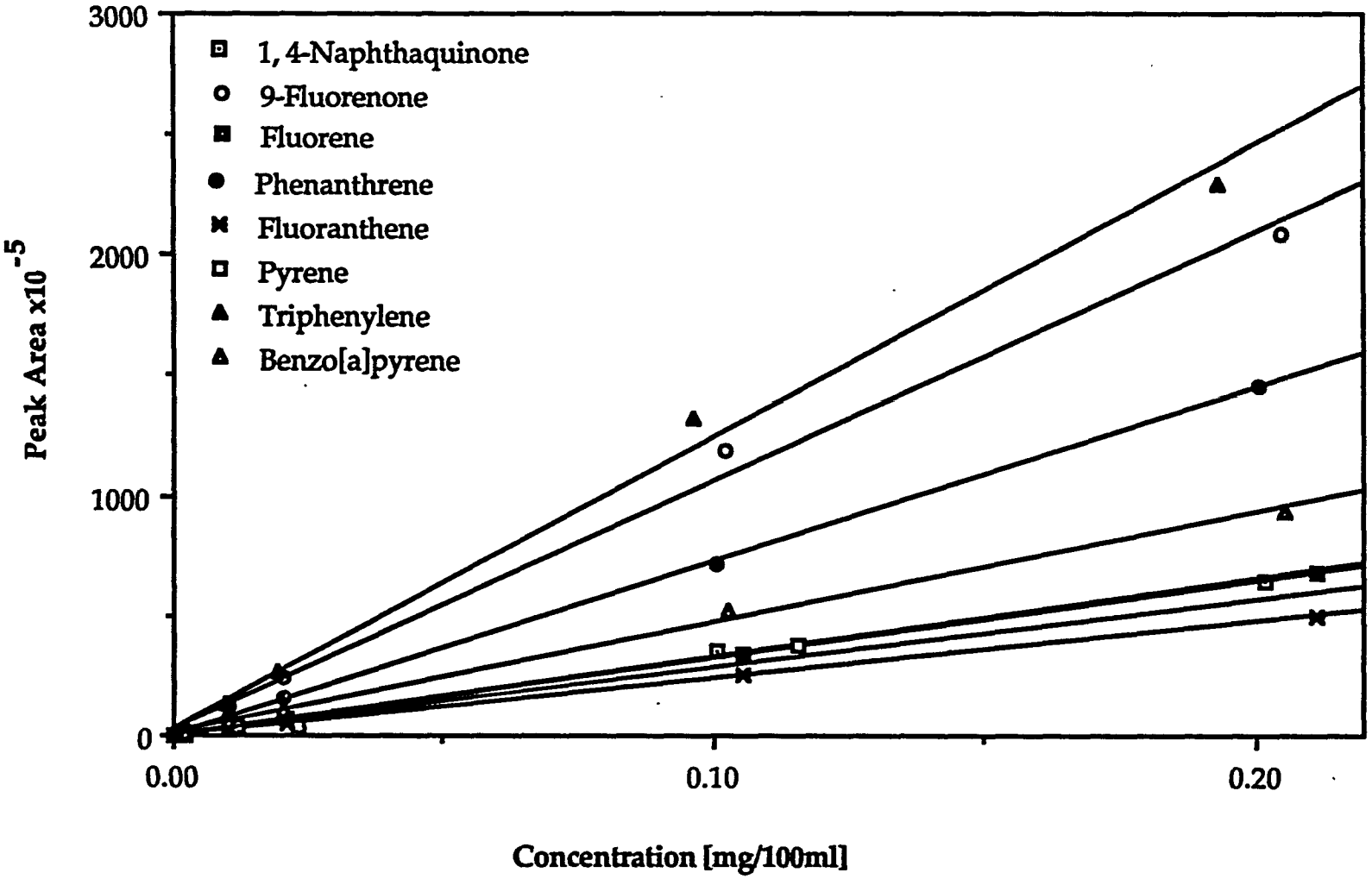


Figure 5. Calibration Curve

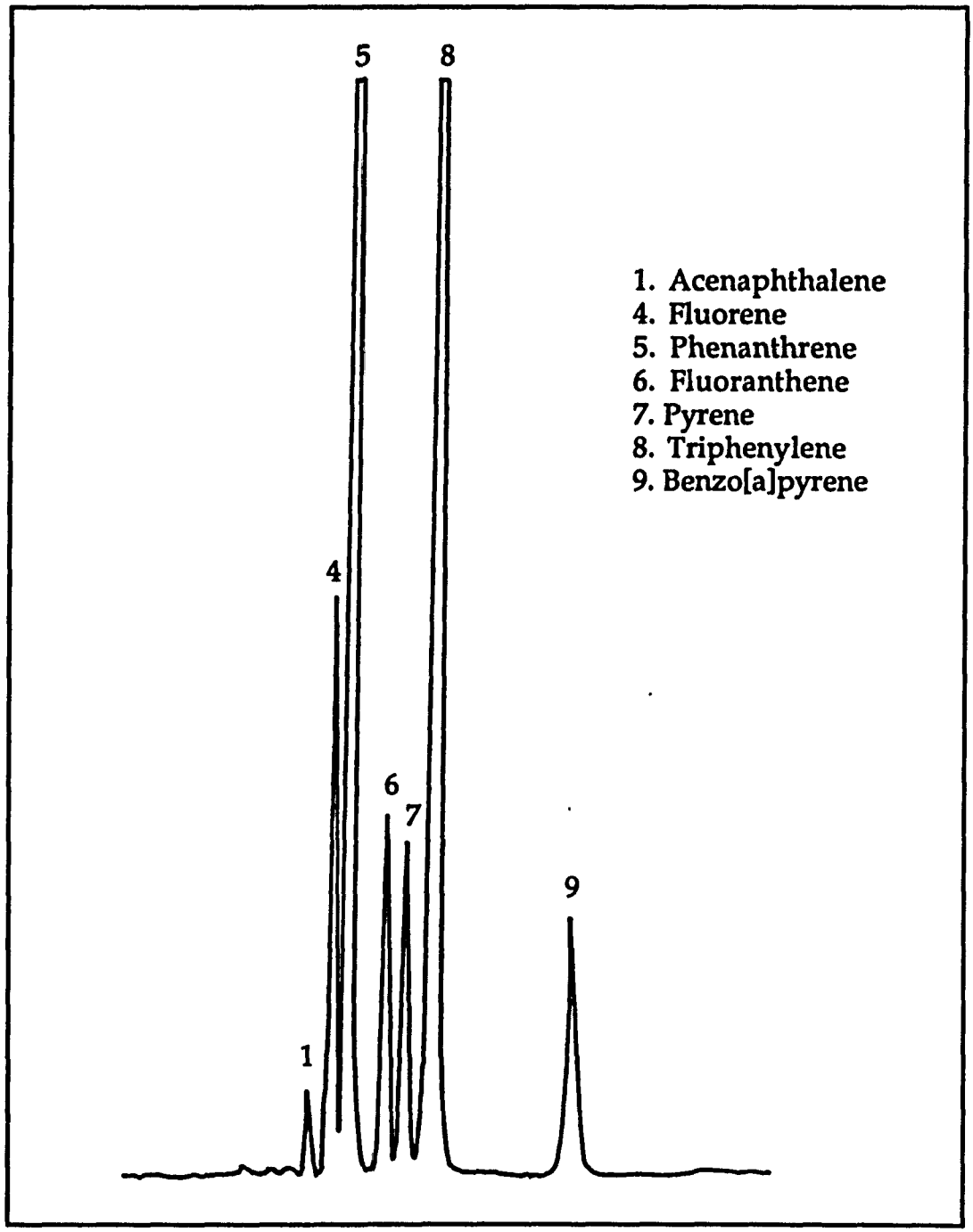


Figure 6. HPLC separation of spiked [30µg/g] fly ash sample after the SCFE; isocratic elution of ACN: Water 80:20, attenuation 128, run time 20 min, wavelength 255 nm.

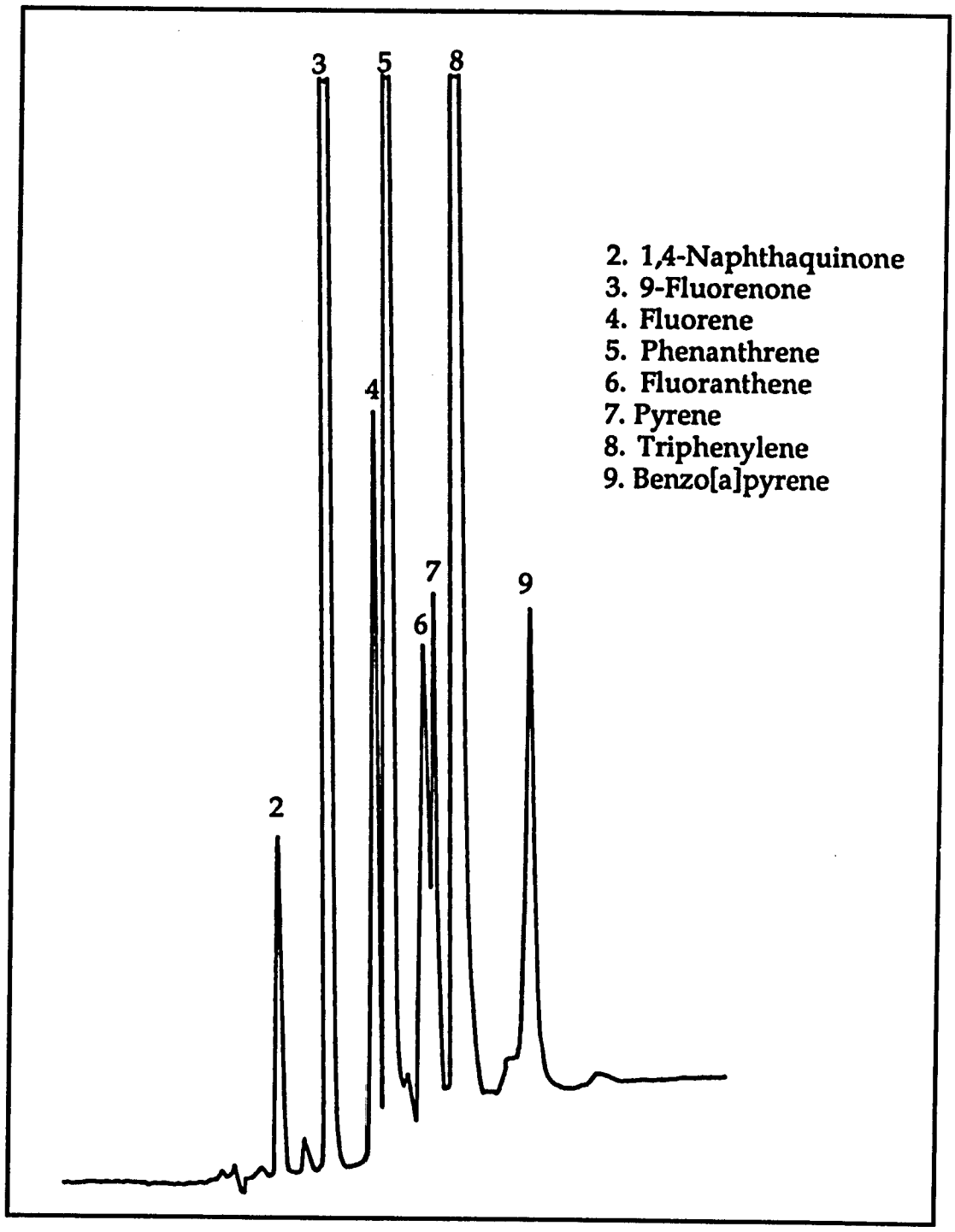


Figure 7. HPLC separation of spiked [1 µg/g level] soil sample after the SCFE; Linear gradient ACN:Water 60:30> 90:10, run time 30 min., attenuation 16, wavelength 255 nm.

and under theses circumstances, the extracted analytes precipitate from carbon dioxide. Thus precipitated solutes can be collected in a suitable trap. A very important consideration in analytical extraction is the provisions taken for collecting the sample during the depressurization process. During this study, two different kinds of traps were evaluated for collecting PAHs.

7.1.1 Solid Adsorbent Traps

Depending upon the exact conditions, it is possible for analyte molecules to nucleate and become entrained in the expanding gas, forming an aerosol which can be easily lost to the atmosphere [163]. It is obvious that the particle size of the resulting precipitated compounds is dependent on the rate of depressurization. By creating a slow depressurizing process, relatively large particles can be produced instead of an aerosol, which makes it easier to collect the precipitated particles. Using a porous barrier to the gaseous flow, the solute particles can be filtered from the stream of carbon dioxide. In addition to this these particles can be efficiently trapped by using a selective adsorbent material.

Solid adsorbents have been extensively used to trap the organic pollutants from aqueous samples [164,165]. Tenax-TA and XAD-2 resins have demonstrated the capability of extracting PAHs from drinking water, and the trapped compounds can be easily recovered from these adsorbents either by thermal desorption or solvent elution. Silica and octadecyl bonded phases have been utilized to separate PAHs from various samples in column and in high performance liquid chromatography. These four adsorbent materials were tested to trap a mixture of four PAHs [phenanthrene (Ph), pyrene (Py), chrysene (Ch) and benzo [a] pyrene (B[a]P)] in this study. The effectiveness of trapping was evaluated by studying two important parameters, efficiency of trapping and ease of elution.

To evaluate the efficiency of trapping, a liquid trap was employed to collect the compounds which were not retained in the solid adsorbent trap during the depressurization. In addition to the eluted sample, analytes were determined in the back up trap, sample matrix [filter paper was sonicated] and the solid adsorbent material after the elution of analytes [solid adsorbent was sonicated]. Results are presented in terms of percentage recoveries in Tables 9-12.

These results indicate that all the traps are 100% efficient in collecting these four PAHs. No compounds were detected from the solution in the Erlenmeyer flask or in the tube which connects the solid adsorbent trap to the back-up trap. Moreover it was found that the extracted compounds were present in the elbow union and in the first two to three inches of the solid adsorbent material. The presence of the analytes in the elbow union can be accounted for the change in direction of the carbon dioxide flow. Absence of the precipitated compounds in the last part of the trap encourages use of a shorter adsorbent trap. But the presence of more volatile compounds in the real samples, as well as safety reasons, prevent the use of a shorter trap. A 6" long 1/4" diameter trap filled with solid adsorbent was chosen as the best solid trap in the rest of the studies.

7.1.1.1 Efficiency of Eluting the Trapped Compounds from the Solid Adsorbents

After extraction, the solid adsorbent was cracked open into a beaker, washed with 40-50 ml of methylene chloride and filtered. The washing of analytes from the adsorbent material is one of the crucial steps in this off-line SCFE and it must be quantitative. In this process, analytes can be lost or contaminants can be introduced into the extracted analytes. The lost of the analytes may be due to incomplete elution or loss in the concentration process. To minimize the loss of analytes in the concentration

Table 9

Evaluation of Silica Trap [6"x 1/4"]

	Percentage Recovery			
	Ph	**Py**	**Ch**	**B [a] P**
Collector	92	98	67	98
Backup trap	00	00	00	00
Filter paper	0.1	0.05	32	01
Sonicated silica [after washing]	00	00	01	00

Table 10

Evaluation of Octadecyl Bonded Phase Trap [6"x 1/4"]

	Percentage Recovery			
	Ph	**Py**	**Ch**	**B [a] P**
Collector	91	98	67	97
Backup trap	00	00	00	00
Filter paper	0.1	00	32	0.8
Sonicated C_{18} [after washing]	00	0.5	0.5	0.5

Table 11

Evaluation of Tenax-TA Trap [6"x 1/4"]

	Percentage Recovery			
	Ph	**Py**	**Ch**	**B [a] P**
Collector	90	96	58	95
Backup trap	00	00	00	00
Filter paper	0.2	00	33	0.5
Sonicated Tenax-TA [after washing]	03	05	11	01

Table 12

Evaluation of XAD-2 Trap [6"x 1/4"]

	Percentage Recovery			
	Ph	**Py**	**Ch**	**B [a] P**
Collector	89	95	64	92
Backup trap	00	00	00	00
Filter paper	0.5	00	30	01
Sonicated XAD-2 [after washing]	02	08	08	10

step, a rotary evaporator was used at a slow rotating speed at a low temperature [40°C].

Quantitative elution was tested from spiked solid adsorbents by Soxhlet extraction after elution. The results are presented in Table 13. show clearly that even though Tenax-TA and XAD-2 resins can quantitatively trap PAHs from the carbon dioxide stream, the slightly less than quantitative elution of the analytes from them results in poor recoveries. In addition, halogenated or aromatic solvents can not be used to elute trapped compounds from Tenax-TA. The polymeric Tenax-TA tends to dissolve in the presence of such solvents [166]. On the other hand silica gel and octadecyl bonded phases demonstrated easy elution and were selected as the best adsorbents for the solid adsorbent traps.

7.1.2 Evaluation of Cold Traps

During the depressurization, in addition to the decrease of carbon dioxide solvent power, a decrease of temperature can be expected due to Joule-Thompson expansion. The resulting temperature is lower than the critical temperature. Further reduction of temperature, well below the critical condition, can enhance the precipitation of the solute. In addition, sudden supercooling can also result in the formation of larger size particles. This suggests that the extracted compounds can be trapped efficiently by allowing the supercritical gas to expand at a temperature which is much lower than the critical temperature. This was tested with three different traps at dry ice temperature. The results are given in Table 14.

It was noted that the percentage recovery depends mainly on the flow rate of the carbon dioxide through the trap [rate of depressurization]. As expected, lower percentage recoveries were observed with faster flow rates which can result in elution of the precipitated solutes from the cold trap as

Table 13

Evaluation of the Elution from Solid Adsorbents

	Percentage Recovery			
	Ph	**Py**	**Ch**	**B [a] P**
XAD-2 resin	82	87	91	86
Soxhlet	08	11	11	12
Tenax- TA	81	88	94	94
Soxhlet	05	06	13	03
Silica	94	100	97	93
Soxhlet	0.4	0.2	04	00
Octadecyl bonded phase	91	97	97	91
Soxhlet	0.5	01	01	00

Table 14

Collector Efficiency in Cold Traps

	Percentage Recovery			
Cold Trap	**Ph**	**Py**	**Ch**	**B [a] P**
1/4 " Tygon tube	52	53	40	50
backup trap	42	35	28	35
1/8" stainless steel tube	70	70	52	58
backup trap	18	20	20	30
1/8" stainless steel tube [with glass beads]	90	93	68	88
backup trap	01	02	00	00

well as formation of an aerosol. Therefore care was taken to open the outlet valve at the same rate throughout the experiment in order to evaluate the effect of tube size on the percentage recovery. The results demonstrate that the percentage recovery depends on the size of the bore of the tube. The inverse relation between the tube diameter and the percentage recovery suggests that the lower pressure gradient exerted in the smaller diameter tube effectively helps to trap the solutes. Moreover a slower rate of gas passing through the smaller tubing reduces the possible loss of sample with the carbon dioxide flow.

A smaller diameter tube filled with glass beads gave best recoveries implying that any barrier to the carbon dioxide flow can yield a better recovery. However, a solid trap with small particles without the cold conditions demonstrated better recoveries in the previous study and eliminated the need of cold temperatures. This mixed mode will be more efficient in the case of highly volatile solutes in which a solid adsorbent trap itself can fail. Use of much lower temperatures can create some additional problems such as condensation of carbon dioxide in the tube and clogging which can prevent carbon dioxide flow. This can create more dangerous situations such as explosion of the tube with loss of solutes.

7.2 Evaluation of Optimum Experimental Conditions for Selected PAHs

There are three variables that one can optimize in the evaluation of a static equilibrium SCFE system namely; pressure, temperature and the equilibrium time. The lower boundary limits of the pressure and temperature are determined by the critical values of the extracting fluid. Obviously the upper bounds are depend on the instrumentation. As a general rule static equilibrium SCFE experiments are not designed more than 100°C above the critical temperature. This restriction is applied because of two facts; first at higher temperatures thermally labile compounds can be

decomposed, secondly at high temperatures fluid density falls and more unusual pressure conditions have to be used in order to achieve liquid-like densities. Even though these two factors can lower the upper bound of the extraction temperature, higher temperature can favor the extraction by increasing the escaping tendency of the solute from the condensed phase due to the logarithmic increase of vapor pressure with temperature.

The competing effects of the reduction in solvent density and the increase in solute volatility with the increase of temperature explain the necessity of evaluating the optimum experimental conditions for the analytes. Knowledge of these conditions can be highly helpful in analyzing unknown samples containing similar types of compounds. Moreover, one has to study the effect of equilibrium time for a complete extraction. Equilibrium time signifies the length of time for an extraction of a particular sample. This is accounted for by the kinetics of the extraction process. Even though the kinetics is not well understood, a general mechanism can be used to explain the extraction process. The extraction process starts with the penetration of SCF into the extraction matrix. The penetrated SCF interacts with the sample matrix and the analytes dissolve in the SCF. Finally, analyte-loaded SCF moves out of the sample matrix.

It has been proved that penetration of SCF into the matrix is a diffusion controlled process [167]. This implies that equilibrium time will depend on particle size. Smaller porous particles will allow faster penetration and equilibrium will be attained more quickly compared to bulky solids. During this study, spiked filter paper was initially used as the sample matrix and it was assumed that it represents a homogeneous matrix. In later studies with environmental solids, samples were sieved in order to get a small particle size, homogeneous matrix. In solubility studies, powdered analytes were used from the standard chemicals without any

pretreatment.

7.2.1 Effect of Equilibration Time

Four different equilibration times were studied, 5, 10, 15 and 20 minutes. All extractions were done at 408 atm and 60°C. Results of these studies are listed in Table 15. These results demonstrate that PAHs [except chrysene] can be quantitatively extracted after 15 minutes. Extraction from a standard solution diluted 10 times gave 94% recovery of chrysene after 15 minutes equilibration time. This demonstrates that the capacity of SCF carbon dioxide for chrysene is low compared to other PAHs. That is, carbon dioxide is saturated with chrysene in the concentrated sample and it will not give a better percentage recovery even if sample is equilibrated with carbon dioxide for a longer period of time. As in the evaluation of traps, the remaining chrysene was found in secondary extractions which confirms the lower capacity phenomenon. This was further studied and a reasonable explanation is given in the following solubility section disscussion. In environmental samples PAHs are found in microgram quantities. Hence a 15 minute equilibration time is sufficient to extract quantitatively these compounds from the environmental samples, provided the sample is present in a powdered form or as a thin film. In the case of bulk solids, the sample has to be ground before the extraction. In addition to faster equilibration with small particles, more surface area exposed to SCF will make better contact with sample matrix resulting in an efficient extraction process.

Table 15

Effect of Equilibrium Time on % Recovery

Time [min]	Ph	Py	Ch	B [a] P
05	70	75	45	68
10	87	88	58	78
15	88	90	64	84
20	87	91	64	86

Table 16

Effect of Pressure on % Recovery at 45°C

Pressure [atm]	Ph	Py	Ch	B [a] P
204	70	72	30	54
272	78	75	35	65
340	80	80	48	68
408	82	87	54	72
476	85	92	58	79
544	89	94	62	88

Table 17

Effect of Pressure on % Recovery at 50°C

Pressure [atm]	Ph	Py	Ch	B [a] P
204	78	76	34	58
272	80	80	45	60
340	85	84	55	70
408	88	91	58	80
476	88	92	63	86
544	89	95	67	91

Table 18

Effect of Pressure on % Recovery at 60°C

Pressure [atm]	Ph	Py	Ch	B [a] P
204	71	78	40	63
272	81	83	42	62
340	85	83	54	70
408	88	90	65	85
476	89	94	71	88
544	90	98	69	97

7.2.2 Effect of Temperature and Pressure

Pressures ranging from 204 to 544 atm were studied at three different temperatures, 45°C, 50°C and 60°C and the results are given in Tables 16-18 From these results two conclusions can be drawn. First, increase in temperature increases percentage recovery. This increment is more significant for benzo [a] pyrene than phenanthrene. The increase of percentage recovery with temperature is due to the increase of escaping power from solid analyte matrix [increase of the vapor phase composition] which leads to a better extraction efficiency. The greater increase of recovery for benzo [a] pyrene to phenanthrene is explained by their vapor pressures.

The second conclusion which can be drawn from these results is that there is an increase of percentage recovery with pressure at isothermed conditions. The increase of pressure at constant temperature results an increase of density of the SCF and hence in solvating power. Furthermore, the increment is more significant at the lower pressures than at higher pressures. This is because the increase of density is steeper at pressures close to P_C than at higher pressures. From these results it can be concluded that 544 atm and 60°C temperature are the optimum conditions for the extraction of PAHs.

7.3 Solubility Studies

The difference in percentage recoveries for pyrene and chrysene, which both have four benzene rings, suggested a study of the effect of PAH structure in the extraction. Pyrene, chrysene and triphenylene, all having four benzene rings, were selected as model compounds for solubility studies. About 0.5-1.5 g of the compound was placed individually in the extraction chamber at a time. This amount of the compound was chosen in order to ensure saturation of supercritical carbon dioxide in the extraction chamber. Both extracted and unextracted compounds were quantitated

separately in order to evaluate the mass balance. Quantitations were done by both GC/FID and HPLC/UV [at the maximum absorbance wave length of each compound]. Mass balances were in the range from 90% to 102%. These results of mass balances implies that PAHs are not being lost in the extraction process. The amount of carbon dioxide used for the extraction was calculated from the density. Hence the molar fraction of the solute in the SCF phase, a measure of the solubility, was calculated. Vapor pressures of the solutes were estimated from the reference data [168]. The enhancement factor was calculated and the results are tabulated in Tables 19-24.

At these two temperatures pyrene demonstrated the highest and chrysene the lowest solubility in SCF carbon dioxide. This variation in solubility can be explained in terms of size [number of π electrons] and the topology [type of ring-linkage]. Based on the type of condensation, the entire group of PAHs can be divided into two groups, cata-annellated and peri-condensed. In cata-annellated PAHs, the tertiary carbon atoms are centers of two interlinked rings whereas in peri-condensed PAHs some of the tertiary carbon atoms are centers of three interlinked rings. Chrysene and triphenylene belongs to the former group while pyrene belongs to the latter group. Annellation can be linear, six-membered rings located on one straight line, or angular, six-membered rings located on different straight lines with the angle between the lines always being 120°. Both chrysene and and triphenylene are angular cata-annellated PAHs but with different angularity. Figure 8. shows the structures of all the possible four-benzene-ring PAHs.

Physical and chemical properties of cata-annellated and peri-condensed PAHs are significantly different. This difference was often observed in chromatographic separations. In GC, HPLC and SCFC experiments it was demonstrated that the peri-condensed compounds are

Table 19

Solubility of Pyrene in SCF Carbon Dioxide at 60°C

P [atm]	Extract [mg]	Mole Fraction	Enhancement
340	16.40	$6.3xe^{-4}$	$1.1xe^{+6}$
408	21.02	$7.8xe^{-4}$	$1.6xe^{+6}$
476	24.20	$8.7xe^{-4}$	$2.0xe^{+6}$
544	29.12	$1.0xe^{-3}$	$2.7xe^{+6}$

Table 20

Solubility of Pyrene in SCF Carbon Dioxide at 45°C

P [atm]	Extract [mg]	Mole Fraction	Enhancement
340	14.88	$5.4xe^{-4}$	$9.9xe^{+6}$
408	16.00	$5.6xe^{-4}$	$1.2xe^{+7}$
476	18.02	$6.1xe^{-4}$	$1.5xe^{+7}$
544	23.54	$7.6xe^{-4}$	$2.2xe^{+7}$

Table 21

Solubility of Chrysene in SCF Carbon Dioxide at 60°C

P [atm]	Extract [mg]	Mole Fraction	Enhancement
340	0.583	$1.9xe^{-5}$	$1.3xe^{+6}$
408	0.685	$2.3xe^{-5}$	$1.7xe^{+6}$
476	0.967	$3.1xe^{-5}$	$2.7xe^{+6}$
544	1.002	$3.5xe^{-5}$	$3.2xe^{+6}$

Table 22

Solubility of Chrysene in SCF Carbon Dioxide at 45°C

P [atm]	Extract [mg]	Mole Fraction	Enhancement
340	0.345	$7.7xe^{-6}$	$1.4xe^{+7}$
408	0.423	$1.1xe^{-5}$	$2.3xe^{+7}$
476	0.547	$1.6xe^{-5}$	$4.2xe^{+7}$
544	0.684	$2.0xe^{-5}$	$5.8xe^{+7}$

Table 23

Solubility of Triphenylene in SCF Carbon Dioxide at 60°C

P [atm]	Extract [mg]	Mole Fraction	Enhancement
340	1.824	$6.2xe^{-5}$	$6.2xe^{+6}$
408	1.986	$6.5xe^{-5}$	$7.9xe^{+6}$
476	2.804	$8.9xe^{-5}$	$1.2xe^{+7}$
544	3.386	$1.0xe^{-4}$	$1.7xe^{+7}$

Table 24

Solubility of Triphenylene in SCF Carbon Dioxide at 45°C

P [atm]	Extract [mg]	Mole Fraction	Enhancement
340	1.598	$4.9xe^{-5}$	$3.6xe^{+7}$
408	1.806	$5.6xe^{-5}$	$5.0xe^{+7}$
476	2.103	$6.3xe^{-5}$	$6.6xe^{+7}$
544	2.684	$7.7xe^{-5}$	$9.2xe^{+7}$

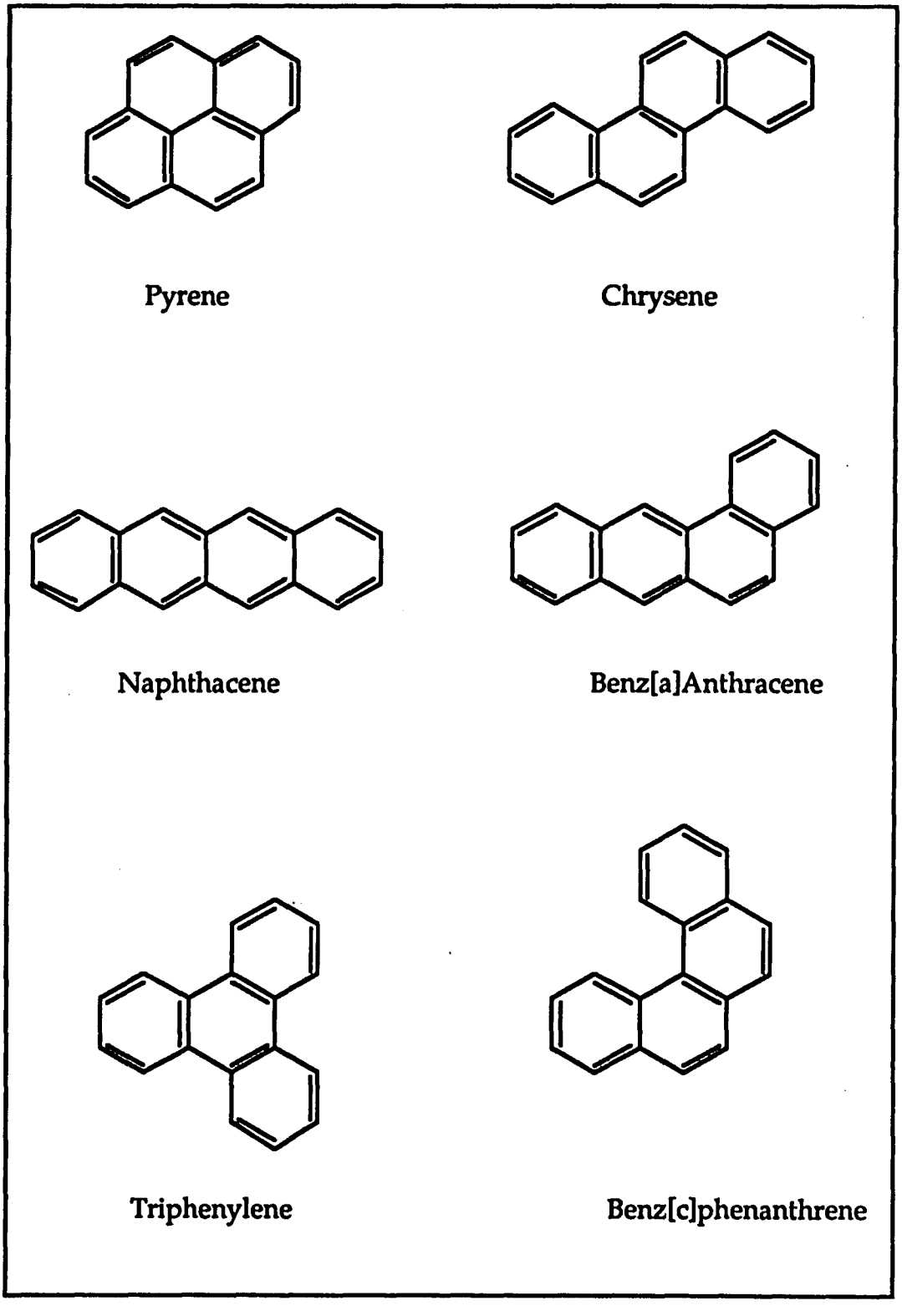
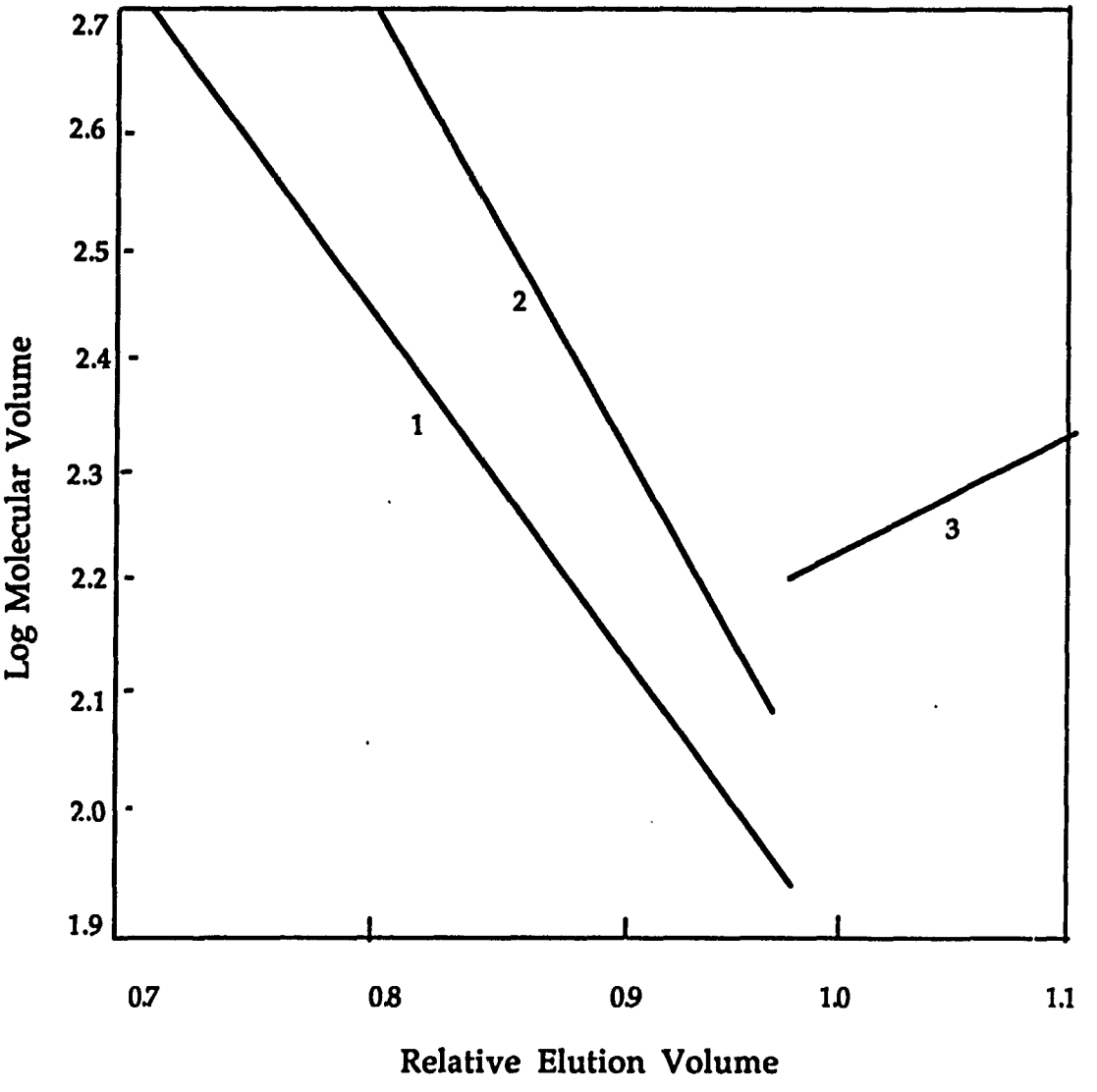


Figure 8. Structures of four-fused benzene-ring PAHs

eluted with a smaller elution volume than their cata-annellated analogs [169-173]. This is further illustrated in gel permeation chromatography [174]. As shown in Figure 9. [174] elution volumes are related to the molecular volumes of the hydrocarbons but this relationship is different for the compounds which have different types of condensation. Note the line which represents peri-condensed compounds is quite different from the lines which represent cata-annellated compounds and non-condensed compounds. As Hains et. al. [174] pointed out, this difference is due to size effects.

Size differences between peri-condensed compounds and cata-annellated compounds can be explained in terms of their condensation. In cata-annellation, four carbon atoms and four π electrons are added to two already present in the system to form a new ring whereas in peri-condensation, new ring is formed by adding three carbon atoms and three π electrons to three already present in the system. Hence, peri-condensed PAHs have fewer π electrons than their cata-annellated analogs and the peri-condensed are smaller in size compared to the cata-annellated. For example, pyrene has only 16π electrons [two peri-condensed carbon atoms] compared to 18π electrons in the cata-annellated analogs, chrysene and triphenylene. This explains the above mentioned pattern of PAH elution in GC, HPLC and SCFC. Presumably also this is the reason why pyrene has a higher solubility in SCF carbon dioxide compared to triphenylene and chrysene.

Within the isoelectronic cata-annellated PAHs, physical and chemical properties differ with the molecular topology. Figure 10. [141] shows the characteristic graphs of the isoelectronic cata-annelated PAHs



1 : Paraffins and mono-ring compounds
2 : Cata-annellated compounds
3 : Peri-condensed compounds

Figure 9. Correlations based on condensation

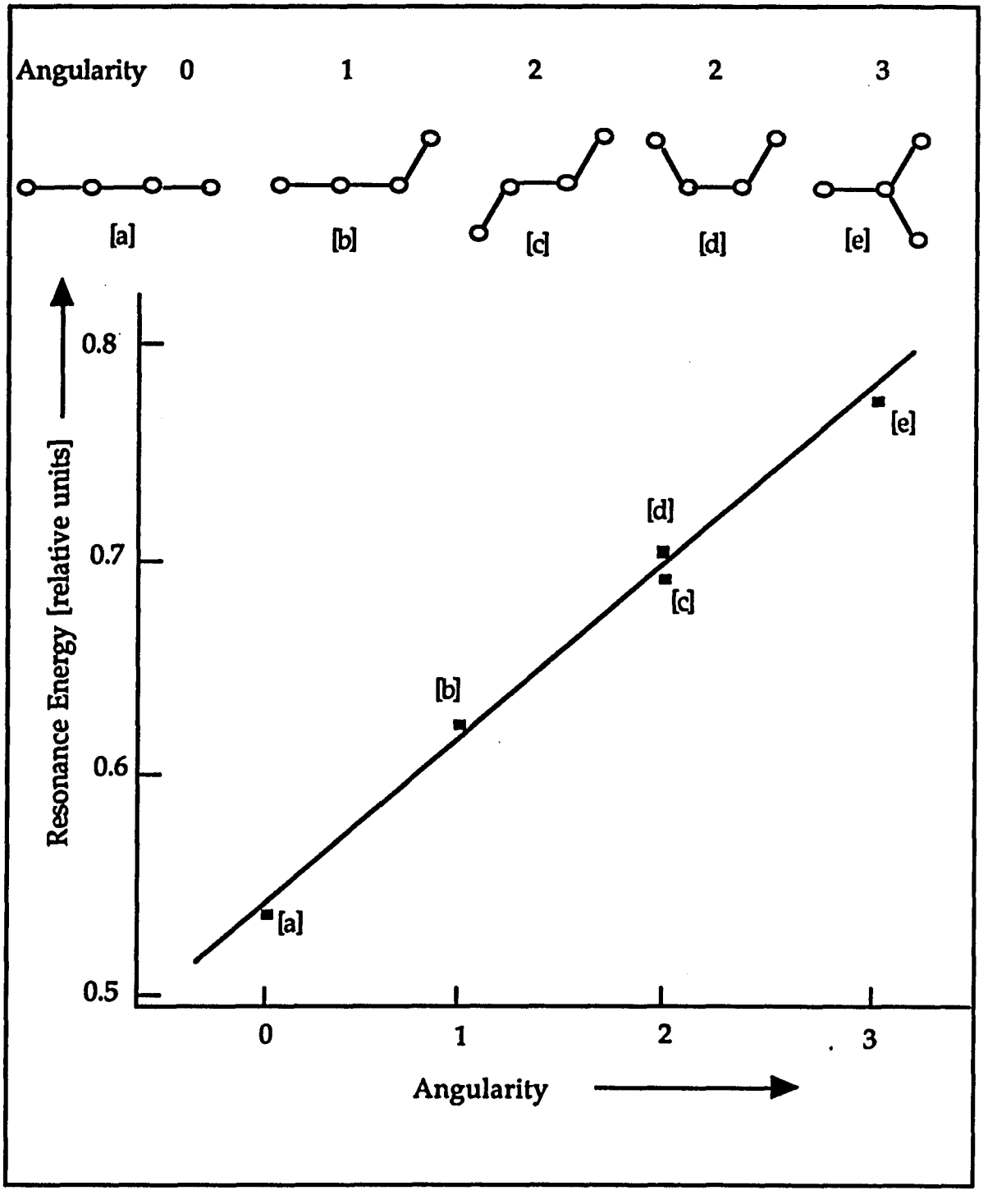


Figure 10. Correlation between resonance energy and angularity of isoelectronic PAHs [from ref. 174]

with four rings. The points mark rings while the lines mark the edges of annellated rings. The characteristic topological property is the angularity, which is the sum of the # of 120° angles. The correlation is linear between the angularity and the resonance energy as the quantity characterizing the stability of PAHs. The linear increase of resonance energy with the angularity is one good example for the variation in properties of the isomers with the topology. The isomer with the highest angularity is the most stable and the linear isomer is the least stable of all.

Topology and size dependence of the properties of the PAHs can be further illustrated by separating the effects of the size and topology on those properties. For example the properties of PAHs of different sizes can be compared with the same topology. Figure 11. **[141]** shows the energy of the para band [cm^{-1}] for various PAHs topologies plotted against the parameter $[n-2]/n^2$. The topologies of the annellation series R1 to R5 are shown on the left-hand side, with the formulas of the first and last members of each annellation series. The parameter $[n-2]/n^2$ describes the size of the PAHs, where n is the number of π electrons in the system. With respect to the annellation series R1 to R3, the arrows indicate the annellation direction. The resonance energy per π electron [REPE] is plotted against $[n-2]/n^2$ in Figure 12. **[141]** Again, linear correlations can be obtained and from these two plots it is clear that the properties of PAHs depend on topology. Hence, the difference between triphenylene and chrysene solubility in SCF carbon dioxide is also verified.

Another approach to explain the difference of solubility in SCF carbon dioxide can forward by comparing the crystalline structure of these analytes. At low temperatures molecular shape [topology] is very important in the condensed phase, because in this phase intermolecular distances are

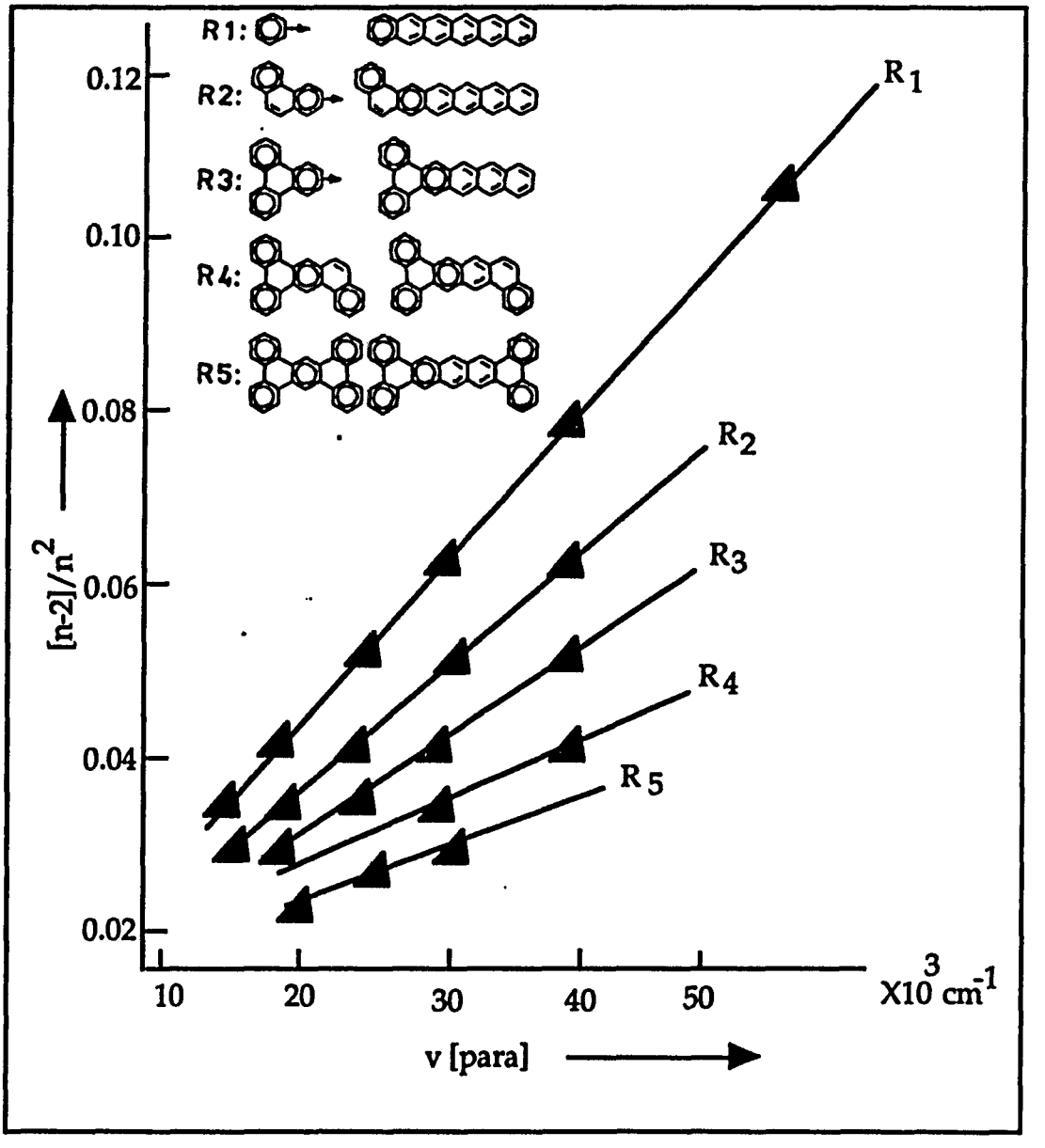


Figure 11. Size and Molecular topology dependence of the energy of the para band [from ref. 141]

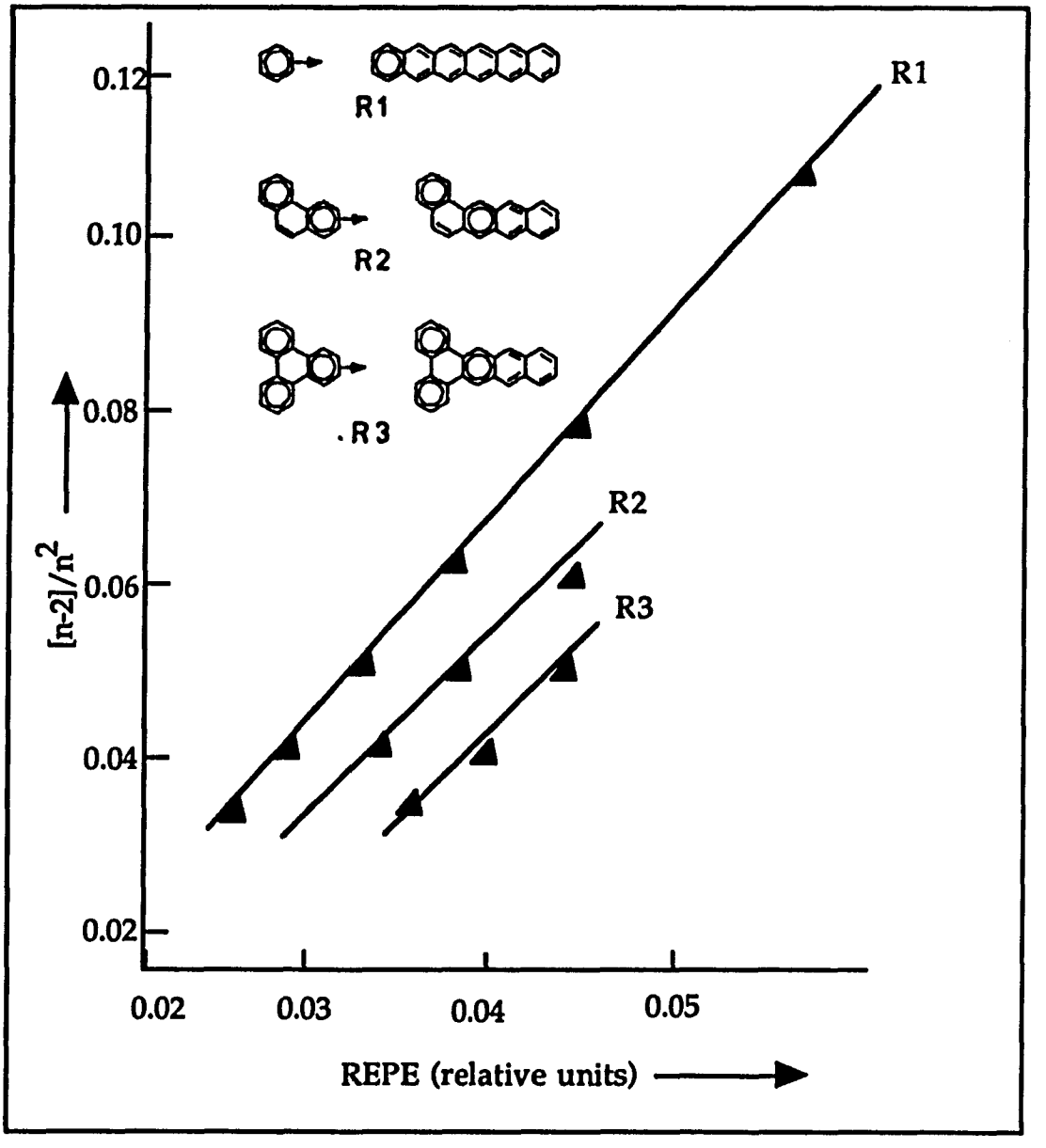


Figure 12. Size and Molecular topology dependence of the resonance energy per π electron [REPE] [from ref. 141]

very small and the intermolecular attractions become very significant. With peri-condensation, molecules tend to approach the shape of a sphere. As the spherical shape is approached the surface area per molecule decreases resulting a weaker inter-molecular attractions per pair of molecules. Therefore, in the condensed phase molecules are loosely bound to each other and the molecules can be easily separated from their crystalline state. In cata-annellated molecules, the surface area increases with the linearity, less branching, and inter-molecular attractions are relatively high, resulting in stronger binding in the crystalline state. This difference in the crystal packing is well observed in the melting point determinations and solubility determinations in a series of any isomeric organic compounds Table 22 [168].

The differences in crystalline structure and kinetics of the extraction process accounts for the trend in solubility of these three compounds and the same arguments can be extended to predict solubility of other isomers in SCF carbon dioxide. In terms of diffusion of carbon dioxide into these crystal types, pyrene has the highest rate of diffusion, and naphthacene has the lowest. Linear naphthacene will demonstrate the poorest solubility of all, and the order of solubility can be predicted as naphthacene < benzo [a] anthracene < chrysene <triphenylene < pyrene. The other isomer which can not be accounted for here, is benzo [c] phenathrene, which is not a planar compound as are the others in Figure 8; therefore additional factors can influence its physical properties and solubility. Correlations of solubility data are given in Figures 13-15.

Table 25

Properties of Four-benzene Fused-ring PAHs

Property	Py	Nap	B[a]A	Ch	B[c]P	Trp
Freezing point [°C]	150.2	357	160.4	258	68	198.1
Boiling point [°C]	394.8	443	437.6	441	---	448.4
Critical temperature [°C]	665	714	706	711	---	740
Refractive Index	1.770	---	1.789	1.785	---	1.756
Density $kg.m^{-3}$ $x10^{-3}$	1.27	1.24	1.174	1.274	---	1.31
ΔH_s kJ mol^{-1}	118	106	118	101.1	125	120
ΔH°_f kJ mol^{-1}	114.8	158.8	170.8	145.3	184.9	151.8
Aqueous solublity [mg/kg]	0.132	---	0.0094	0.0018	---	---

Py: Pyrene; Nap: Naphthacene; B[a]A: Benzo[a]Anthracene; Ch: Chrysene; B[c]P: Benzo[c]phenanthrene; Trp: Triphenylene

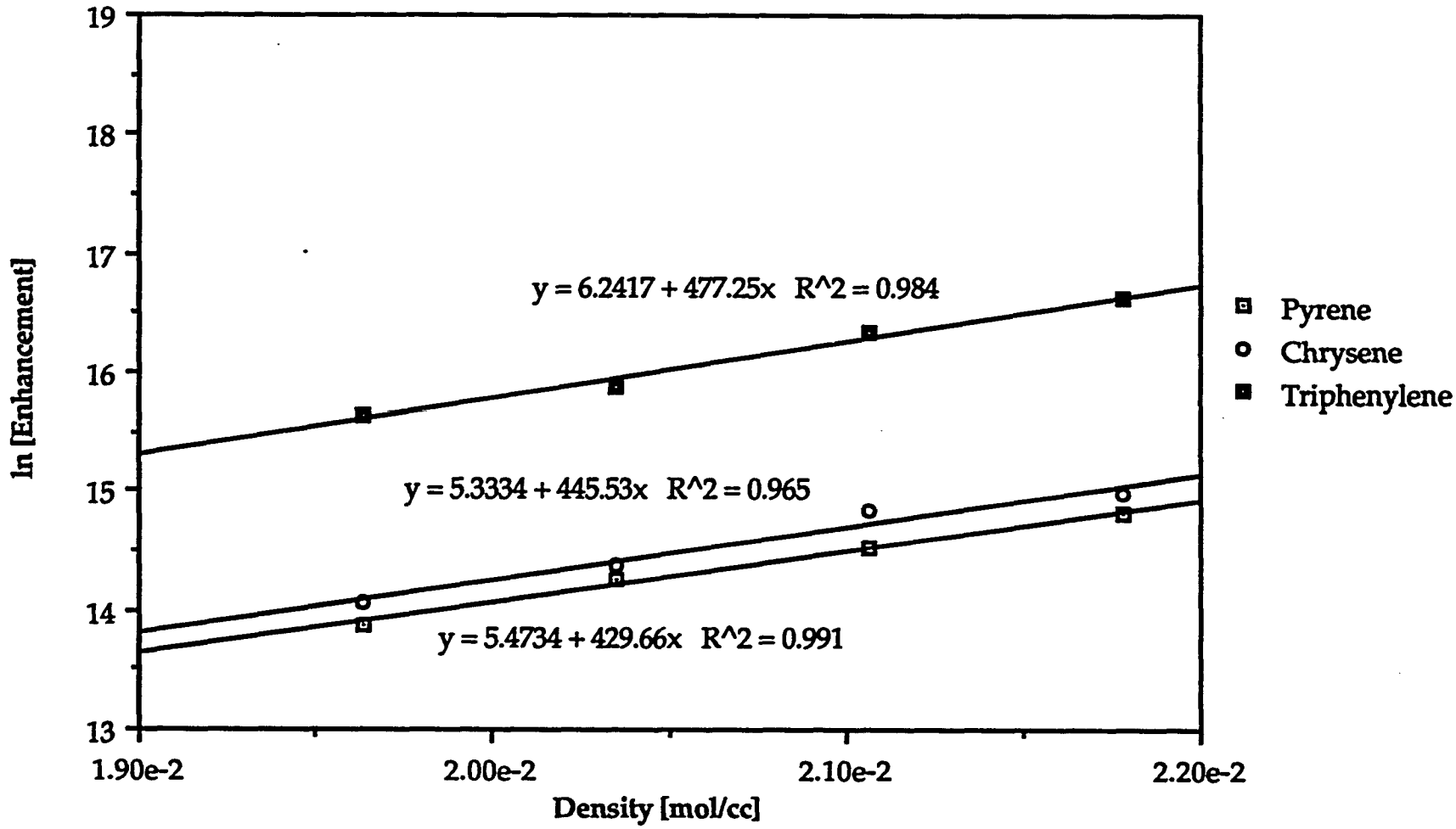


Figure 13. Density and Enhancement correlation at 60 C

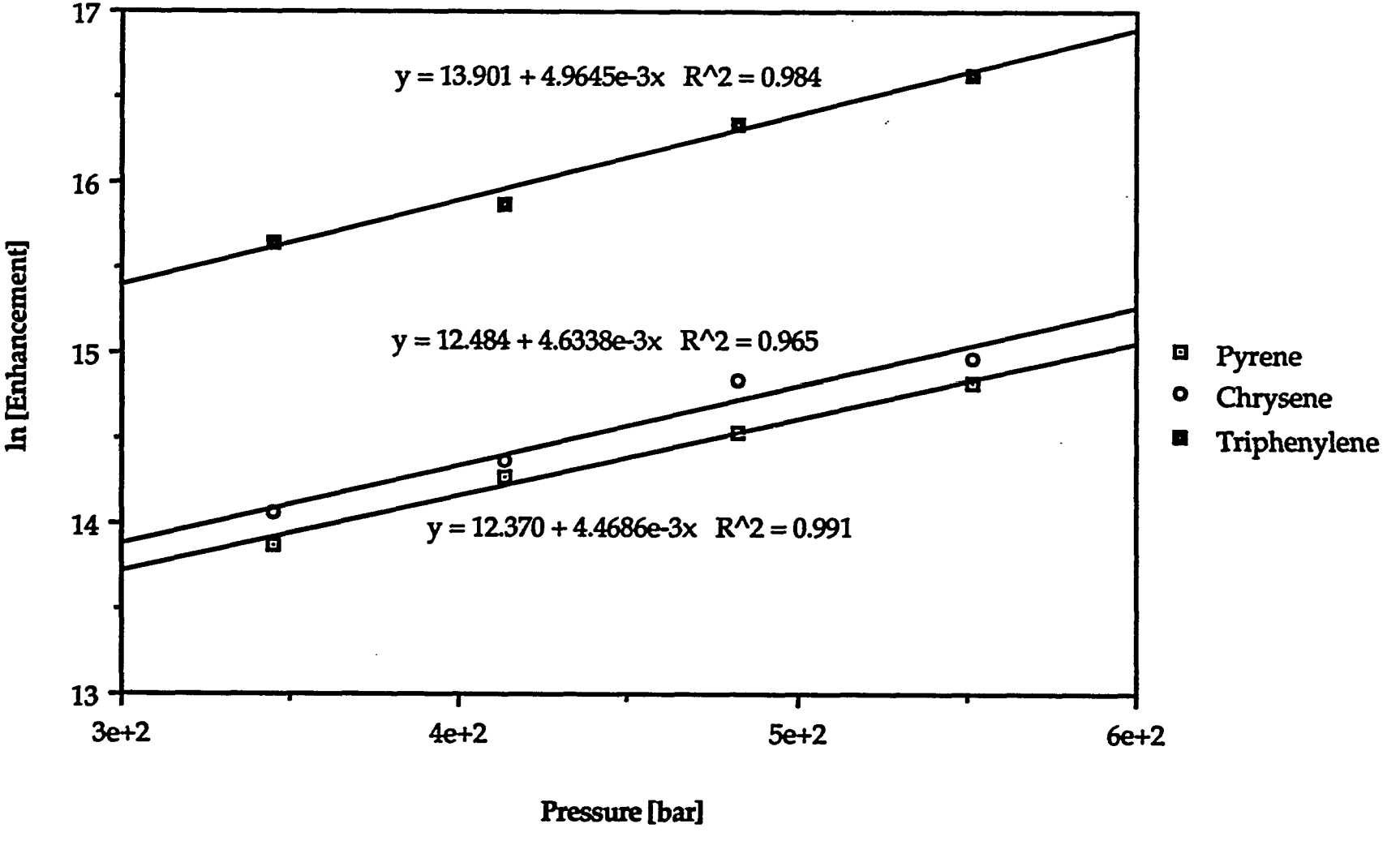


Figure 14. Pressure and Enhancement correlation at 60 C

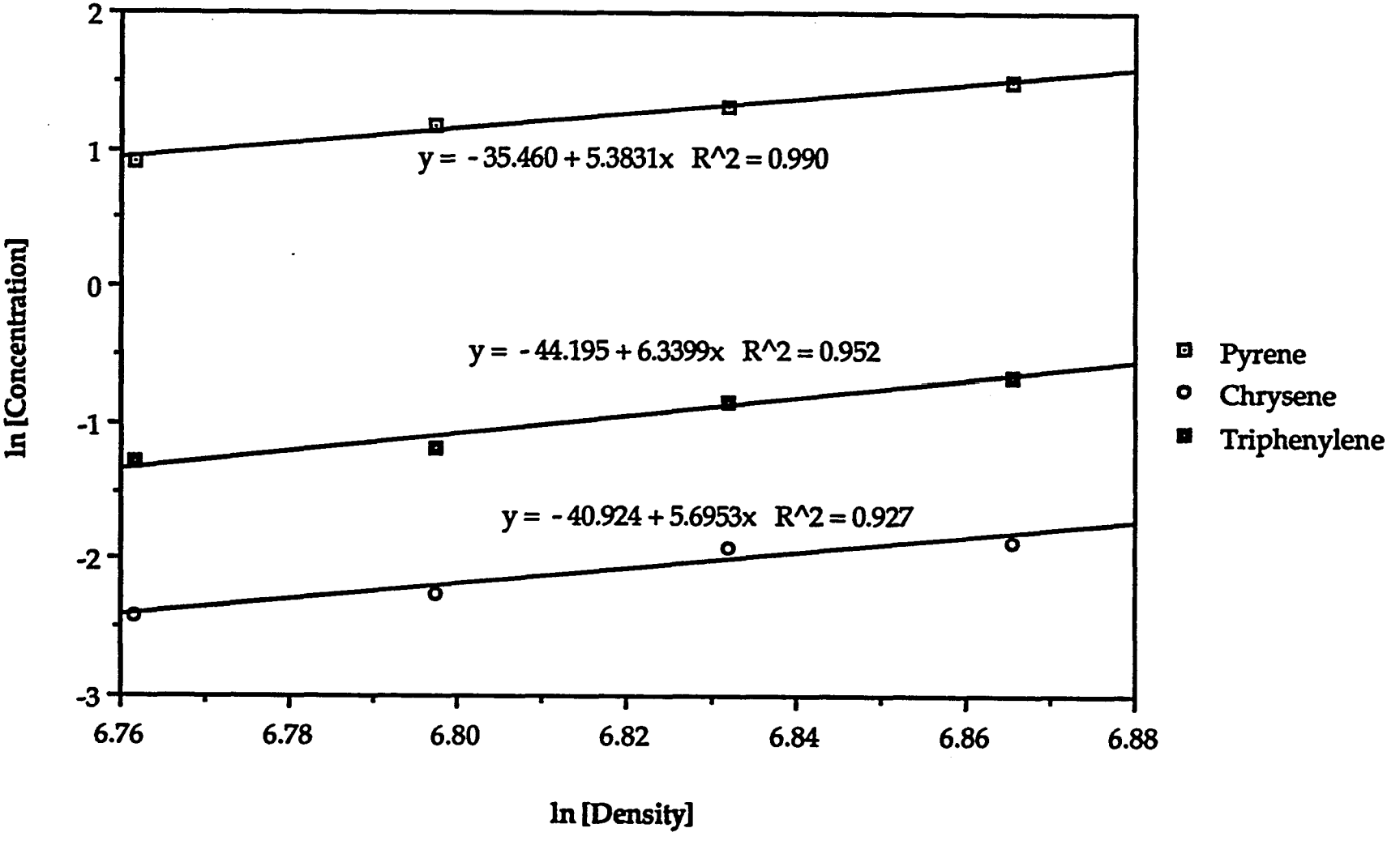


Figure 15. Concentration and Density correlation at 60 C

7.4 Effect of Density

From the previous experiments evaluating optimum extraction condition, it is clear that the extraction efficiency is mainly governed by the density of the fluid and the vapor pressure of the solute. The density of the pure supercritical fluid can be altered both by temperature and pressure. It is interesting to study the effect of density of the fluid on the percentage recovery of solutes. To investigate the density effects, corresponding pressures were calculated for the density in the range of 0.464 to 0.974 g/ml [reduced density of 1.00 to 2.10] over the temperature interval 313-363°K using an equation which represents carbon dioxide above the critical conditions [173]. Calculated pressures as a function of density and temperature are plotted in Figures 16,17. The linear increase in pressure with temperature at fixed density explains the fact that higher temperatures where the supercritical fluid loses its liquid-like density are not suitable. The logarithmic increase of pressure with density at fixed temperature explains the fact that the variation of the density is very low at high pressures.

An experiment was designed to study reduced densities from 1.7 to 2.1 over the temperature interval 313 - 363°K. One gram of the spiked chromosorb W was extracted at the corresponding temperature and pressure for 15 minutes. Results are given in Tables 26-31. As the results reflect, percentage recovery of PAHs increase with SCF density at constant temperature. Since there is no apparent change in vapor phase composition of PAHs, this increase is purely due to the increase of SCF density. As the SCF density increases, interaction between PAHs and carbon dioxide molecules also increase, leading to a favorable extraction. It is interesting to compare the slopes of recovery isotherms. For a particular PAH, isotherms have apparently equal slopes, Figure 18, but differ with different PAHs, Figure 19. Presumably, the magnitude of the slope is a measure of carbon

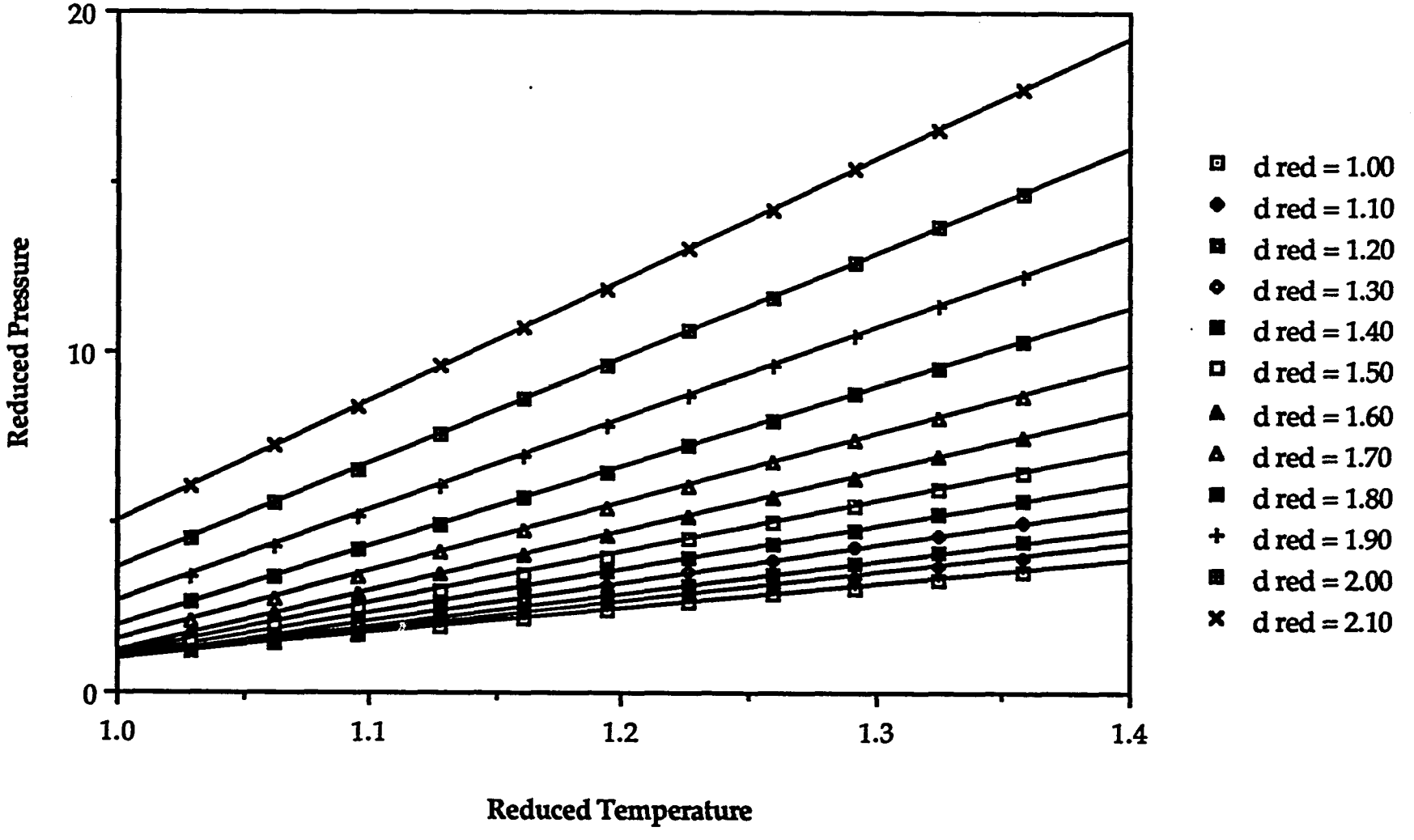


Figure 16. Variation of reduced pressure with reduced temperature at fixed density

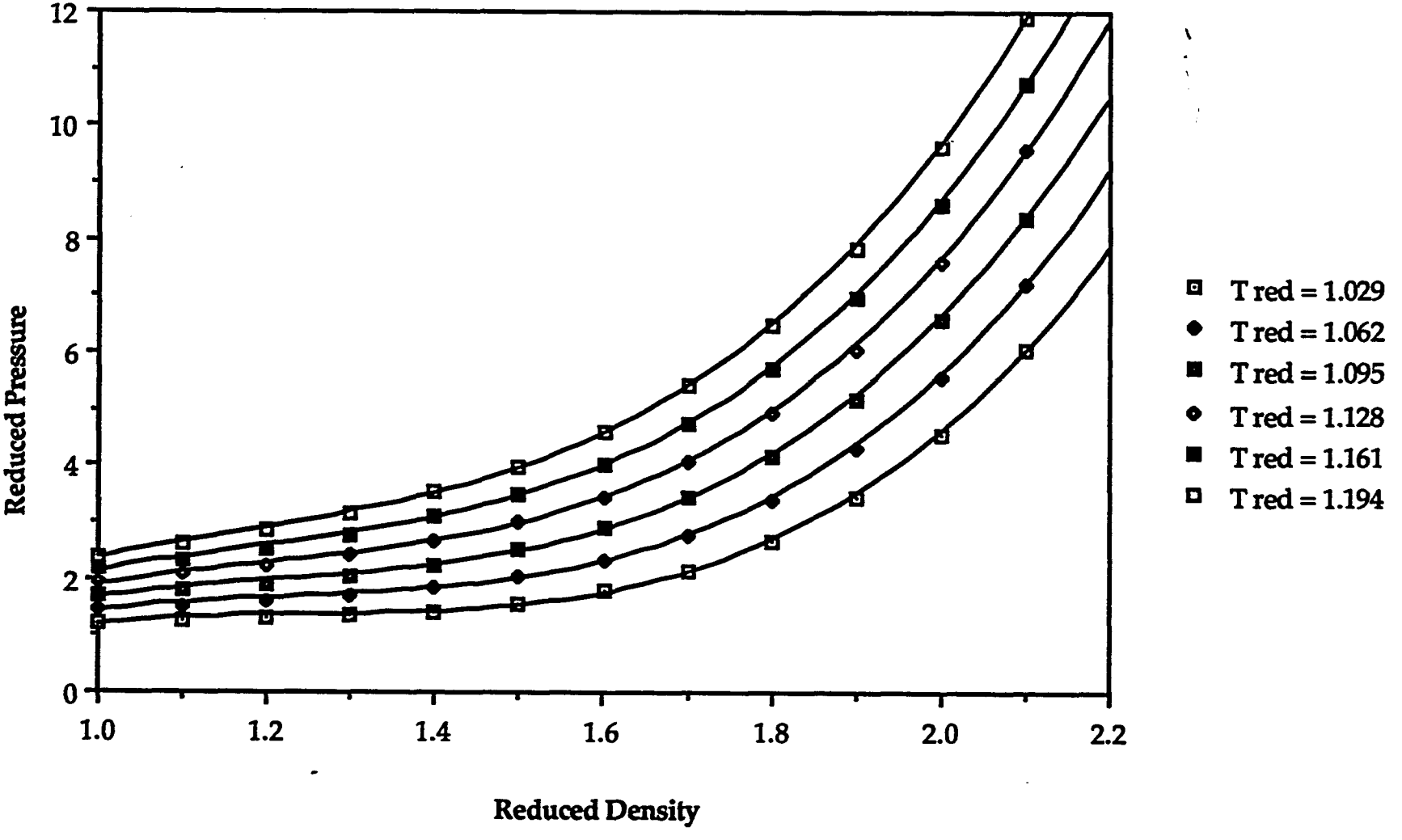


Figure 17. Variation of reduced pressure with reduced density at fixed temperature

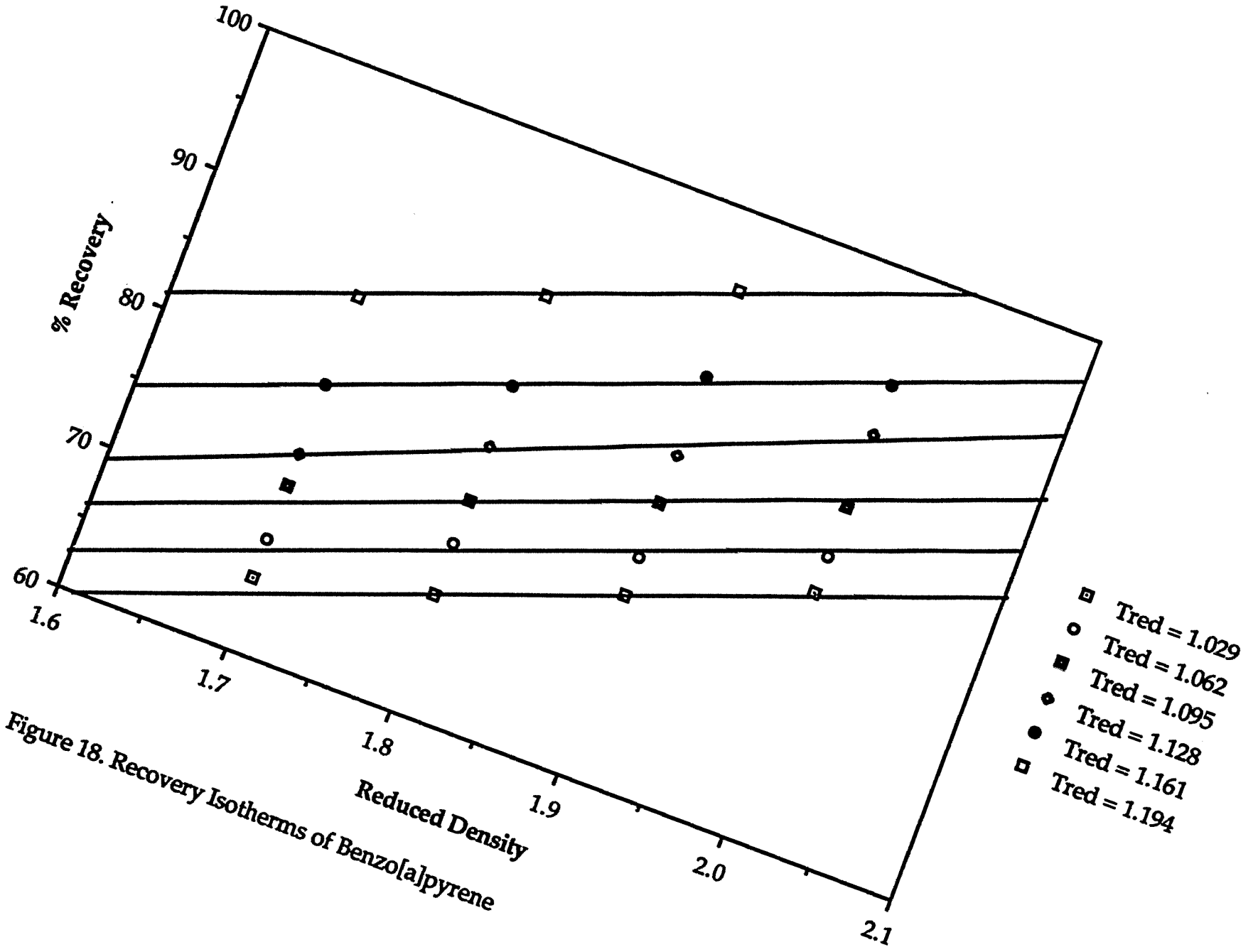


Figure 18. Recovery Isotherms of Benzo[a]pyrene

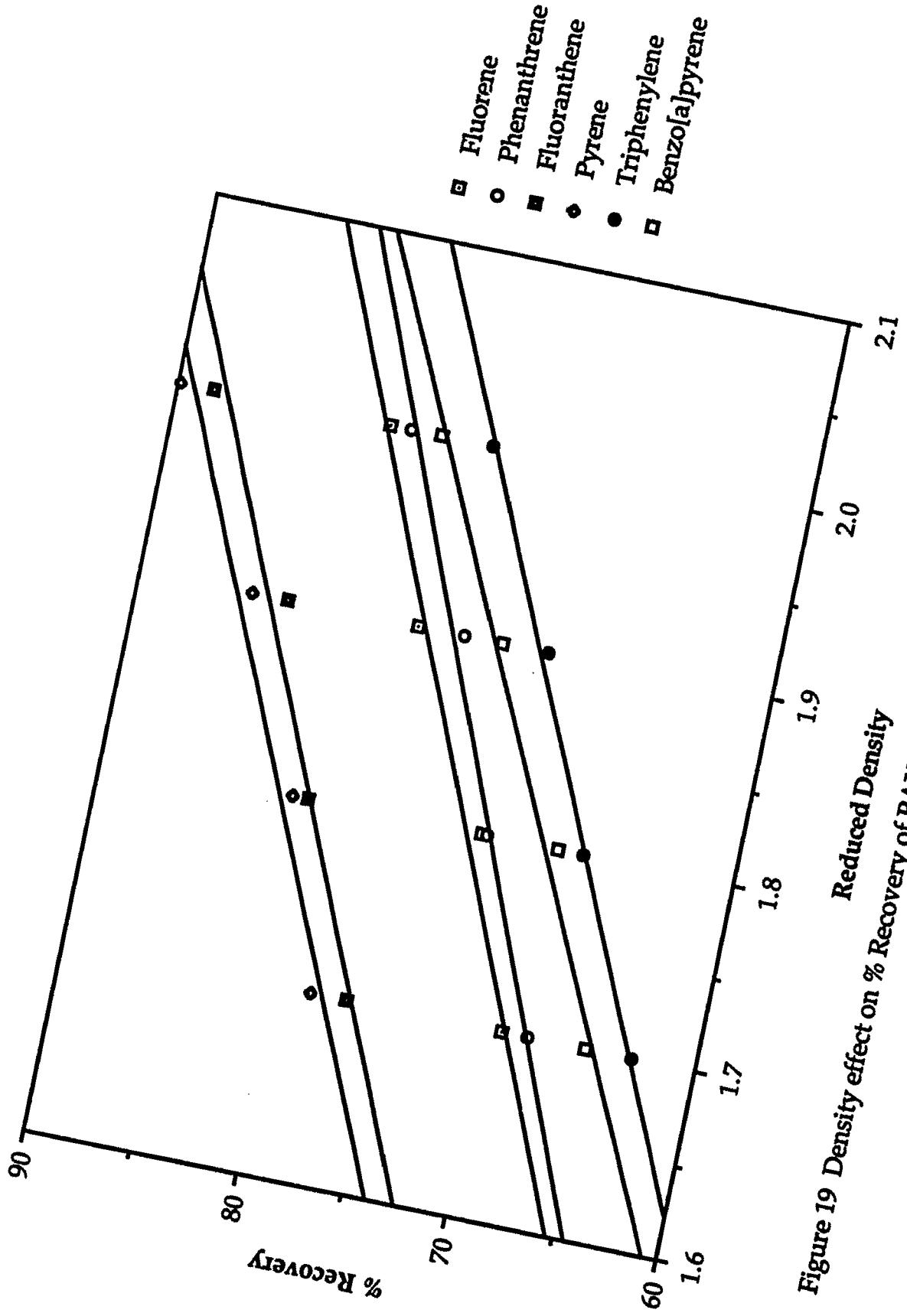


Figure 19 Density effect on % Recovery of PAHs

Table 26

Density Effect on % Recovery of Fluorene

	ρ_r			
T_r	1.7	1.8	1.9	2.0
1.029	69	72	77	80
1.062	71	75	79	82
1.095	75	78	82	85
1.128	78	81	86	88
1.161	82	85	89	92
1.194	87	91	95	---

Table 27

Density Effect on % Recovery of Phenanthrene

	ρ_r			
T_r	1.7	1.8	1.9	2.0
1.029	68	72	75	79
1.062	71	76	79	82
1.095	74	77	81	85
1.128	77	81	84	89
1.161	82	85	89	93
1.194	88	91	94	---

Table 28

Density Effect on % Recovery of Fluoranthene

	ρ_r			
T_r	1.7	1.8	1.9	2.0
1.029	77	80	83	88
1.062	79	83	88	93
1.095	83	85	91	94
1.128	86	89	94	98
1.161	89	92	97	101
1.194	92	97	101	---

Table 29

Density Effect on % Recovery of Pyrene

	ρ_r			
T_r	1.7	1.8	1.9	2.0
1.029	78	80	85	90
1.062	81	85	86	94
1.095	85	88	92	97
1.128	88	93	95	100
1.161	91	95	100	101
1.194	93	97	101	---

Table 30

Density Effect on %Recovery of Triphenylene

	ρ_r			
T_r	1.7	1.8	1.9	2.0
1.029	63	67	71	75
1.062	66	69	73	77
1.095	69	73	76	82
1.128	73	76	81	85
1.161	78	80	85	90
1.194	85	86	93	---

Table 31

Density Effect on % Recovery of Benzo [a] pyrene

	ρ_r			
T_r	1.7	1.8	1.9	2.0
1.029	65	68	73	78
1.062	68	72	76	80
1.095	72	75	80	84
1.128	74	79	83	89
1.161	80	83	89	94
1.194	85	90	94	---

dioxide-PAH interaction. Furthermore the gap between two isotherms of a particular PAH is a measure of the enhancement of PAH vapor phase composition or the difference in vapor pressure within the temperature interval.

Extraction of Fly ash

Three different fly ash samples were studied. Five grams of each fly ash sample Parma, Bologna and Montour were individually extracted at 544 atm 60°C for 15 minutes. From these samples, several high molecular weight hydrocarbons and phthalates were identified by GC/MS analysis, but no PAHs were identified. Soxhlet extraction of 25 g of these samples also proved the absence of PAHs. A separate GC/MS study at Lehigh university suggests that there are not any PAHs in the Montour sample [176]. A previous investigation reported the presence of several PAHs in the Parma and Bologna samples [74]. Most probably these PAHs decomposed during the four year storage in our laboratory. A new fly ash sample was obtained from Lehigh University [Montour fly ash sample] and used for the spiking studies. The concentrations of the spiked samples are given in the experimental section. Estimated percentage recoveries from the extractions are given in Table 32. From these results it is clear that certain PAHs can not be quantitatively extracted from the fly ash matrix under these experimental conditions. Benzo [a] pyrene and acenaphthylene demonstrated the poorest recoveries.

Another problem was suggested involving the extraction of pesticide residues from fruit wrappers [waxed papers]. Liquid extraction methods produce a large quantity of saturated hydrocarbons [wax] and the determination of pesticides from such a matrix is extremely difficult unless the sample is further purified or a specific detection method is employed. We hoped that this problem could be solved by performing a selective

Table 32

% Recovery of PAHs from Spiked Montour Fly Ash

	Spiking Level [µg/g fly ash]			
Analyte	**0.3**	**3**	**30**	**300**
Acenaphthylene	40	46	52	56
Benzo [a] Pyrene	ND	54	62	64
Fluoranthene	80	93	94	98
Fluorene	78	83	91	90
Phenanthrene	72	82	86	93
Pyrene	77	86	95	89
Triphenylene	ND	80	89	87

SCFE under controlled conditions. As a preliminary study, wax papers were fortified with a mixture of PAHs and extracted at low pressures [102-204 atm]. Interestingly, it was found that nearly all PAHs were extracted with the wax even at low pressures.

Although selective extraction was not successful, these observations encouraged us to test saturated hydrocarbons as modifiers for SCF carbon dioxide in extraction of PAHs. A piece of wax paper [~0.25g, 20% wax by weight] was inserted with the spiked fly ash sample and extracted at 612 atm 60°C for 15 minutes. Extracted samples were quantitated by HPLC /UV in which the UV-transparent saturated hydrocarbons did not interfere with the PAH signals. However, repeated injection of these extracts caused an increase in the analytical and guard column back pressures implying retention of wax particles. Hence, wax paper was replaced by a single liquid hydrocarbon and three different hydrocarbons [hexane, dodecane and hexadecane] were tested separately.

It is interesting to note that non-polar modifiers can enhance the extraction efficiency of PAHs from fly ash matrix [Table 33]. This increment may be explained in terms of the enhancement of the polarizability of the SCF phase. Polarizability of pure carbon dioxide itself is very low. Compared to carbon dioxide, straight chain alkanes have relatively high polarizabilities which increases with the number of carbon atoms in the chain. This increase in polarizability can induce a stronger interaction between the solutes and modified SCF carbon dioxide leading to a better recovery.

Though the enhancement is significant, the extract contained a large quantity of saturated hydrocarbons and phthalates which interfered with the GC/FID determinations; no significant problem was encountered in HPLC/UV determination. The increase in PAH recovery from the sorptive

Table 33

Effect of modifiers on % Recovery

	Modifier			
Analyte	**none**	**hexane**	**dodecane**	**Hexadecane**
Acenaphthylene	56	54	58	55
Benzo [a] Pyrene	64	70	74	76
Fluoranthene	98	100	97	102
Fluorene	90	94	92	95
Phenanthrene	93	94	93	93
Pyrene	89	98	102	105
Triphenylene	87	90	95	94

fly ash matrix with carbon number of the modifier is very encouraging. However a tremendous increase of total peak area [excluding the area of the modifier] and in the number of peaks in GC/FID detection, demonstrates the poor selectivity of the extraction process towards PAHs. Extraction at low pressures was attempted to clean up the dried spiked fly ash matrix, but it was found that a considerable fraction of high molecular weight hydrocarbons still remains in the matrix. With increase in pressure in the primary extraction, low molecular weight PAHs were extracted and selective fractionation could not be achieved. Cleaning of the spiked fly ash matrix [at low pressures ~136 atm] with the modifier demonstrated a loss of low molecular weight PAHs.

A few samples were Soxhlet extracted after SCFE but the total of spiked benzo [a] pyrene and acenaphthylene could not be accounted for. Overall a maximum of 78% recovery was obtained for benzo[a]pyrene, whereas for low molecular weight PAHs [except acenaphthylene], quantitative recoveries resulted. These low recoveries may be due to the strong adsorption of these PAHs into the highly sorptive matrix. In addition the spiked PAHs can undergo specific chemical reactions with the matrix components which can lead to a loss of some spiked PAHs [177]. Compared to other PAHs, which give reasonable high recoveries, this possible reaction may be specific for certain PAHs.

The low recovery of acenaphthylene was investigated, and it was found that some acenaphthylene was lost during the concentration process by rotary evaporation because of its relatively high volatility. Another possible loss of acenaphthylene is from the fly ash itself within the equilibration time prior to extraction, when the spiked sample was kept at room temperature. If the spiked samples were kept at a low temperature the possibility of losing acenaphthylene could be minimized.

Extractions of very low level spiked samples demonstrate semi-quantitative results implying that the matrix has irreversibly adsorbed some PAHs. Or this may be accounted for by the reduced sensitivity of the HPLC/UV detection under these conditions. This was tested by injection of stock and diluted solutions repeatedly into HPLC/UV and it was found that there is a larger deviation of the results [RSD of 4-12% vs 2-6% for the other concentrations]. Low concentration solutions had to be concentrated to 0.1 ml for quantitation whereas all other solutions were concentrated to only 1 ml. This concentration causes another problem, i. e., the concommitant concentrating of interfering materials which resulted in a high uncertainty in quantitation. In these cases, the purity of the chromatographic peaks were tested and those peaks with the purity indexes greater than 1.5 were rejected and considered as not detectable with a suitable accuracy.

Extraction from Soil Samples

Railroad soil samples [total organic content 13.3%] were extracted at the optimum extraction conditions. The extract contained several PAHs including fluorene, phenanthrene, pyrene and triphenylene. A secondary fractionation, developed by Lawrence and Weber [178,179] for PAHs partitioned from saponified fish or meat samples, was attempted to isolate the PAHs because the resulting SCFE fractions contained high molecular weight hydrocarbons which interfere in the GC/FID method. Therefore quantitation was done by HPLC/UV only [Table 34, Figures 20-24] Soxhlet extraction of this sample with methylene chloride led to a worse situation, in which an oily "tar like" residue [maybe burned oil] was extracted which was not suitable for analysis by any chromatographic technique. The extract remained of oily nature even after fractionation by a silica column. The SCF extract had a yellowish color; methylene chloride modified extract had a brown color; and methanol modified SCF extract had a dark brown [almost black color]. The pure SCF extract did not exhibit an oily nature

Table 34

Amount of PAHs [μg/g] Extracted from Railroad Soil Sample

	Soil Weight [g]			
PAH	**2.52**	**5.02**	**2.49**	**Mean [RSD]**
Fluorene	0.78	0.72	0.81	0.77 [4.33%]
Phenanthrene	0.91	0.88	0.85	0.88 [2.27%]
Pyrene	1.23	1.29	1.27	1.26 [1.85%]
Triphenylene	0.43	0.48	0.52	0.48 [6.25%]

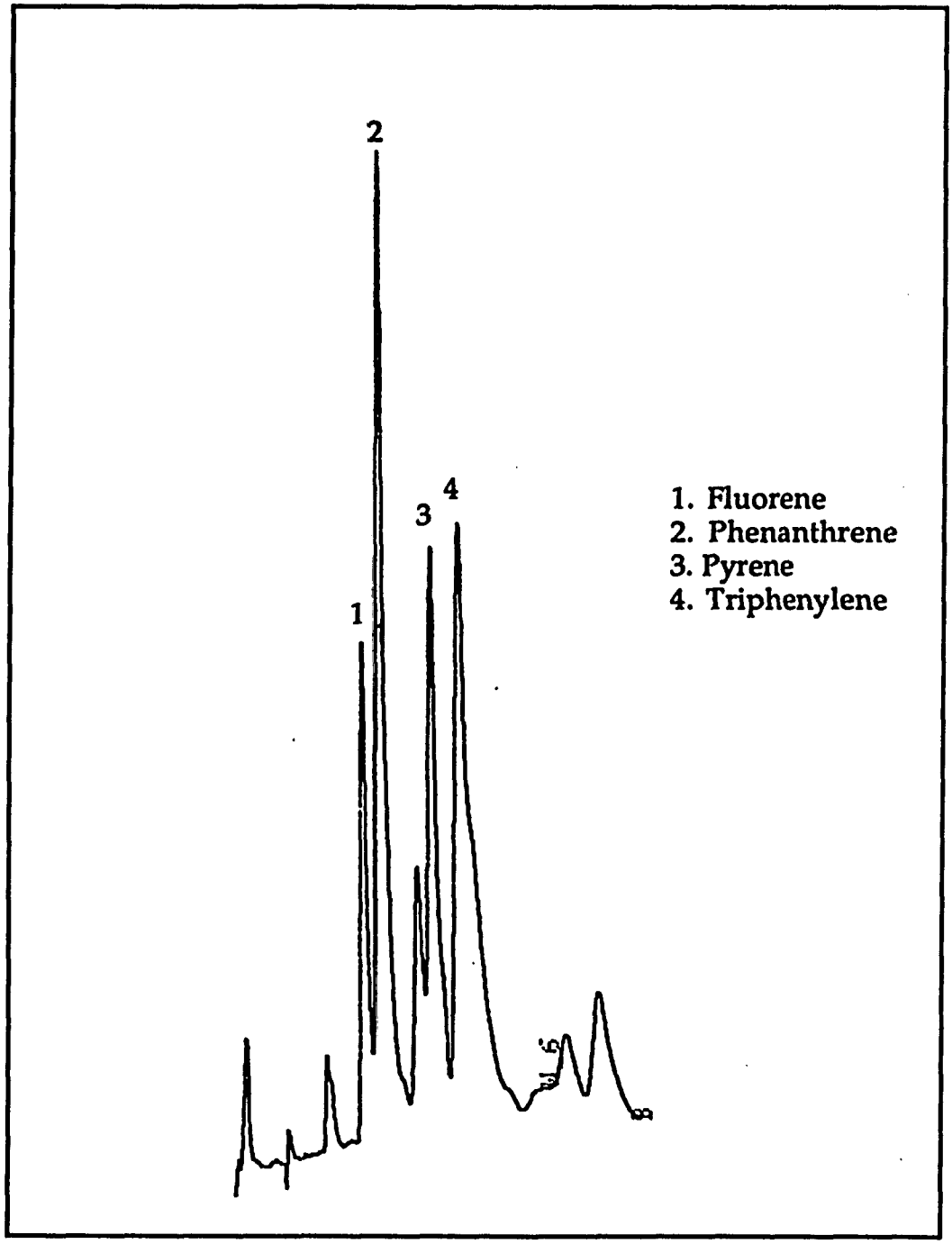


Figure 20. HPLC separation of SCFE railroad soil sample, Linear gradient ACN:Water 60:30>90:10, run time 30minutes, attenuation 16, wave length 255nm.

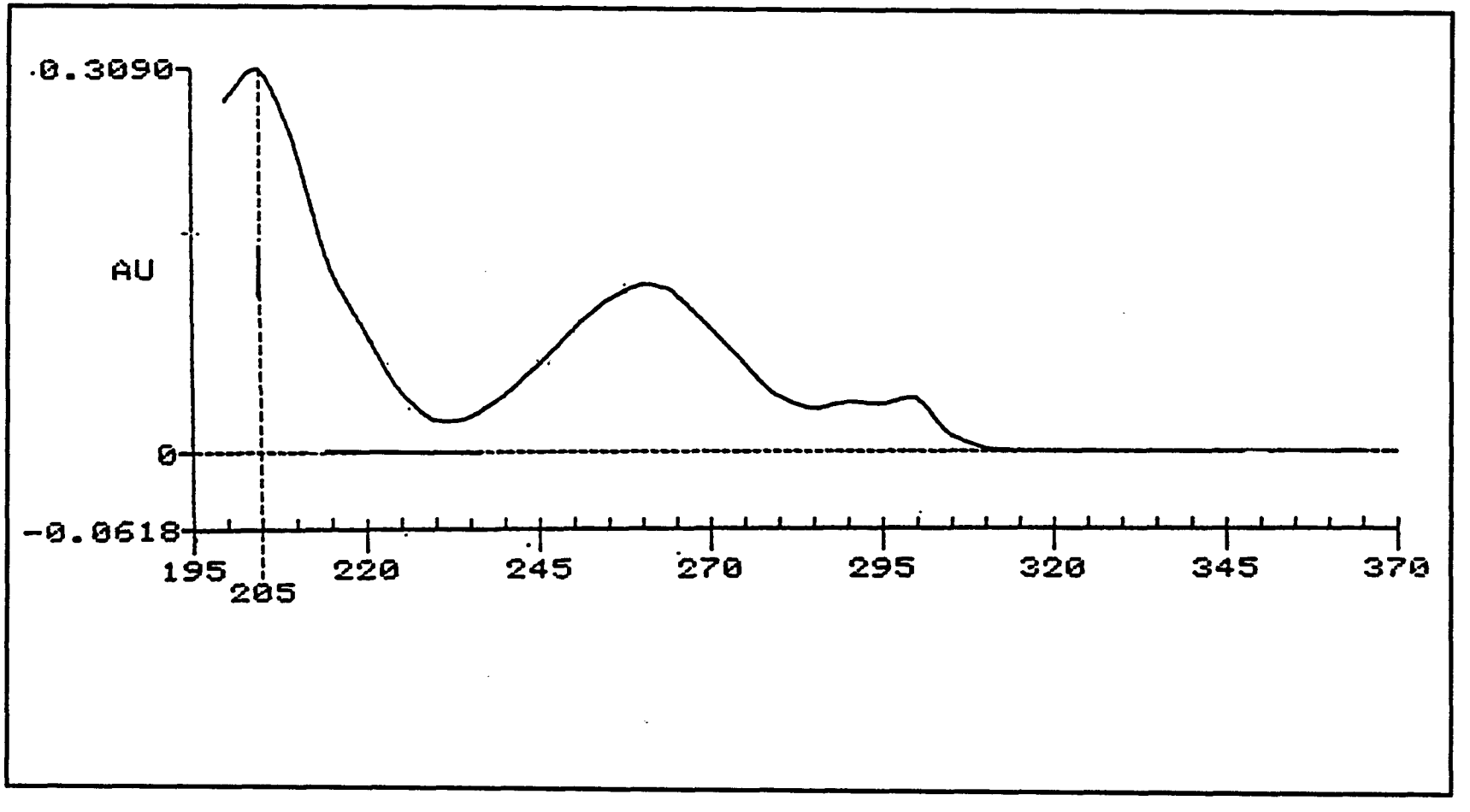


Figure 21. Identification of peak # 1 in Figure 20 by diode-array detector

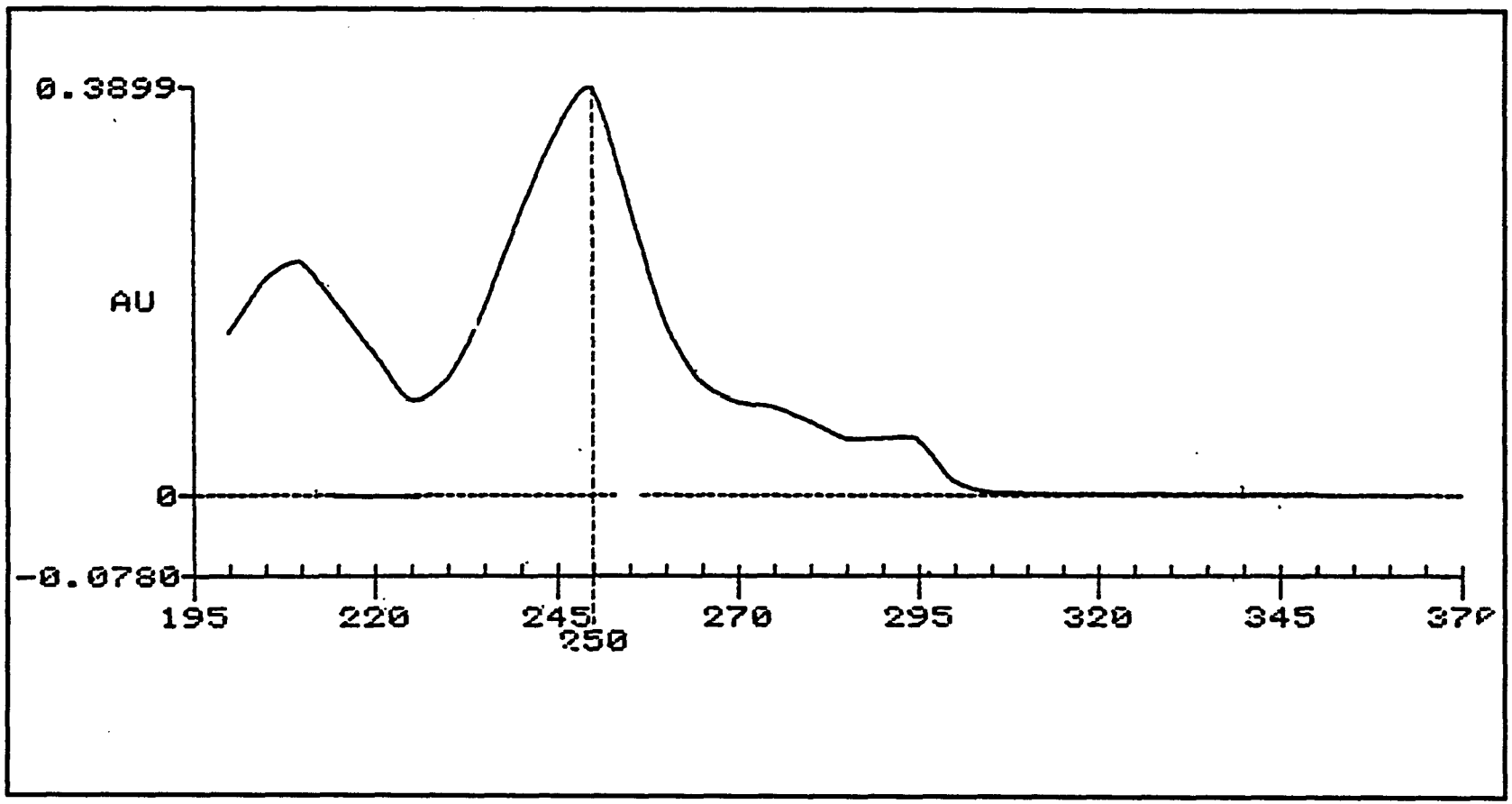


Figure 22. Identification of peak # 2 in Figure 20 by diode-array detector

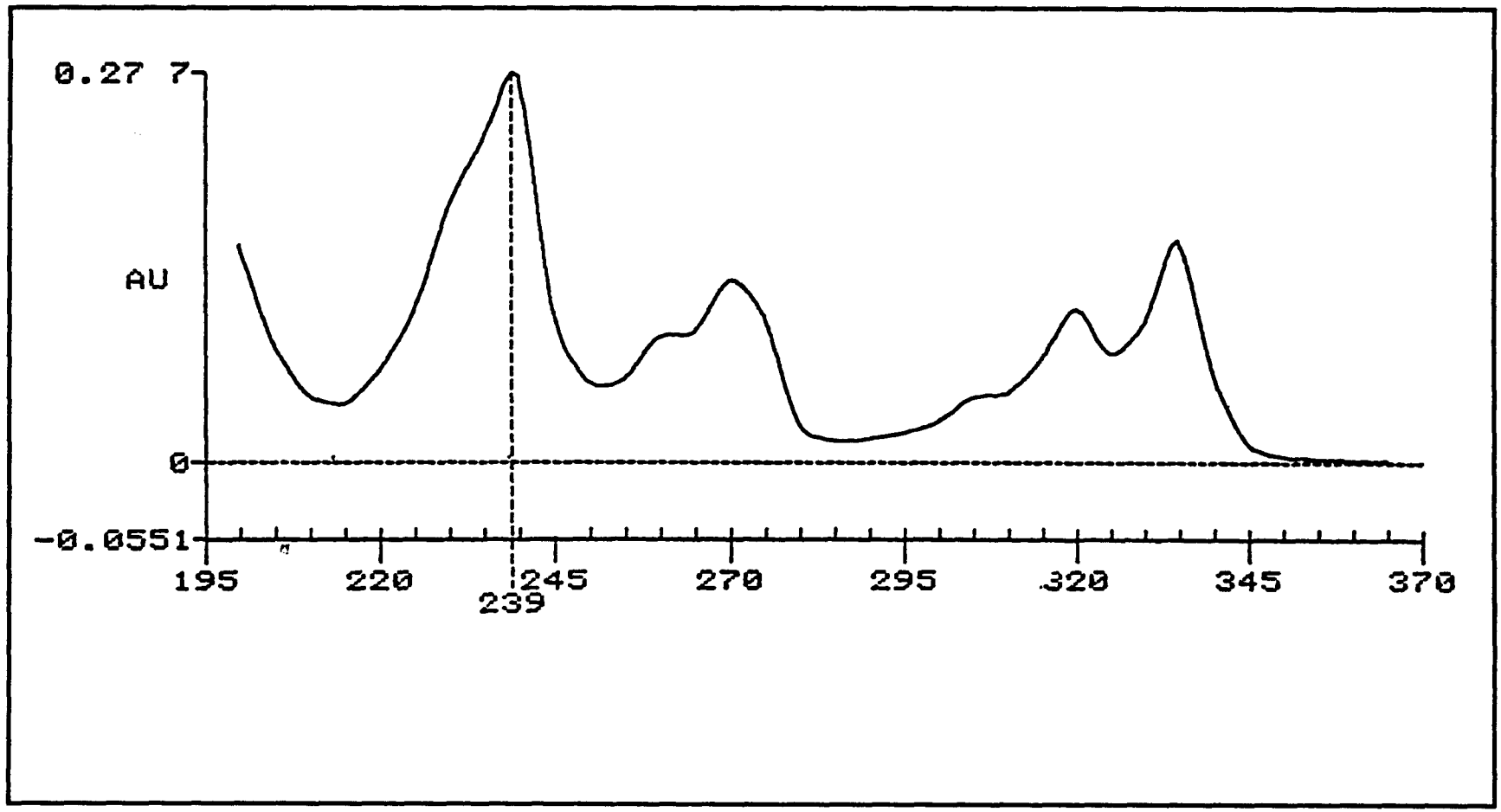


Figure 23. Identification of peak # 3 in Figure 20 by diode-array detector

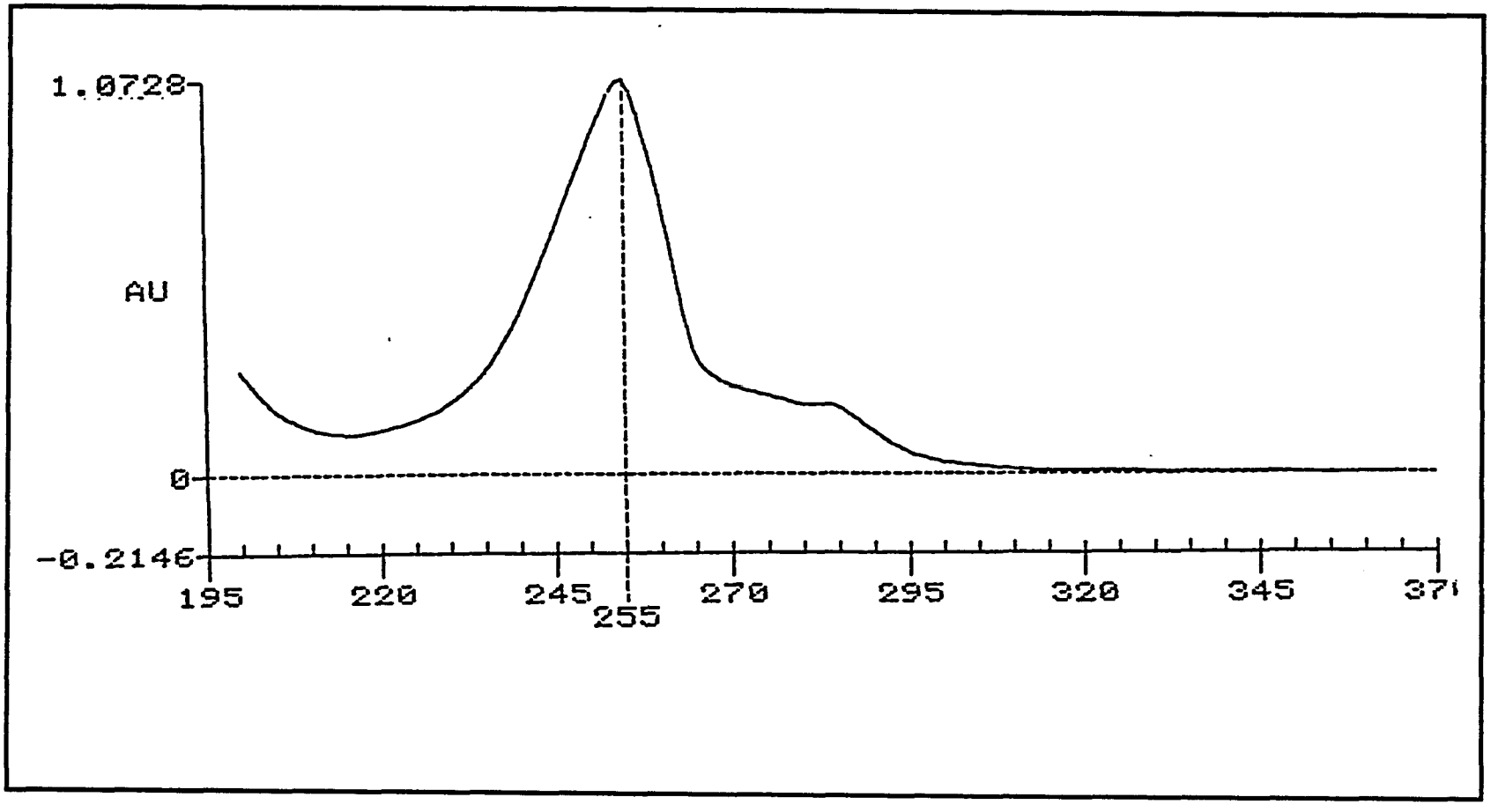


Figure 24. Identification of peak # 4 in Figure 20 by diode-array detector

whereas the two modifiers produced oily extracts. This qualitative experiment proves the capability of the modifiers to improve the efficiency of the extraction, but also that selectivity of the SCFE is lost to a certain extent.

A much cleaner soil sample was collected from Kissena Park Queens N. Y. [total organic content 5.536%]. This sample was extracted by both Soxhlet and SCFE methods and it was found that the sample did not contain any PAHs. Quantitation of a SCF extracted blank soil sample proved the absence of interfering materials for HPLC/UV analysis of the interesting PAHs. This was used as the matrix for spiking studies. A new stock solution was used for the spiking; acenaphthylene was not used as a standard but two oxy-PAHs were introduced. The concentrations of the spiked samples are given in the experimental section. All the extractions were done at 612 atm, 60°C for 15 minutes. Quantitative recoveries were obtained even in the absence of modifiers [Table 35]. Benzo [a] pyrene still gave slightly lower recoveries and the spiked samples with very low concentrations exhibit similar problems as discussed above in the spiked fly ash extract determinations. In addition to these problems, at higher detector sensitivity the changing mobile phase produces a drifting baseline leading to a high uncerteinty in the quantitations.

Table 35

% Recovery of PAHs and Oxy-PAHs from Spiked Soil

	Spiking Level [μg/g soil]				
Analyte	**0.1**	**1**	**10**	**100**	**1000**
Benzo [a] Pyrene	ND	70	76	83	82
Fluoranthene	82	90	98	103	101
Fluorene	78	86	93	98	94
9-Fluorenone	80	86	84	97	98
1,4-Naphthaquinone	75	87	93	94	87
Phenanthrene	77	86	89	92	93
Pyrene	ND	89	97	105	100
Triphenylene	ND	85	94	101	93

Conclusion

Off-line supercritical fluid extractions developed specifically for analytical sample preparation and analyses are described. The analytical SCFE method has been evaluated with the emphasis on the efficiency of the extraction and the collection steps. Experimental parameters were evaluated to optimize the extraction of middle-sized PAHs. The efficiency of extraction was evaluated as a function of temperature and density. Structural effects were considered to explain the differences in solubility of four-benzene fused-ring PAHs. As demonstrated by quantitative recovery of standard PAHs, SCF carbon dioxide provides a powerful alternative to liquid solvents for the extraction and recovery of PAHs. The extractions are simple, inexpensive and rapid to perform. Four to five extractions can easily be performed within two hours. Since carbon dioxide is used as the SCF, solvent disposal problems and toxicological problems of exposure to the solvent are insignificant compared to conventional extraction methods. Extracted materials are not exposed to the light or to excessive heat which reduces the possiblility of photo- or thermo- decompositions. Extractions from spiked samples are much cleaner and selective HPLC-UVD determinations eliminated extra sample handling and tedious separation processes. Overall this method is much superior for the extraction and analysis of middle-size PAHs.

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