ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS; PHENANTHRENE, FLOURENE, FLUORANTHENE AND NAPHTHALENE IN TAP WATER

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ABSTRACT

The purpose of this study was to determine whether the presence of industry or petrochemical facilities near water way sources affected the quality of tap water. The viability of SPME in analysis of contaminated water systems was studied. The instrumentation that was used was SPME/GC-FID. We determined that the water treatment process was highly efficient because no detectable levels of Polycyclic Aromatic Hydrocarbons(PAHs) in the tap water collected from different sources, in addition to this we came to a conclusion that SPME could be used to monitor in Tap drinking water because it has high sensitivity and good selectivity.

INTRODUCTION

Polycyclic aromatic hydrocarbons PAHs are the largest group of suspected carcinogens and possible mutagens. They are a group of more than a hundred organic compounds of two or more carbon rings derived from benzene.(7) The term PAH is not used in the strictest chemical sense because all PAHs are not aromatic, e.g. Fluorene. The health effects that can be caused by the exposure to PAHs depend on how much has entered the body, length of the exposure and how the body responds to the PAHs. These effects may be either short term or long term. Studies of workers exposed to mixtures of PAHs and other compounds have noted an increase risk of skin, lung, bladder and gastrointestinal cancers (2). The drinking water contaminants that can have chronic effects are chemicals such as disinfection by products, solvent and pesticides, radionuclides and minerals such as arsenic. Some chronic effects of drinking water contaminants are cancer, liver or kidney problems, or reproductive difficulties.

Elevated concentrations of PAHs in the air and water can lead to significant environmental effects. Entry of PAHs in the environment can be categorized into three groups i.e. individual emissions, which include furnaces, automobile and other exhausts, fireplaces and wood stove, and cigarette smoke. Industrial emissions include coal and oil- fired power plants, waste incinerators, coke and ashphalt production, aluminium smelting and carbon black production and wood preservatives (7). Natural emissions are forest and brush fires, volcanic eruptions and decaying organic matter. In addition to these PAHs may be found in low levels in foods such as roasted coffee, roasted peanuts, refined vegetable oil, grains, vegetables and fruits (2). US Environmental Protection Agency (EPA) has listed 16 PAHs as priority pollutants in wastewater and 24 PAHs in soils, sediments, hazardous solid wastes and ground water (4). Some of the priority pollutants include naphthalene, acenapthylene, acenapthene, fluorene, phenantrene,

anthracene, pyrene, fluoranthene, chrysene, etc. Some contaminants come from erosion of natural rock formations, others are substances discharged from factories, applied to farmlands or used by consumers in their homes. PAHs can break down by reacting with sunlight over a period of days or weeks. Some PAH particles can readily evaporate into the air from soil or surface waters. Most of them do not dissolve easily in water this is because as a rule, when PAH compounds grow in molecular weight, their solubility in water decreases, solubility in fat tissues increases and their melting and boiling points increases. They stick to solid particles and settle to the bottoms of lakes and rivers. Microorganisms can break down PAHs in soil or water after a period of weeks to months. PAHs enter water directly from the air with dust and precipitation, or on particles washed from the soil by runoff. PAHs dissolved in water can be taken up by plants, and released into soil and water when plants die, decompose or are burned. PAHs also find their way directly into the aquatic environment through discharged from various human activities, including domestic and industrial sewage effluents; spills and leaks of PAH containing materials such as oil; runoffs from paved roads, parking lots and the grounds of wood preservative plants; offshore drilling; and leaching and disposal of refinery effluents. PAHs are slow to degrade in the environment and sediments in particular are "sinks" where chemicals tend to concentrate. It should be noted that PAH contamination tests might result in false positives because an anthropogenic ally-contaminated system also produces PAHs in site through its own natural biological processes. Knowledge of sources and pathways of pollutants in the environment is important for effective pollution control (1).

The sources of drinking water (both tap and bottled water) include rivers, lakes, streams, ponds, reservoirs, springs, and wells. As water travels through the ground, it dissolves naturally occurring minerals. In some cases water can pick up substances resulting from the presence of

animal or human activity, as well as radioactive materials. Presently States and water suppliers are working systematically to assess every source of drinking and to identify potential sources of contaminants. Contaminants that may be present in water before any treatment include: microbial, inorganic, organic, pesticides and herbicides and radioactive contaminants. In order to ensure tap water is safe to drink, EPA prescribes regulations which limit the amount of certain contaminants in water provided by public waterway systems. An example of treatment process is the treatment of water from the Mississippi river. The purification process begins with the addition of a coagulant chemical, commonly called polyelectrolyte at the river station. This polyelectrolyte causes fine suspended particles to coagulate or gather into larger particles. Water then treated with these polyelectrolytes travels through several large pipelines from the river pumping stations to the water plants. As it enters the plant it is treated with ferric sulphate and lime. Ferric sulphate is also a coagulant chemical used to aid the polyelectrolyte in coagulation and clarification process. Lime also known as calcium oxide is used for pH adjustment, softening and corrosion control. The water is then gently mixed by large mechanical paddles in two flocculation basins where the suspended particles gather together into large particles. This flocculated water then travels into settling basins where the particles settle. The settled particles forms sludge layers, which are removed from the basins through a series of valves and pumps. The clarified water then exists the settling basins and is treated with free chlorine and anhydrous ammonia. This produces chloramines, which is used for residual disinfection. This water then enters an additional settling basin for further settling and also to allow enough contact time with the disinfectant. After exiting the second settling basin the water is treated with sodium hexametaphosphate which is used to hold the lime in solution thus keeping from deposition on the filter or the media and fluorosilicic acid which is used to add fluoride to the drinking water to

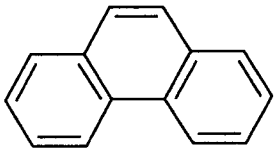
aid in prevention of dental cavities. The final step in the purification process is filtration through 44 rapid sand filters. These filters consist of graded gravel toped first with a layer of and and then with a layer of anthracite. After filtration, the purification process is complete and drinking water is pumped out to customers. The quality of finished water and river water is tested daily at the Water Quality Laboratory of the Sewerage and Water Board. Samples of drinking water from various points in the distribution system are then analysed for chemical and microbial parameters regularly. This parameters are pH, alkalinity ,hardness, fluoride ,etc,(8).The Lafayette utilities system water source is the Chicot Aquifer, a large , natural underground "Lake" in southwest Louisiana .It is a stable , plentiful and protected fresh water supply.LUS worked with the Louisiana Department of Environmental Quality's Office of Groundwater several years ago to put together a Wellhead Protection Program.In this program ,potential sources of contamination within a one mile radius of public supply water wells was identified.The treatment process of this water from the aquifer involves transporting it from the aquifer to the treatment plants through underground pipelines.Once this water reaches the plant, it is cleaned through a three-stage process that includes softening, filtering and disinfecting before it reaches the taps.

Our hypothesis was based on the assertion that some of the contaminants present in water before treatment and especially microbial and organics would vary depending on the source of the water. Further after treatment some of these contaminants would still be present in drinking water in low levels depending on the effectiveness of the treatment process. However this is not favourable because long-term exposure to low levels of some PAHs has been reported to be carcinogenic. We also wanted to verify the viability of SPME as a method for drinking water analysis. Currently EPA has not established maximum contaminant levels for individual PAHs but has set a maximum contaminant level for total PAHs of 0.2 ppb. Local quality water reports

do not report the maximum contaminant level for individual PAHs and total PAHs. Low levels of PAHs have been found in some drinking water supplies in the US. Drinking tap water samples were collected from suburban of Baton Rouge and New Orleans and tests carried out to determine whether and how the water needs to be treated, as well as the to assess the effectiveness of the treatment process. The main supply of drinking water are aquifers and the Mississippi river and these sources both have a high chances of being contaminated with PAHs from storm runoffs, incomplete combustion of petroleum products and underground oil spills. Among the top priority pollutants, the following PAHs, fluorene, naphthalene, phenanthrene and flouranthene were studied.

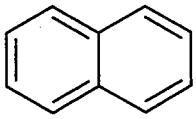
STRUCTURES AND PROPERTIES OF THE FOUR PAH'S STUDIED.

PHENATHRENE



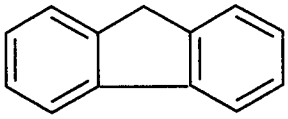
BP 338
SOLUBILITY1.18g/m^3
MW178.2g/mol

NAPTHALENE



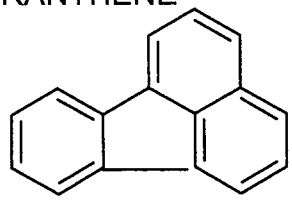
BP 218
SOLUBILITY 30.2g/m^3
MW 128.2G/MOL

FLUORENE



B.P 383
SOLUBILITY1.90g/m^3
MW 166.2g/mol

FLUORANTHENE



BP 217
SOLUBILITY 0.260g/m^3
MW 202.3g/mol

http://chrom.tutms.tut.ac.jpsample/PAH/pah.html

EXPERIMENTAL APPROACH

SAMPLE COLLECTION, HANDLING AND STORAGE

Samples of tap drinking water were collected from La Place, Harvey, Lafayette, Geismar, Lobdell, Illinois Chicago, Houston Texas, New Orleans and Gretna. In addition to this surface water from the City Park Lake near Dalrymple Drive was collected. Samples were collected using grab sample bottles that were 1 litre amber glass, fitted with a screw cap lined with Teflon so as to protect the samples from light. The bottle and cap had been rinsed with acetone and dried so as to minimize contamination. The samples were then stored in a dark refrigerator thermo stated between -10°C and 4C°.

EXPERIMENTAL METHODOLOGY

The method that was used for extraction of analyte was the Solid Phase Microextraction (SPME). The fibre was thoroughly activated by heating in the injector of the GC at 270 °C for 30 minutes. Extraction of the analytes from the sample matrix was done by liquid immersion, which works by partitioning of organic compounds between aqueous phase and the fibre to preconcentrate the analyte on the fibre through adsorption. The fibre that was used was the 65µm coated with polydimethyl siloxane. This was then interfaced with the GC-FID. The oven had a column length of 30m and i.d of 0.25µm and a silica film thickness of 0.5µm.The operating conditions of the GC-FID were set as follows: A split less mode was used for the SPME injections with the purge valve closed for 3 minutes .The inlet temperature was set to be 270°c for the SPME injections and that of the FID detector was set at 300°C. The carrier gas helium had a flow rate of 0.7ml/min, a linear velocity of 30cm/s and a pressure of 3.5psi at 50°C. For thermal desorption of the SPME, the fibre was left at the injector for 5 minutes. The GC-FID column temperature program was as follows. The column temperature held initially for 50°C for

1minute, increased to 100°C at 10°C per minute, then to 250° at 60°C/min then to 300° at 3°C/min and held for 5minutes.

PREPARATION OF STANDARD SOLUTIONS

Stock solutions of the following PAHs Phenanthrene, fluorene , naphthalene and fluoranthene were prepared by weighing 0.1grams of each respective PAH in a 100ml volumetric flask and dissolved in HPLC grade Acetone so as to prepare a 1000ppm solution of each PAH. This was then diluted to various concentrations so as to prepare the calibration curve for each PAH. Napthalene and Phenanthrene were diluted in aqueous media to make solutions of 750,500,250 100 and 50ppm solutions. However due to the low solubility of fluorene and flouranthene the solutions prepared were of 75,50,25,1,0.5ppm and 400,200,100,50,25ppm respectively. A spiked solution that contained all the pure standard analytes was prepared by weighing 0.1grams of each pure PAH and dissolved in acetone in a 100ml volumetric flask so as to prepare a solution of 1000ppm.This was then diluted further with deionized water to a final concentration of 10ppm. Direct injection under split less mode of each of the stock solution of the PAH to be analysed was done so as to obtain the retention time of every PAH. This was still verified by injecting the spiked solution of the various analytes. The SPME was then conditioned according to SUPELCO conditioning requirements and used to carry out the extraction of each of the water samples mentioned and for the preparation of the various calibration curve for each PAH.

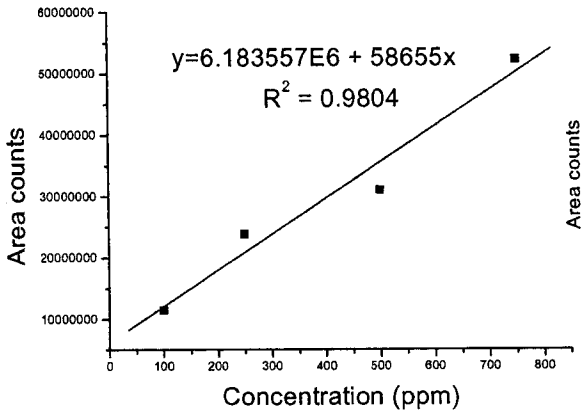
DATA AND RESULTS

It was observed that the solubilities of the different PAHs decreased with increase in molecular weight. In this regard different concentration ranges for preparing calibration curves for High molecular weight PAHs were chosen.

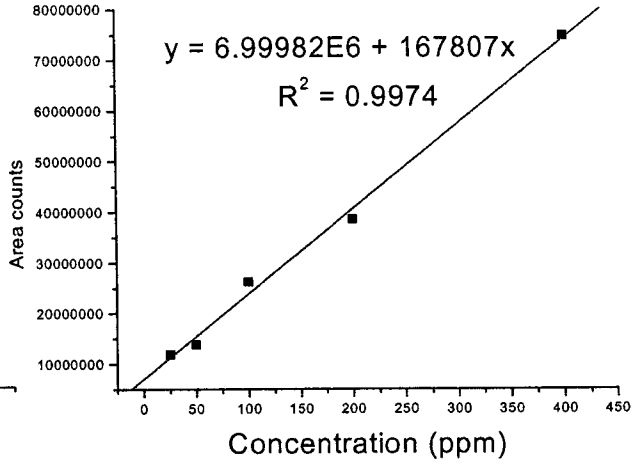
The calibration curves were checked regularly by injecting two of the standards solutions of different concentration to determine the reproducibility. One of the standard solutions for each calibration curve was near but above the method detection limit.

Working calibration curves

Naphthalene

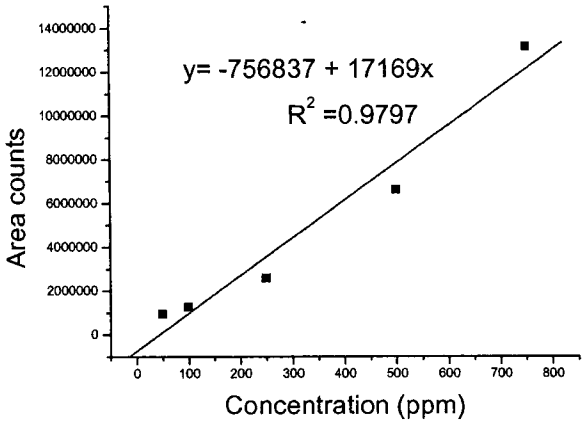


Fluoranthene

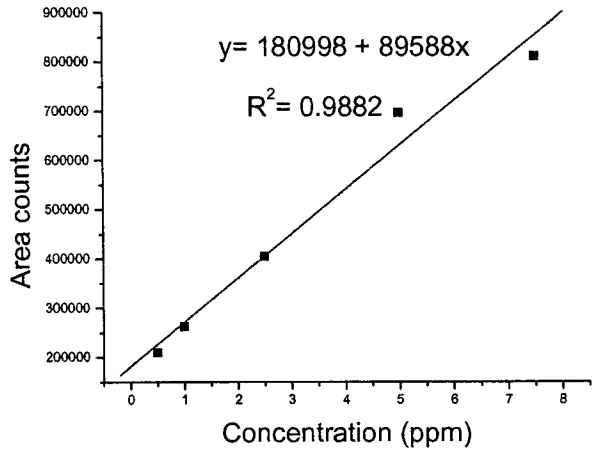


Working calibration curves

Phenanthrene



Flourene



Analyte	Concentration (ppm)	Area Counts
Phenanthrene	50	936912
	100	1264516
	250	2573021
	500	6622205
	750	13148216
Flourene	0.5	209560
	1	262613
	2.5	404616
	5	695835
	7.5	810584

Analyte	Concentration (ppm)	Area Counts
Naphthalene	100	11475392
	250	23848426
	500	31000700
	750	52258128
Flouranthene	25	1.19E7
	50	1.38E7
	100	2.62E7
	200	3.85E7
	400	7.47E7

Calibration of PAHs from water by SPME

PAH	Slope(10^{-6})	Intercept(10^{-6})	R^2
Naphthalene	58655	6.183557	0.9804
Flourene	89588	0.180998	0.9882
Phenathrene	117169	-0.756837	0.9797
Fluoranthene	167807	6.99982	0.9974

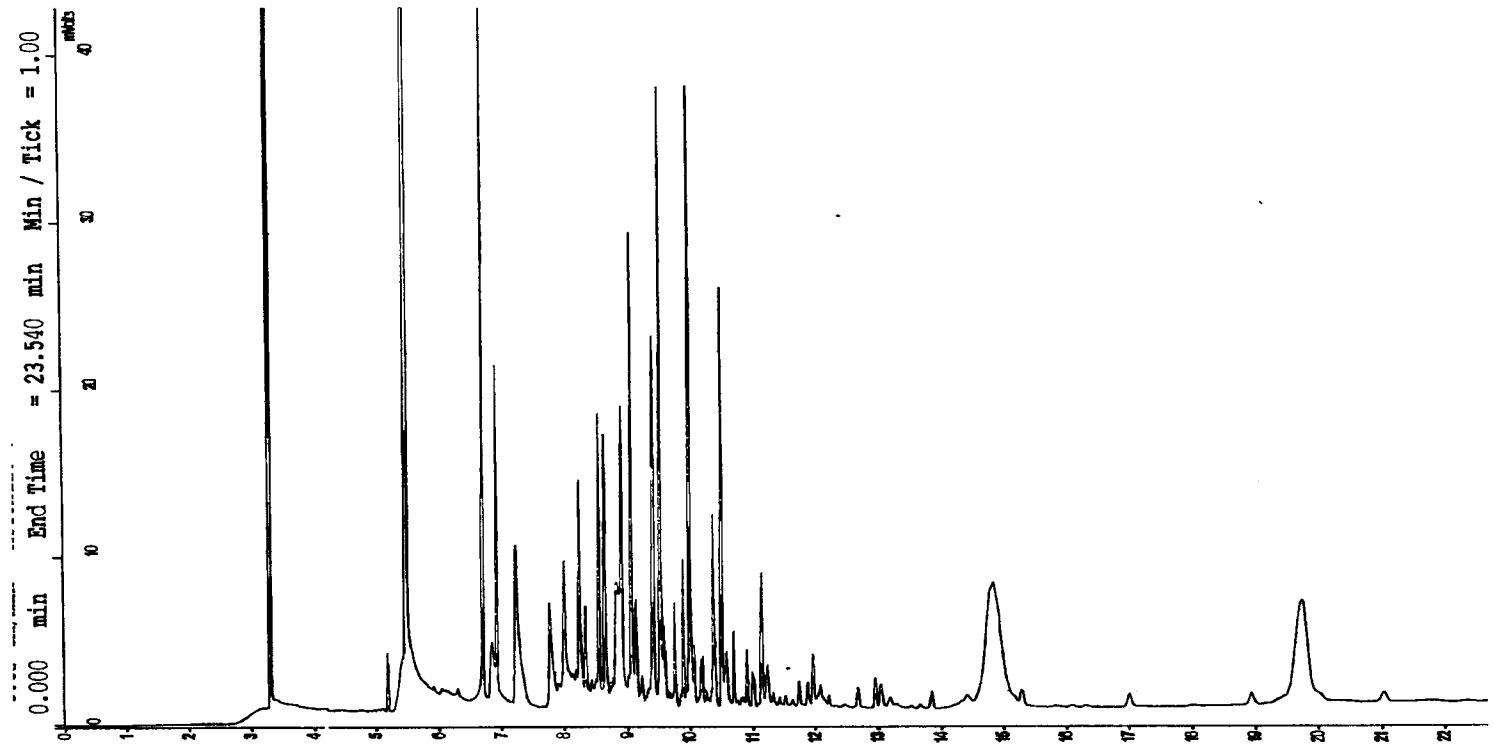
Analyte	Molecular weights	Solubities (g/m^3)	Boiling Points(^0C)	Retention times(Min)
Naphthalene	128.2	30.2	218	8.49
Acenapthene	154.2	3.93	279	9.75
Flourene	166.2	1.9	295	9.88
Phenanthrene	170.2	1.10	336	10.50
Flouranthene	202.3	0.26	480	11.89

Identification of analytes.

The retention times of PAHs in water samples were to be compared with those in reference chromatogram for the standards solution mixture. For unknown compound with retention times within limits to that of a standard compound the identification was considered positive.

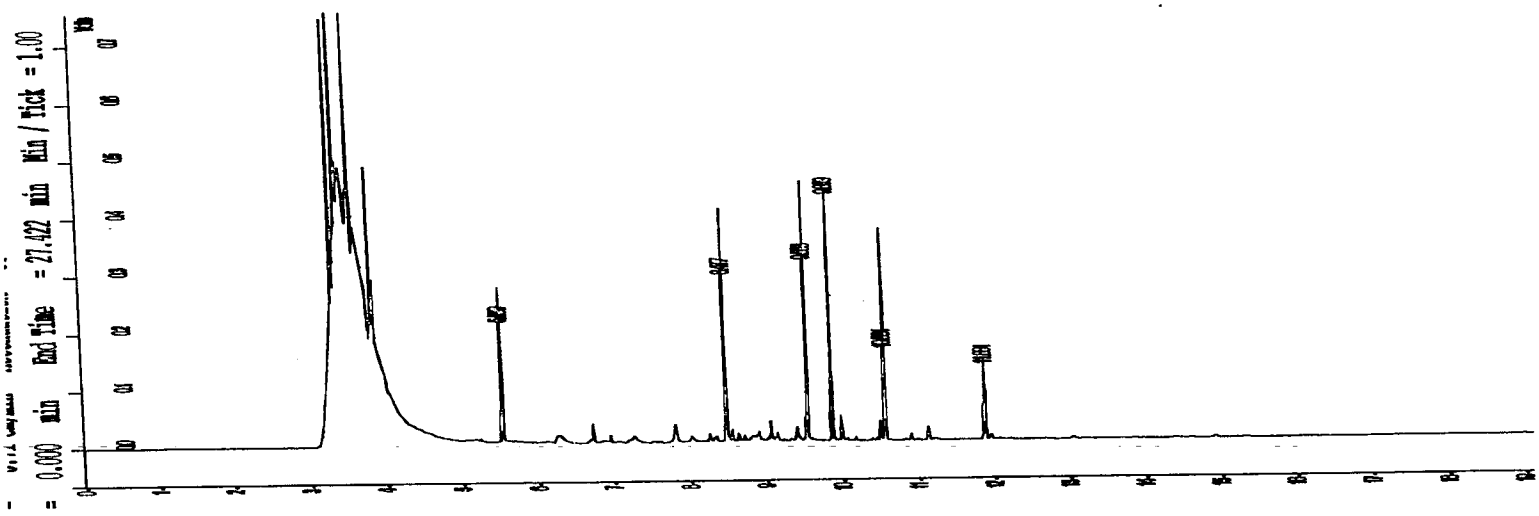
Drinking tap water samples collected from Harvey, Laplace, Gretna,Lafayette,Baton Rouge and New Orleans, were analysed for PAHs. However, none of the water samples collected had detectable levels of PAHs of interest. A sample of water collected from the City Park Lake was also analysed and no PAHs were detected. Below are some chromatograms obtained for some of the samples.

Chromatogram for water sample (Harvey)



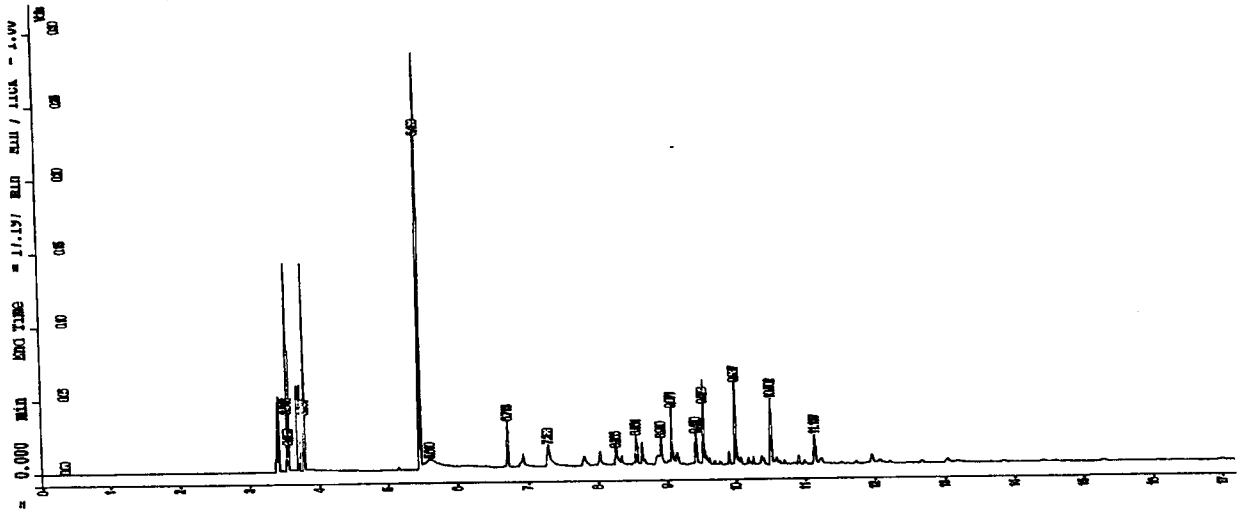
Retention times (min)

Chromatogram for Standards (Mixture)



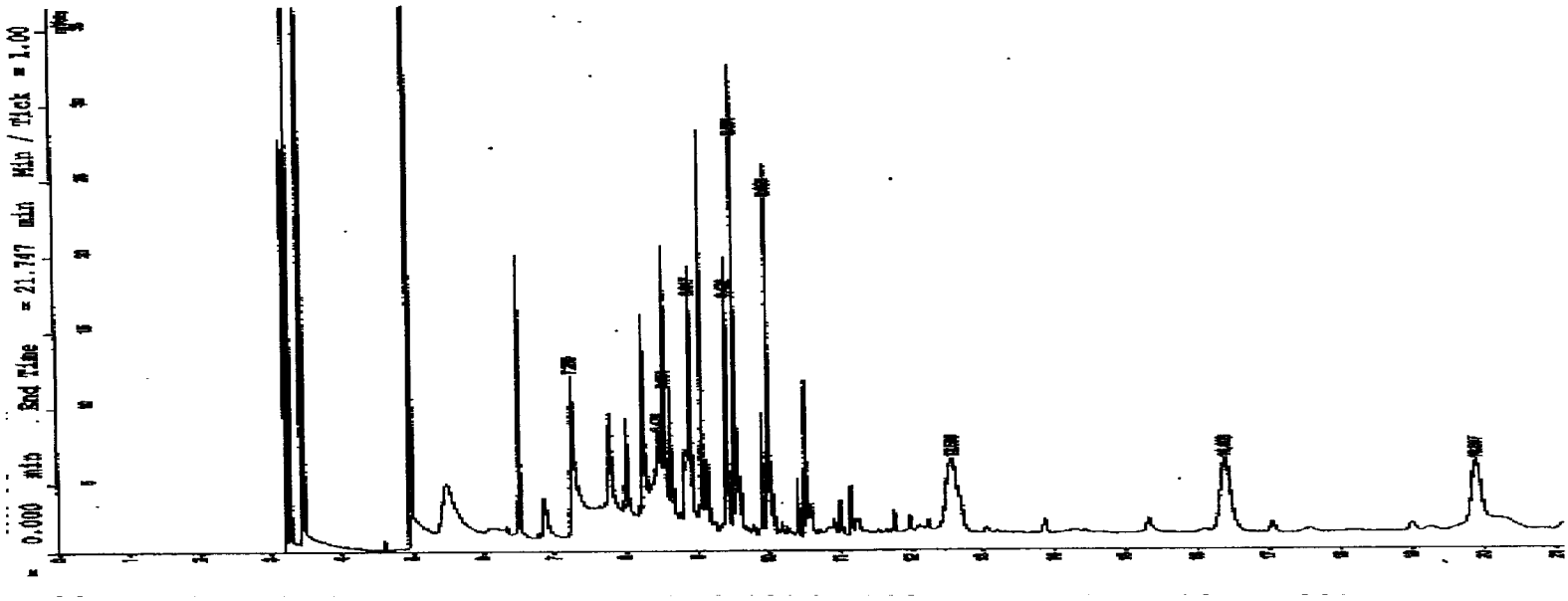
Retention times (min)

Chromatogram for water sample (Gretna)



Retention times (min)

Chromatogram for water sample (City Park lake)



Retention times (min)

Discussion.

The objective of this study was to analyse for PAHs in drinking tap water. From the chromatograms of the drinking water samples, no peak was identified with same retention time as the standards. Water samples were also spiked with appropriate standards to ascertain the presence of PAHs for peaks that eluted near same retention times as the some of standards. The two peaks occurring early in the chromatograms are solvent and air peaks, while the others may be organic contaminants other than PAHs that could be present in low levels and bleeding of the fibre. Therefore it can be concluded that the water treatment process is effective, and the levels of PAHs if any were below detectable limits. The FID has very low detection limits and SPME

has very good selectivity and therefore appropriate for this analysis. The amount of compound adsorbed on the fibre decreased with increase in PAH molecular weight. The difference in PAH recovery is due mostly to the decreasing solubility of PAHs in water with the increasing of their molecular weight. The low recovery is also caused by the affinity of the specific PAH for the relatively polar solid matrix. The distribution constants are very different, the adsorption onto a fibre is kinetically favoured for low molecular weight PAHs but thermodynamically favoured for high molecular weight PAHs [18]. The response (slope) decreases because their solubility into water decreases with increase in high molecular weight. The response could also be decreased as a result of carryover from the SPME fibre. The process, which releases analytes from the solid matrices, is difficult to optimise, because the interaction between analytes and matrices is poorly understood and it usually varies according to the complexity of analyte and matrix types. It is noted that thin fibres are more suitable for SPME of high molecular weight PAHs. It should be noted further that PAHs contamination tests might result in false positives because an anthropogenically-contaminated system also produces PAHs in situ through its own natural biological process [8]. There has been a decrease in levels of PAHs in drinking water due to improvement of waste stream treatment, increased usage of by products and / or overall decrease in by product production. However detailed study with continuous monitoring of these PAHs is recommended.

PAHs have been observed to increase in water bodies near highway due to increased vehicle usage. The surface water sample from City Park Lake showed no detectable amounts of PAHs of interest, a plausible reason could be that high molecular weight PAHs (Fluoranthene, phenanthrene) sink to the bottom after attaching to solid particle and also because there had been no storm runoff at the time of sample collection. The three to four ring species are produced by

incomplete combustion e.g. from car engine. For two to three ring species (Fluorene and Napthalene), produced by non- combustion process such as petroleum spills, they are easily degraded by photochemical process or micro organisms [4].

In determining the choice of fibre to use, the molecular weight and polarity of the analytes were considered. For the low molecular weight PAHs like Napthalene and Fluorene, the 100 um polydimethyl siloxane coated fibre was appropriate while for high molecular weight PAHs (like Fluoranthene and Phenanthrene) the 7 um PDMS fibre would give effective extraction yields. The general purpose 65 um PDMS/DVB fibre was used since the cross linked phase is more stable at high temperature and when several extractions are to be done.

Other plausible analytical techniques that should be used for this work include, Supercritical Fluid Extraction with or without GC/Flame ionisation Detection or GC/MS Detection.

Solid phase extraction with or without planar chromatography and densitometric detection

High performance liquid chromatography/ ultraviolet spectroscopy.

Current studies in biotechnology indicate that certain micro organisms can be used to degrade PAHs and other related environmental pollutants. These metabolites can then be used to synthesize optically active compounds that can be used by pharmaceutical and chemical industries to synthesize new drugs, polymers and other products of commercial importance [12].

APPLICATIONS

SPME offers some advantages for example it is fast and reduces sample preparation time by 70%, minimizes the use solvents and their disposal, its economical and reusable and very versatile. Some typical application for SPME are industrial applications such as surfactants, environmental analysis of water samples, flavour analysis of food products, forensic analysis of arson samples, toxicological analysis of blood alcohol and drugs in urine/serum and head analysis of the trace impurities of polymers and solid samples. SPME-GC/FID has been used in other areas apart from environmental studies. These are areas such as the analysis of aroma compounds of two different palm wine species "Matango" and "Raffia" from Cameroon [13], other application include analytical method for monitoring air borne trimethylamine, protocol for the analysis of high concentration of benzene, Toluene, Ethyl benzene, Xylene, isomers in water [14], Determination of benzene and halogenated benzene in pure and octanol saturated water [15]. Several investigations have established that SPME can be effective for monitoring drugs and drug metabolites in biological fluid and that SPME may accelerate the development of new pharmacological, food and beverage applications [5].

FURURE RESEARCH WORK

If a portable instrument is available, the SPME fibre can be immediately desorbed after sampling in the GC injection port, and storage of the sample on the fibre is not necessary. If the instrument is not movable to the field, the sample has to be carried to the laboratory. Collection and transportation of bulky and/or heavy samples of water can be avoided by using SPME for field extraction. The fibre can be exposed to the matrix directly where the sample is located, and only

the SPME sampler, with the fibre sealed in an appropriate way, has to be transported to the laboratory. In this case minimization of the sample losses from the SPME fibre is crucial for reliability of the results. Dedicated SPME sampler for field application has to be designed to preserve the integrity of the sample during the transportation between the sampling location and the laboratory. A portable field sampler which can concentrate and store organics from the field and perform indoor sampling is essential for tough sample handling problems, to reduce total costs and easier sample extraction, to decrease waste disposal, increase occupational safety through solvent less extraction procedures and lessen the variability of analytical process with ready to use and controlled products. These features will help to eliminate various drawbacks including high costs and excessive sample preparation times.More studies can be done such as optimisation of SPME extraction, matrix effects, change of extraction time and temperature, pH and ionic strength studies. This system can also be used for other fibre phases.

Conclusion

Analysis of Tap water samples and city park lake water sample was achieved and no detectable levels of PAHs were realised. Separation of pure standards was achieved using SPME/GC-FID and four calibration curves for the PAHs; Naphthalene, Fluorene, Phenenthrene and Flouranthene prepared. The method detection limits was about 1 ng/s while the theoretical limit of detection for FID is 10^{-12} g/s. Advantages of this analytical technique are; Inexpensive, Minimum sample preparation, Direct sampling operation from source, and very good selectivity. Future application of this solvent free methodology of extraction are encouraging for the monitoring of PAHs in Tap water.

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