CHAPTER 1

INTRODUCTION

The determination of organic contaminants in water is fundamental to the solution of the environmental protection problems. Solvent extraction is widely employed to isolate the analytes into a water-immiscible solvent. The basic factors that affect the quantitative recovery are the nature of the solvent used, the volume ratio of solvent to water sample, and the performance of the extraction i.e., batch-wise or continuous extraction. The exhaustive macroextraction which involves relatively large volume of solvent and preconcentration step is often the source of difficulties e.g., emulsion, false positive, interference and time consumption.

The simple one step microextraction was developed to resolve these problems. It is a very rapid and flexible method, requires no preconcentration, uses minimal glass-

wares and sample handling. The microextraction is also an economic extraction procedure.

The next step in the analysis of organic priority pollutants in water and wastewater is to characterize and determine each of the component present. High performance liquid chromatographic technique (HPLC) plays an important role on this step. It offers many advantages over the gas chromatographic technique, as follows :

(1) It operates at lower temperature (below 80 ^{o}C) while GC involves very high temperature of the column and detector. Condensation of the less volatile compound at the detector can cause trouble.

(2) It is highly selective for separation of isomeric compounds.

(3) It has available selective and highly sensitive detectors, such as ultraviolet and fluorescence detectors.

1.1 THE PURPOSES OF THIS STUDY

Microextraction procedure was developed for determination of Polynuclear Aromatic Hydrocarbons (PAHs) in water system. The following effects on the percent recovery of the organic priority pollutants, i.e., anthracene, fluoranthene, fluorene and pyrene, were studied.

1. The effect of shaking time

2. The effect of the extracting solvents.,i.e. toluene, hexane, and methylene chloride

3. The effect of the sample to solvent ratios,i.e., 10:1, and 50:1

4. The effect of salts, i.e., sodium chloride, and anhydrous sodium sulfate

5. Determination of the optimal absorption wavelength for each PAH which can be used to increase the sensitivity of this technique.

Quantification of the compound of interest was performed by the high performance liquid chromatographic technique using an UV-visible detector and the internal standard method.

1.2 BACKGROUND

Polynuclear aromatic hydrocarbons (PAHs) are homologs of benzene in which three or more aromatic rings are joined in different configurations (1). Their physical properties are mostly white crystalline solid and their boiling points are in the range of 200-400^{o}C. Although they are sparingly soluble in water because of nonpolar and neutral properties, they can be dissolved in many organic solvents i.e. methanol, hexane etc.

It has been known for many years that certain PAH posses carcinogenic property (2) and was first recognized by the London Surgeon Percivall Pott two centuries ago as responsible for cancer of the scrotum in chimneysweepers.(3) The others biological properties of PAHs are mutagenicity and covalent binding to macromolecules.(3) PAHs degrade slowly, persist in the tissues for long time, and are usually toxic.(1) The U.S.EPA has proclaimed that PAHs is one of the 65 priority toxic pollutants and in 1970 WHO in Europe also recommended that a concentration of PAHs should not exceed 0.20 μg/L in water.(4-5)

The environmental prevalence of PAHs is largely a consequence of PAH formation as the products of incomplete combustion and incomplete pyrolysis, from materials containing carbon and hydrogen. (1) Therefore, there are two different sources of PAHs

(1) man-made source, i.e., industrial wastes, vehicular emissions etc. Some PAHs are the raw materials in the manufactures of celluloid, carbon black, fungicide and insecticide.

(2) natural source such as forest fires and bacterial synthesis.(1)

The determination of PAHs in water systems is at present being studied with great interest and the analyst is confronted by three major problems:(1)

(1) The concentration of individual PAH ranges from less than 1 ppt in groundwater supplies to greater than 1 ppm in heavily contaminated sewages. These concentrations necessitate the application of some extraction or preconcentration techniques to raise the concentration to a level at which identifications can be made and quantitative analyses can be carried out.

(2) Serious handling error can arise where the concentration of the solute is less than 1 ppm due to losses or contamination in sampling or indeed in any step of the analytical processes.

(3) PAHs may represent as little as 0.01% of the organic fractions present in the water sample, the analytical scheme must be devised so that the PAHs can be analysed without any interference from other pollutants.

The analysis of PAHs in water system consists of two steps:

(1) extraction and preconcentration (6-26)

(2) qualitation and quantitation (27-45)

There are several extraction and preconcentration methods which can be used in determination of the PAHs e.g. adsorption (6-15), coupled column liquid chromatography (16), headspace (17) and liquid liquid extraction (18-27).

Adsorption method The adsorption on a solid adsorbent is used in order to isolate compounds dissolved in water. It is performed by passing the water sample through the adsorption column and then eluted with a

solvent. The appropriate adsorbents used were macroreticular resin (6-8), activated carbon (9-11), Tenax-GC (12-14) and open-pore polyurethane foam (15).

Junk et.al.(7-8) used the porous polymer resins in order to adsorb large number of model trace organic compounds in water. The accuracy and the reliability of this method depended on the method of evaporation as well as the vessel shape. The % recoveries of PAHs in the concentration range 20-500 ng/L were 98.

Lagana et.al. (9) proposed the determination of six PAHs in water sample by using a short column packed with graphitized carbon black. The best recoveries of them (53-109%) were obtained with toluene-benzene-acetonitrile (5:2:3) as the eluent.

Bruner (10) also examined the properties of different graphitized carbon black as traps for the extraction and preconcentration of PAHs from water. The best results were obtained with carbopack F, eluted with toluene at 100^{o}C.

Stenberg (11) showed the difference in adsorptive properties for PAHs and PAH derivatives and then compared the extraction by vacuum sublimation and the soxhlet extraction of PAH adsorbed on carbonaceous materials.

Leoni and Puccetti (12) had investigated the extraction of organic micropollutants such as pesticides and PAHs from surface and drinking water by using Tenax-GC. The recovery of such substance was over 90 % at optimum condition.

Pankow et.al. (13-14) improved the capabilities of adsorption/thermal desorption (ATD) with Tenax-GC in the determination of trace nonpolar aqueous organic compounds at the nanogram per litre level. The recovery of naphthalene obtained from gas chromatograph/mass spectrometer/data system (GC/MS/DS) was 81%, with 2% precision. .

Navratil et.al. (15) had tested the column of open-pore polyurethane foam for the ability to remove and concentrate PAHs from water, compared with Amberlite XAD-2 resin. The result showed that over 90 % recovery was

achieved for the 1-L of solution determined.

Coupled column liquid chromatography The principle of coupled column /HPLC is the enrichment of PAHs on an adsorption column, directly eluted from this column onto an analytical column, and separated by reversed phase HPLC. The two columns are joined together by switching valve. The advantages of this method are: it can be used with the small volume of the sample and sample handling for extraction and concentration is eliminated.

Oyler and his coworkers (16) described for the quantitation of PAHs in water at the nanogram to milligram per litre level. The procedure involved forcing an aqueous sample through a glass microfiber filter connected in series with a 7x50 mm C-18 HPLC column. The column containing the PAH material was then connected to a C-18 analytical micro-packed reversed phase HPLC column and was eluted with an acetonitrile-water gradient. Fractions corresponding to each UV peak of each PAH were collected and these fractions were then injected directly into a GC equipped with a sensitive photoionization detector (PID).

Headspace technique In headspace analysis, the volatile and semi-volatile PAHs were purged with a stream of inert gas or nitrogen gas and passed through a resin or cryogenic traps. The desorption was performed by thermal or flash heating and then analysed by GC.

Hertz et.al. (17) had developed a procedure for the determination of hydrocarbons in oil spills. Dynamic headspace sampling and the complementary analytical techniques of GC were utilized for quantitation of low molecular weigth PAHs.

Liquid liquid extraction The liquid-liquid extraction is a well-known sample preparation technique. It involves the partition behavior of the analyte between the two immiscible phases i.e. aqueous and organic phases. This technique can be classified into two categories:

(1) Macroextraction,1000 mL of water sample will be extracted with 100-150 mL of organic solvent. Since the large volume of the solvent used, the preconcentration step is necessary and the loss of volatile compounds can occur.(18)

Kasiske et.al. (19) analysed three types of water (ground, surface, and drinking water) with macroextraction followed by GC and HPLC. A 1-L sample was extracted three times with 30 mL cyclohexane and the combined extract was concentrated to 0.5 mL in a vacuum rotary evaporator.

Grob et.al. (20) had investigated the liquid-liquid extraction and the stripping method for the recovery of organic pollutants from water at concentration of 10 ppt. It can be concluded that this procedure was impractical according to the loss of the pollutants and the enrichment of the solvent impurities.

(2) Microextraction, a new liquid-liquid extraction, which used a small amount of solvent (0.2-10 mL) to extract 10-1000 mL of water sample, was developed by Rhoades and Millar (21) in 1965. The investigation of the concentration of volatiles in fruits was performed by using 0.25 mL of solvent for 50 g small fruit sample.

Rhoades and Ogawa (22,23) summerized the advantages of the microextraction over the macroextraction

as followed: the technique was easy to perform and very rapid, it required no preconcentration step, minimal glasswares and sample handling, and it was economical.

Rhoades and Nulton (22) extracted 10-100 mL of wastewater in volumetric flask with 200-1000 μL of solvent. The ratio of solvent : wastewater ranged from 1:40 to 1:100 was performed for analysis of priority pollutants i.e., volatile aromatics, phthalates, PAHs, and phenols. The precision, percent recovery, speed and its convenience were preferable than exhaustive macroextraction procedure.

Thrun et.al.(24) extracted benzene, toluene, ethyl-benzene and o-xylene from water by using microextraction. The effect of solvent to sample ratio (1:20 and 1:100), salting out with sodium sulfate, and the presence of other organic substances in the matrix were all evaluated.

Murray et.al. (18,25) used the microextrction procedure to analyze trace amount of organic compounds in water and found that the recoveries of these compounds approached a maximum when 1 mL of hexane was used to

extract 1 L of water containing 10-100 µg of contaminants. Large volumes of hexane would have a diluting effect with no appreciable increase in recoveries. The % recovery of naphthalene was about 27 , with RSD of 5.8% .

Thielen and his coworkers (26) applied the micro-extraction and capillary column GC techniques for repetitive analyses of wastewater discharge in plant discharge streams.

Tong and Karasek (27) identified seventy-six components in the extracts of three different diesel exhaust particulate sample by GS/MS.

JohnDennis et.al. (28) used capillary GC with FID and HPLC with fluorescence detector for a number of PAHs in five food samples. The capillary GC method was favoured for analysing a large number of PAHs, whereas the HPLC method was prefered for the individual analysis of a smaller number of PAH isomers.

Sorrell and Reding (29) presented the cyclohexane extraction, HPLC and UV detection of the PAHs in the

environmental water sample. This method could effectively quantitate fifteen PAHs in raw or finished water at 1-3 ng/L concentration.

Krustulovic et.al. (30) used a variable wavelength micro UV detector in combination with a fixed wavelength detector for routine analysis of selected PAHs in environmental samples by HPLC.

O'Haver and Parks (31,32) described the derivative and wavelength modulation techniques to determine low amount of benz [a] anthracene in the presence of excess chrysene and pyrene in the presence of excess anthracene without any prior separation. These techniques were especially useful for isomers that were difficult to separate chromatographically.