



CHAPTER 1

INTRODUCTION

1.1 MICROEXTRACTION

Solvent extraction is a widely employed as clean up and concentration steps in the procedures for analysis of a variety of organic substances in water and wastewater. The Environmental Protection Agency (EPA) recommends this method for separation and concentration organic priority pollutants in water.(1) The extraction procedures which have been employed vary depending on the nature of the solvent used, whether the extraction is performed continuously or batch-wise, and the ratio of the volume of organic solvent used to the volume of aqueous sample taken. Generally, the variation in batch-wise extraction is the sample to solvent ratio. A large volume of the organic solvent is required for increasing the percent extraction. The macro-extraction can involve contacting approximated 1 liter of aqueous sample as many as three times with 200-250 mL of organic solvent and it allows stand until the phase separation is complete. After removing the solvent, the extract must often be concentrated prior to analysis to achieve the desired sensitivity. The preconcentration step is made by using rotary evaporator or micro Snyder column. However, preconcentration is time-consuming and it can introduce serious errors from loss of

the analyte due to volatilization. The impurities in the solvent are also concentrated so that the resulting sample contains both the original impurities in water and in solvent.

On the other hand, so called microextraction, a one step extraction involving the extraction of small volume of water (10-100 mL) with an even smaller volume of organic solvent (10 mL or less) has been developed. The concentration of the analytes in organic phase accompanies the extraction and a separate preconcentration step can be avoided. Thus, in a matter of ten minutes or so, an aqueous sample can be taken, extracted and an aliquot of the extract taken for analysis. Owing to it is easy to perform, flexible and required minimal glassware and sample handling, then it is used for analysis many class of pollutants.

The advantages of the microextraction method over the macroextraction can be summarized as follows :

1. The method is very rapid.
2. Minimal use of glassware and special apparatus.
3. Sampling handling is minimized. Extract preparation is easily and readily accomplished by the analyst, there is no need for a "sample processing crew". Error and accidents, e.g., spills, etc. do not pose serious problems because an extract can be prepared immediately.
4. Solvent concentration is not necessary; thus, impurity in the solvent is not concentrated and no loss of solutes.
5. Economic.

1.2 THE PURPOSES OF THIS STUDY

In this study, MICROEXTRACTION technique was developed for determination of Polynuclear Aromatic Hydrocarbons (PAHs) in water system. The studies of various effects on percent recovery of microextraction were :

1. The effect of the shaking time, i.e., 2, 4, ...min.
2. The effect of the extracting solvents, i.e., methylene chloride, cyclohexane, and carbondisulfide.
3. The effect of the sample to solvent ratios, i.e., 9:1, 5:5, and 2:8.
4. The effect of the salting out with sodium chloride and sodium sulfate.

Analysis can be performed by using a gas chromatograph equipped with flame ionization detector (FID) and the internal standardization was used for the entire study.

1.3 HISTORICAL

It has been known for many years that certain PAHs possess mutagenic or carcinogenic properties after being metabolized (2), degraded slowly, persisted in the tissues for long time, and are usually more toxic. PAHs can act by interfering with metabolic processes and some metabolites are more toxic than the pure compounds. The U.S. EPA addressed PAHs as one of the 65 priority toxic pollutants.(3)

PAHs can enter the environment from several sources. The major sources appear to be from incomplete combustion or incomplete pyrolysis process which uses materials containing carbon and hydrogen. The amounts and types of individual chemicals that formed are dependent upon the starting hydrocarbons and the conditions of combustion or pyrolysis. The combustion of fossil fuels such as heat and power generation, refuse burning, industrial activity (coke ovens and coal refuse heaps), and vehicular emissions (especially diesel) become a large source of PAHs in environment. The other sources can be formed naturally such as lightning-ignited forest and they also occur naturally as minerals or by bacterial synthesized. Some PAHs are used as a dye intermediate, in the manufacture of some plastics, creosote, synthetic resins, lampblack, celluloid, carbon black, insecticide and fungicide and has been detected in the cigarette smoke and wood smoke.(4)

The PAHs found in water can originate from many different sources. A small amount of PAHs originates from endogenous or natural sources, the predominant sources of PAHs in water are man-made such as, petroleum spills, sewage, industrial wastes and washout from atmospheric pollution. Although PAHs have been shown to be strongly carcinogenic, it has never been definitively determined that the levels of PAHs found in drinking water are harmful. A drinking water standard for PAHs as a class has been developed. The 1970 World Health Organization European Standards for drinking water recommends a concentration of PAHs not to exceed 0.2 $\mu\text{g}/\text{L}$.(1) They found that there was insufficient data to propose a criterion for the protection of freshwater or of saltwater aquatic life. For the protection of human health, the concentration is preferably zero. An additional lifetime cancer risk of 1 in 100,000 is posed by a concentration of 0.028 $\mu\text{g}/\text{L}$.

The determination of PAHs in water systems is at present being studied with great interest since a large numbers of PAHs have been shown to be high carcinogenic. The observation in the early part of this century that certain constituents of coal and its by-products were tumor producing and potentially carcinogenic and then the initial search for the carcinogenic constituents of coal is occurred. Bloch and Dreifuss (5) obtained evidence that the carcinogenic factors was probably of the polynuclear aromatic hydrocarbons. Coke and Kenenaway (5) tested a large number of hydrocarbons known to occur in coal tar and succeeded in discovery of the first carcinogenic constituents of coal tar,

3,4-benzopyrene and other polycyclic aromatic hydrocarbons. The chemistry, metabolism and cancer activity of PAHs were studied by many scientists. However, the analytical investigations on these carcinogenic components, in particular, PAHs into the environment did not begin in earnest until the early 1960s with the work of Bornoff and his associates in Germany.(6) From that day to the present day, the number of different analytical methods which have been applied to the environmental samples containing PAHs as well as synthetic mixtures of PAHs was overwhelming. The analyst was confronted by a number of problems in the analysis of PAHs in water samples.

The first problem was that the concentration of PAHs was very low, the concentration range from less than 1 ppt (pg/g) in pure ground water supplies to greater than 1 ppm ($\mu\text{g/g}$) in the heavily contaminated sewage. The concentrations necessitated the application of some extraction or preconcentration technique to raise the concentrations to level at which identification and quantitative analyses can be made.

The second problem occurred when handling solutions where the concentrations of the solute was in a range less than 1 ppm. Serious errors can arise from contamination or losses in the sampling step and in any steps of analytical process.

The third problem was that PAHs may represent as little as 0.01 % of the organic fraction present in the water samples,

thus the analytical scheme must be devised so that the PAHs can be analyzed without interference from other pollutants.

Most analyses of PAHs in water system are carried out in two steps. The first step involving clean up and preconcentration steps, and the second qualitative and quantitative analyses of PAHs. Many principles and techniques have been developed for clean up and concentrate PAHs in water samples.

The adsorption principles, by using a solid adsorbent such as C₁₈ bonded phase, Tenax GC, XAD-resins, polyurethane foam or carbon black.(7)

The liquid-liquid extraction techniques, the traditional method for extraction and concentration organic compounds from water.(8)

The other techniques such as headspace analysis (9,10), thermal desorption (11) and coupled-column liquid chromatography (12). After PAHs have been separated, a number of methods for detecting and measuring the amount of PAHs present were available. A number of analytical techniques have become available for the analysis of PAHs in water systems. Two approaches are possible :

(1) An initial chromatographic separation followed by identification.

(2) A total analysis by spectroscopy.

In general the complexity of the sample limits advantages of the one step spectroscopic approach. The problem of separating and analyzing a class of compounds that contains no functional group and has a large number of structural isomers is a difficult one. All the chromatographic methods have been applied to this problem with varying degrees of success. The factors which must be considered in comparing and evaluating the various analytical techniques are

1. The separation efficiency should include complete isolation of PAHs from the other organic pollutants and the resolution of the PAHs fraction into its various compounds.
2. The lower limits of detection must be sufficient to resolve and identify the PAHs.
3. Ease and speed of analysis.

The ultraviolet or fluorescence detection are convenient methods subsequent to high performance liquid chromatography (13,14) or thin layer chromatography (15-17), the flame ionization detection or mass spectrometer are generally used with gas chromatography. (18)

Burnham et. al.(19) developed a method for extraction of trace PAHs and other organic contaminants from potable water by using macroreticular resins. The samples were passed through XAD-2 or XAD-7 column, then the sorbed compounds were eluted with diethyl ether. The percentage of compounds sorbed were determined by UV spectrophotometer.

Leoni et.al.(20) used Tenax GC for the extraction of PAHs and pesticide from surface and drinking waters, and then analyzed with GC. In the absence of other contaminants and under condition standardized at the time as optimal, the recovery of such substances was, on average, over 90 %, both for the pesticide and for PAHs.

Junk et.al.(21) used simplified resin sorption subsequent with GC/FID for measuring the organic components in water. The resulted showed that recovery of PAHs about 98% in the concentration range 20-500 ng/L.

Navratil (22) prepared open-pore polyurethane column by in-situ polymerization of toluene-carbon tetrachloride solutions of an isocyanate and polyol. The column have been hasted for ion exchange properties, solvent compatibilities, and ability to remove and concentrated PAHs from water. Solutions containing 1 microgram of pyrene per liter of water was determined by UV spectrophotometer and recovery of pyrene was approximately 100 %.

Das and Thomas (23) used variable wavelength fluorescence detector for HPLC to analyze nine major PAHs in the recycled waste waters from the quenching operation in a coke oven plant. The sample was soxhlet-extracted with cyclohexane. The fluorometric detection limit closed to subpicogram levels and precision studied gave a relative standard deviation ranged from 0.32 to 2.66 %.

Basu and Saxena (24) used the polyurethane foam plug for concentrating trace quantities of the six representatives of the PAHs from large volumes of finished and raw waters. The retention efficiencies of the individual PAHs on the foam were not less than 88 % from finished water and 72% from raw water.

Giger and Schaffner (25) determined the PAHs by using capillary GC. The samples were isolated by a sequence of solvent extraction, gel filtration and adsorption chromatography. Precision and accuracy of five individual PAHs were presented. Recovery were reported in range 80 to 100%.

Lagana and Rotatori (26) concentrated six PAHs in aqueous samples, using a short column packed with graphitized carbon black (GCB). The adsorbed compound were eluted by passing through a column with toluene-benzene-acetonitrile (5:2:3) and analyzed by using GC/FID. The result showed that GCB can be used successfully for the recovery of PAHs.

Jackson (27) used supercritical fluid chromatograph (SFC) approach to PAHs analysis. The SFC with fused-silica columns was successfully used in analyzing the real samples. The results showed that the SFC offered higher resolution than capillary GC.

Tong and Karasek (28) identified the three extractes of different diesel exhaust particulate samples. The PAHs have been isolated from the other compounds by HPLC fractionation. GC/MS was used for identification and quantification was used WCOT

column GC/FID. The quantitative results obtained showed high reproducibility, precision, and good reliability.

Tahboub and Pardue (29) described the use of first- and second-derivative of multiwavelength spectra with matrix least squares data processing to resolve mixtures of component with overlapping absorption spectra. Procedures were evaluated for PAHs in the presence of a light scattering component. The results showed that the multiwavelength first- and second- derivative spectra offered higher degree of selectivity than absorption spectra. PAHs were quantified in the ranges of 0.2 to 2.0 ug/mL.

Mieure and Dietrich (30) examined the macroextraction of organic pollutants from water systems. Methylene chloride was selected as the extraction solvent. The advantage of methylene chloride, the effect of salting out with sodium chloride, and the enrichment of the sensitivity by evaporation extracting solvent before analysis were evaluated.

Lao et.al.(31) used solvent extraction for extracting the PAHs from wood preservative sludge samples, and then injected the extract into GC/MS for qualitative identification and into GC/FID for quantitative determination. The chromatogram showed that the effluent contained very high concentrations of PAHs which were toxic to marine life.

Jungclaus et.al. (32) identified PAHs and other organic contaminants in the effluents from two tire manufacturing plants by extracting with methylene chloride,

followed by GC/MS. Some PAHs, i.e., naphthalene, fluoranthene and pyrene in concentration 0.1 mg/L were detected.

Ogan and Slavin (33) analyzed 16 PAHs in aqueous samples. These 16 PAHs of environmental concern, since 15 of them were included on the EPA priority pollutants list. After extraction, the concentrated samples were analyzed by reversed phase liquid chromatography with fluorescence detector. The method was applied to the analysis of several environmental samples and several of these compounds were quantified at concentration below 10 ng/L in the original sample.

Grob et. al. (34) have examined the potential of liquid extraction for the recovery of organic pollutants from water. A 1-liter sample was extracted with 100 mL of organic solvent. If the extraction efficiency was assumed to be 100 %, and if the extract was then reduced to 2 μ L of a single injection onto a capillary column, the solute was concentrated by a factor of 50,000. However, the impurities in the solvent were also concentrated by this factor. Grob concluded that the combined effect of the losses of the pollutants and the enrichment of the impurities made this procedure impractical. To avoid the problems created by large volume reduction, microextraction was developed. In this method, 1 L of water was extracted by less than 1 mL of solvent. After extraction, the extract can be analyzed directly. Proponents of this method preferred it due to only single extraction was required. Since the large sample to solvent ratio was used, the concentration of solutes in organic phase accom-

panied the extraction and the concentration step can be avoided. Thus, in ten minutes or so, a sample can be taken, extracted and aliquot of the extract was taken for an analysis. Grob compared the closed looping method with the rapid microextraction by using GC/FID analysis, the results showed that in the low and medium molecular weight regions, stripping was 3-4 times more efficient than liquid extraction, while for high molecular weight substances, i.e., PAHs, a stripping method rapidly loss efficiency.

Mieure (35) presented the rapid and sensitive method which it was suitable for determination of the organohalides in drinking water, natural water, and effluent water. The method was based on the microextraction subsequent with electron capture gas chromatographic determination. The effect of sample to solvent ratio and salting out effect were studied.

Richard and Junk (36) described the rapid microextraction method for the determination of halomethanes in water. The procedure involved vigorous shaking 10 mL of sample with 1 mL of pentane with subsequent electron capture /gas chromatographic analysis. Less than 0.1 $\mu\text{g/L}$ of halomethanes, i.e., chloroform, bromoform, and bromodichloromethane in a 10 mL water sample was easily detected.

Dressman et.al. (37) compared three microextraction procedures to the purge-and-trap method for the determination of trihalomethanes in drinking water. The results showed all three microextractions offered a similarly sensitive and accurate

alternative to the purge-and-trap method. However, the extraction method was more convenient to implement and used than purge-and-trap method.

Murray (38) developed an extraction flask for extraction with a small volumes of solvent using Grob's method. A two necks 1-L flask with a capillary tube sealed to a shortened center neck was used. Nine hundred eighty milliliters of water and 200 uL of hexane were shaken manually for 2 min. The flask was then tilted, so that by addition of more water through a sidearm the solvent layer was forced into the capillary and can be readily removed. Murray compared a rapid microextraction with two macro methods, i.e., a distillation-solvent extraction and a continuous extraction for analyses of trace amounts of organic compounds in water by gas chromatography. The results showed microextraction gave as good a recovery but not better than two macroextractions. Since a microextraction was so rapid while two macroextraction methods required several hours in preparation.

Rhoadas and Nulton (39) described a microextraction in which the sample to solvent ratio ranged from 40:1 to 100:1. The use of this extraction method for extracting the priority pollutants, e.g., volatile aromatics, phthalates, phenols, and polynuclear aromatic hydrocarbons was evaluated. Results obtained during an EPA verification analysis of variety of industrial process waters and effluents were discussed.

Thrun and Oberholtzer (40) studied various effects on the extraction efficiencies of microextraction technique to extract benzene, toluene, ethylbenzene, and o-xylene from water into pentane. The effects of sample to solvent ratio (20:1 and 100:1), salting out with sodium sulfate, and the presence of other organic substances in the matrix were evaluated.

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