



CHAPTER 1

INTRODUCTION

Ethylbenzene and chlorinated aromatic hydrocarbons are produced annually by chemical companies in U.S.A. (1, 2). Ethylbenzene is used as a solvent or diluent in the paint industry, agricultural sprays for insecticide and as a component of automotive and aviation gasoline. It may be introduced into an environment by the vaporization during solvent used, pyrolysis of gasoline and emitted vapors at filling stations (1). For monochlorobenzene and dichlorobenzenes, they are used as a process solvent and as a raw materials or intermediates in the manufactures of other chemical products such as pesticides, phenols, dyestuffs, etc. The discharged streams from those manufactures are the source of the entry of these organics into environment (1). The chlorinated aromatic compounds are relatively unreactive and biologically non-degradable, these toxic compounds may remain in the environment for weeks or months and may be bioaccumulated in fish and animal (2). Furthermore, they may migrate in aerosol or vapor phase over extended distances and may be deposited by natural processes as rain or gravity (2).

To control this type of pollution, it is important to have the ability to identify and quantify these trace organic compounds in water. There are various methods used for monitoring the trace organic priority pollutants in water and waste water e.g.,

direct aqueous injection (3), solvent extraction (4-7) , steam distillation (8-9) , adsorption technique (10-14), purge and trap (15-20), headspace technique (21-29) , etc. Each method has advantages and disadvantages which relate to equipment needs, desired limits, sample matrix and analysis speed. The two methods that the United States Environmental Protection Agency (EPA) recommended for the determination of trace volatile and semivolatile organic priority pollutants in water were purge and trap (16-17,30) and liquid - liquid extraction (30-32). However, at such the low concentration level of ppb or ppm, these two methods required the sample preparation including isolation and pre-concentration which must be performed prior to the analysis to achieve the desired sensitivity (32-34). This pre-concentration step can cause serious problems drawback to the qualitative and quantitative analyses, e.g., the loss of the organic constituents, the enrichment of the original impurities in water and solvent, the interference of impurities in the stripping gas, the large amount of water passing the absorbent, time consumption, etc. (32-35).

The headspace analysis technique, therefore, seems to be an attractive alternative for quantitative analysis of organic substances in water due to it is a simple, rapid, sensitive, reliable method and required no pre-concentration step (35-38). The advantages of this technique can be summarized as follow :

1. Headspace is a convenient way to isolate and concentrate many volatile and semivolatile organic compounds for gas

chromatographic analysis. The sample does not have to be vaporized for the gas chromatographic analysis due to low concentrations of the components already exist in the vapor phase.

2. No overloading or contamination of the column with high boiling or non-volatile material occurs.

3. There is also no pre-concentration step required for the determination of trace organic compounds in water. Minimum detection limits are frequently in the mid-ppb concentration using a flame ionization detector.

4. It is an economic method.

In order to develop the headspace analysis technique for the determination of some semivolatile organics i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene in water, various parameters which affect the sensitivity would be studied and evaluated for the optimum condition of the headspace analysis. The parameters studied were:

1. The equilibration times of the sample i.e., 0, 3, 5, 10,....., etc. minutes.

2. The temperature for equilibrating sample i.e., 30.0°, 40.0°, 50.0°, 60.0° and 70.0° C.

3. The liquid to gas phase ratios i.e., 5:55, 10:50, 15:45, 25:35, 35:25, and 50:10.

4. The headspace gas injection volumes i.e., 0.50, 1.00, 1.50, 2.00 mL.

5. The salting out effect with sodium chloride and sodium sulfate.

In addition the accuracy and precision of this technique were also studied and evaluated prior to use it in the analysis of these compounds in the real water samples. The gas chromatograph equipped with a flame ionization detector (FID) was used for the study.

HISTORICAL

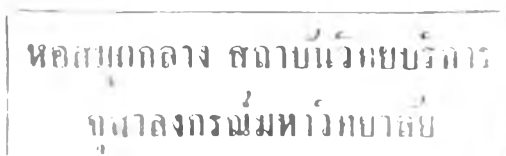
Ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene are a group of semivolatle organic compounds that has been classified as priority pollutants by EPA (30). The information on their toxicities and metabolic studies have been documented (1, 39-40). The human exposure to dichlorobenzene is reported to cause hemolytic anemia and liver necrosis (1). In addition, the dichlorobenzenes are toxic to nonhuman mammals, birds, and aquatic organisms and impart an offensive taste or odor to the water (39). For ethylbenzene, the major effects following acute and chronic exposure include liver and kidney pathologies and nervous system disorders (39). It has also been classified chlorobenzene in EPA's Group as a possible carcinogen due to it has been shown to cause mutagenic effects in higher plants and certain microorganisms (39). Hence, the concentration of ethylbenzene in water recommended by EPA should not exceed 1.4 $\mu\text{g/L}$ and the concentration of monochlorobenzene and dichlorobenzenes in water should not exceed 500 $\mu\text{g/L}$ (1).

The headspace technique used in the analytical work was accomplished more than 20 years ago and the first application of the headspace analysis for the quantitative determination of organic substances was the investigation on the enzymatic generation of the volatile components of raspberries (22,24).

McAuliffe (25) described the basic fundamental of the analysis of volatile organic components in water with unknown partition coefficients by multiple gas extraction. This analysis was based on successive gas chromatographic analyses after repeated equilibration of helium with aqueous sample containing dissolved hydrocarbon. The method gave qualitative separation of hydrocarbon from highly water-soluble organic compounds. The results were shown that normal alkanes were partitioned into the gas phase higher than 96% owing to their low solubility in water, the cycloalkanes partitioned less into the gas phase than do alkanes, and the aromatic hydrocarbons which were relatively high solubilities in water with relative to their vapor pressures, remained principally in the water phase when equal volumes of water and gas were equilibrated.

The first successful application of headspace analysis to the determination of alcohol content in blood was described by Curry and co-worker (26). A 2 mL of blood sample was equilibrated and the equilibrium gas phase of ethanol was analyzed. This success contributed to the widening acceptance of this method and promoted the development of the appropriate instrumentation (22).

Hanna and Marek (27) reported on the analysis of



toluene, benzene, ethylbenzene and trichloroethylene in blood using headspace gas chromatography. One g of solid NaCl, 2.00 mL of internal standard and 1.00 mL of blood were shaken in a close vessel with rubber membrane and cap for 30 min at 70°C and 1.00 mL of the headspace gas was analyzed by GC/FID. The results were shown that the method had a relative standard deviations of 5 - 9 % and it was suitable for use in assessing industrial exposure or acute accidental or suicidal intoxication.

Drozd and Novak (35) conducted a comparison of headspace analysis, liquid-liquid extraction and purge and trap. The results from the study were also discussed.

Dietz and Singley (38) compared the headspace method to the purge and trap method for determination of chlorinated hydrocarbons in drinking water, well water, industrial water and lake water. The chromatograms obtained from the purge and trap method were of much poorer quality than those observed using the headspace technique e.g., peak tailing and detector base line noise. With headspace technique, 25 samples per day could be routinely analyzed, while only 8 - 12 samples per day could be analyzed with the purge and trap. In addition, for samples that contain high levels of volatile organics, the purge and trap system could exhibit the carried over effect. Therefore, the headspace method was preferable to purge and trap technique for routine sample analyses of volatile hydrocarbons.

Kolb, Auer and Pospisil (28) analyzed volatile halogenated hydrocarbons from aqueous solutions by headspace gas chromatography

with fused silica capillary column and an electron capture detector with detection limits below the ppb level. The quantitative analysis of these compounds by means of the internal standardization method, external standardization method and the standard addition method was discussed and was compared with the multiple headspace extraction procedure, which was based on a repeated headspace extraction of the sample.

Kazuo, et al. (41) used the headspace technique to determine chlorinated and brominated organic compounds in drinking water. After equilibration of volatile halogenated compounds at 20°C in the headspace vial , the headspace gas was sampled and injected into a gas chromatograph equipped with an electron capture detector. By using a Silicone DS 550 column, nine compounds were fully separated in the following order CHCl_3 , CH_2CCl_3 , CCl_4 , CCl_2CHCl , CHBrCl_2 , CCl_3NO_2 , CHBr_2Cl , Cl_2CCCl_2 , and CHBr_3 . Recoveries of these compounds added to the raw water and tap water were 95-106 %.

Meier (42) analyzed organohalides in water by headspace gas chromatography with detection limits ranging from 0.01 $\mu\text{g/L}$ for CCl_4 to 20.0 $\mu\text{g/L}$ for CH_3Br ; and from 0.005 $\mu\text{g/L}$ for CCl_4 and 1,1,2,2-tetrachloroethane to 0.07 $\mu\text{g/L}$ for CH_3Br by the purge and trap method.

Antonius et al. (43) suggested that headspace gas chromatography using splitless coupled capillary columns of CP-WAX 51 was suitable for determination of volatile aliphatic and aromatic hydrocarbons in refinery effluents. The method provided sufficient separation and high sensitivity; the relative standard deviations

were $\pm 5.7 - 16.4 \%$ and the detection limit was 10 ppb.

Dieter and Claus (44) discussed the instrumentation, gas chromatographic parameters and problems, and their solutions in headspace gas chromatograph of volatile halogenated hydrocarbons. The application of the technique in water control was described.

Pugen (45) developed headspace technique for the determination of organic compounds in water. A 40 mL water sample containing 15 g of anhydrous Na_2SO_4 at $65 \pm 0.1^\circ\text{C}$ under reduced pressures was determined by this technique with detection limits for acetadehyde, 2-chloro-1,3-butadiene, and benzene of 0.016, 0.001 and 0.001 mg/L, respectively. The linear response was observed for a concentration range of 10^{-3} to 1 mg/L . The sensitivities and recoveries of the method were less than 5 and were higher than 90 %, respectively.

Jones (46) discussed the headspace technique for analysis of complex liquid samples. The application of the technique to analysis of complex liquid samples was also illustrated by analysis of industrial samples, analysis of flavor and fragrance compounds, and analysis of chemical process waste.

Keeley, et al. (47) studied the sorption of benzene and toluene on poly(tetrafluoroethylene) (PTFE) during headspace analysis. The solubilities of benzene and toluene in aqueous NaCl solutions were determined at 25°C in the presence of both PTFE and glass covered magnetic stirring bars. The difference in the results was attributed to the absorption of the aromatic hydrocarbons on the PTFE covered stirring bars.

McNally and Grob (48) applied headspace analysis to determine the solubility limit values of members of the chlorinated alkanes, chlorinated alkenes and chlorinated aromatics listed as the EPA Priority Pollutants.

Comba and Kaiser (49) described an improved headspace method for the determination of volatile contaminants at ng/L level in water. Detection limits at the 1.0 ng/L level or better could be determined for CCl_4 using a capillary column and electron capture detector. This method was also applicable to drinking, surface, and ground waters for measurement of haloform, halomethanes, and haloethanes.

Croll and Summer (50) used headspace technique for determination of trihalomethanes in water. Headspace vapors were withdrawn from the sample container at ambient temperature and injected into GC equipped with electron capture detector. Relative standard deviation of less than 2% was observed for treated river water samples and the results were comparable to those of an established liquid-liquid extraction method.

McNally and Grob (36) have written a review of the environmental applications of static and dynamic headspace analyses. The characteristics of static and dynamic headspace analyses were discussed. Some examples of the environmental applications of these two techniques were also illustrated.

Kolb (51) has written a review with 8 references containing two headspace gas chromatographic analysis methods for determination of volatile halogenated hydrocarbons in water. The 2-

column method, in which a capillary column with electron capture detector and a pack column with a FID were used, was suitable for the automatic routine analysis. The single capillary column with FID and cryofocusing environmental method had good separation efficiency and was suitable for the determination of a large number of compounds.

Kaiser and Oliver (52) described a rapid method for quantitative determination of volatile halogenated hydrocarbons in water. This method was based on the equilibration of the analyzed water with a small volume of gaseous headspace under reduced pressure at elevated temperature. After equilibration, the headspace was returned to atmospheric pressure and the headspace sample was analyzed with GC/ECD. Less than 10 ng/L of halogenated hydrocarbons including chloroform in a 60 mL water sample was easily and rapidly detected.

Kaing and Grob (53) used the headspace technique for the determination of volatile compounds i.e., benzene, toluene, chlorobenzene, ethylbenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene in soil. The precision and accuracy of the headspace procedure were determined and the relative standard deviation for 3 grams of soil sample spiked with 5.1 ppm pollutants mixture in a 20 mL vial was less than 3% . This technique was concluded to be a simple, precise and accurate method for the analysis of volatile compounds in soil.