

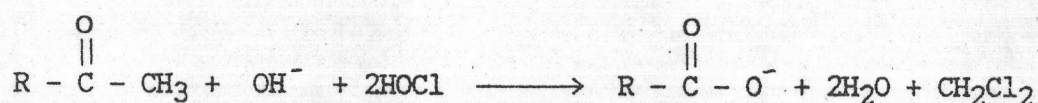
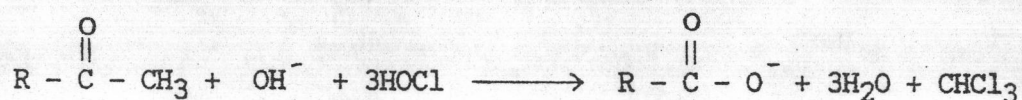
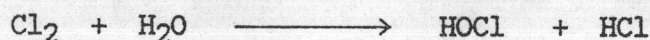
## CHAPTER I



### INTRODUCTION

#### 1.1 Problem Definetion.

Volatile chlorinated hydrocarbons, possess 1 or 2 carbon atom (s), such as methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene, are extensively used as a solvent or diluent in many industries for oils, fats, waxes, lacquers, varnishes, rubber, paints and plastics, and as a raw materials in the manufactures of other chemical products especially flouorocarbons. They are also used as a propellant, a fumigant ( agriculture spray ) to control weeds, fungi in soil and insect pests, a fire extinguishing agent and a dry-cleaning agent (1,2,5). Product residues and the waste water from those manufactures are the source of the entry of these organics into the environment. In addition, some volatile chlorinated hydrocarbons are produced during water treatment by reaction of chlorine, used for disinfection or oxidation, with the naturally occurring organic compounds in the water as a following (1,3)



The chlorinated compounds are relatively unreactive and biologically non-degradable. These compounds may retain in the environment for months or years and may be bioaccumulated in fish and animal (2). Furthermore, they can migrate to the atmosphere and may be deposited by natural processes as cloud or rain.

Methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene are a group of volatile chlorinated hydrocarbon compounds that has been classified as priority pollutant by EPA (1,30). The toxicity and metabolism of these organics have been studied by many investigators and shown to be mutagenic and carcinogenic substances (1,2,4,5). The primary health effect is central nervous system depression with anesthesia, inebriation, narcosis and subsequently health effect is hepatotoxicity, nephrotoxicity and carcinogenicity. (55) Henderson(4) compared toxicity and activity of halogenated hydrocarbons in nonhuman animals e.g., rabbits and mice and revealed that carbon tetrachloride was the most toxic in these compounds. Volatile chlorinated hydrocarbons have been shown to be rapidly adsorbed on oral and inhalation. They can affect the membrane of mitochondria and endoplasmic reticulum and inhibit enzymes activity in Krebs' cycle. The results of performing lead to fatty liver, kidney damage and contribular necrosis. Hence, the concentration of these organics in water are determined to protect harmful effects i.e., chloroform recommended by World Health Organization (WHO) should not exceed  $30.0 \mu\text{g/L}$  in drinking water (10) and national primary drinking water regulation by EPA established maximum contaminant



levels for carbon tetrachloride, trichloroethylene and 1,1,1-trichloroethane of 5 , 5 and 200  $\mu\text{g/L}$ , respectively. (7)

Analytical methods for determination of trace amounts of these chlorinated hydrocarbons in water generally require a preconcentration step prior to gas chromatographic ( GC ) analysis. Several preconcentration techniques have been developed for monitoring these pollutants e.g., solvent extraction (3), direct aqueous injection (51), purge and trap (13-17), headspace technique (19-21), etc. Each method has advantages and disadvantages which relate to equipment requirements, detection limits, sample matrix, sample volume, analysis speed and complexity. The method that the United States Environmental Protection Agency ( EPA ) recommended for the determination of trace volatile organic priority pollutants in water was purge and trap technique (7). This method can detect volatile chlorinated compounds in low concentration level of part per billion(ppb) or part per million (ppm) for the suitable condition (7, 8,13-17) but it necessarily required complex equipment to separate the organics from water and bring about serious problem drawback to the qualitative and quantitative analyses e.g., the loss of the organic constituent, the interference of impurities in adsorbent trap or stripping gas, poor resolution and peak tailing caused by a too long stripping time, the large amount of water passing the adsorbent and time consumption ( 8, 39 ).

## 1.2 Hypothesis.

The headspace analysis technique seems to be an attractive alternative for quantitative analysis of volatile chlorinated hydrocarbons in water because it is a simple, rapid, sensitive and reliable method (11,19-23). This method is based on the fact that when a water sample that contains organic compounds is sealed in a vial, organics will equilibrate themselves between the sample phase and the headspace gas phase. The gas phase is subsequently removed for GC analysis. Distribution of compounds between the two phases depends on temperature, vapor pressure of each compound, sample matrix influencing on compound activity coefficients and the ratio of the headspace gas to the liquid volume in the vial. The advantages of this technique can be summarized as follows (8,11,19,22)

1. A headspace technique is an easy means for isolating and concentrating many volatile organic compounds in water, soil or sediment for gas chromatographic analysis. The sample do not have to be vaporized by high temperature gas chromatograph injector due to low concentration coponents of sample already exist in the vapor phase.

2. No overloading or contamination of the GC column with high boiling, non-volatile or ionic materials occurs.

3. There is also no complicated equipment required for sample preparation and it indicates high precision and minimum detection limit in ppb level.

4. It is an economical method.





### 1.3 Literature Reviews.

The headspace technique was successfully used for the determination of volatile organic substances more than 30 years ago and the first application of the headspace analysis studied on the enzymatic formation of volatile compounds in Raspberries (26). Weurman showed that gas chromatographic analysis of headspace proved useful for the quantitative determination of small amounts of volatiles in aqueous solutions and of enzymes producing compounds such as iso-propanol, ethyl acetate and acetone under the optimum conditions.

Curry and co-worker(25) described the first successful application of headspace analysis to the determination of some volatile poisons as ether, acetone, ethanol, paraldehyde and chloroform in blood. A 1 mL of blood and 0.5 g of solid potassium carbonate were equilibrated in the closed apparatus, which had total volume of approximately 7 mL. The potassium carbonate served to decrease the vapor pressure of water and a 1.0 mL air sample was then taken in a hypodermic syringe from apparatus and was injected into the gas chromatograph for quantitative analysis.

Multiple equilibrium gas extraction exemplified by the analysis of hydrocarbons in water was described by Mc Aullife (27). This analysis was based on successive gas chromatographic analyses after repeated equilibration of helium or nitrogen gas with an aqueous sample containing dissolved hydrocarbons such as fresh water,

sea water, subsurface brines and biological fluids. This method gave qualitative separation of hydrocarbons from highly water-soluble organic compounds and good results for analysis of normal alkanes which partitioned 96 % or greater into the gas phase owing to their low solubilities in water when equal volumes of gas and water were equilibrated. However, cycloalkanes partitioned less than 90 % into the gas phase and the aromatic hydrocarbons remained principally in the water phase because they relative had high solubilities in water in relative to their vapor pressure.

Nunez (11) and Drozd (6) described the theoretical and practical aspects of static headspace analysis. They showed that the headspace analysis was a suitable method for the determination of volatile organics in liquid and solid samples because of its high sensitivity, precision, reliance, accuracy and simple operation. In addition, this technique could detect organic compounds in part per billion ( ppb ) level and no overloading and contamination of the chromatographic column with water and high-boiling compounds or non-volatile materials occurred. An automatic static headspace procedure was explained by the equilibrium sample gas was sucked up by vacuum into the a calibrated sampling loop and upon turning over the eight way stopcock into the second operating position, the contents were purged into the gas chromatograph. However, this technique failed when analytes with very low vapor pressure or high boiling point were analysed.

Kolb (34) studied an application and the sensitivity of



headspace technique for the analysis of some organics in liquid and solid samples. The increased sensitivity of the method could be achieved by the addition of salt into the samples and using a more selective gas chromatographic detector, for example, an addition of magnesium sulphate caused the detection limit of acetic acid and propionic acid in aqueous solution decreased from 1000 and 250 ppm to 80 and 15 ppm respectively, and the analysis of some aromatic hydrocarbons in water that could be succeeded with a flame-ionization detector ( FID ). In addition, he also reported the operation for the determination of vinyl chloride monomer in all types of PVC and the residual solvents in adsorption material and printed foils.

Kaiser and Oliver (19) analysed volatile halogenated hydrocarbons such as  $\text{CHCl}_3$ ,  $\text{CHBrCl}_2$  and  $\text{CHBr}_2\text{Cl}$  in water by headspace gas chromatography with glass column packed with 10 % OV-1 Gas Chrom Q, 80/100 mesh and  $^{63}\text{Ni}$  electron capture detector. The result showed the good reproducibility and the detection limit in 0.1 to 10  $\mu\text{g/L}$  range for 2 mL cold water sample in 60 mL volume separatory funnel with teflon stopcock (2-mm. bore) at 70 °C equilibration temperature, for 30 minutes with pressure of 10 torr using water pump suction and the headspace injection of 5  $\mu\text{L}$ .

Droz and Novak (29) used headspace gas analysis for quantitation by standard addition method and capillary column gas chromatography with splitless sample introduction to permit the reliable determination and identification of ultra-trace amounts of

volatile hydrocarbons in aqueous samples. The equilibration of each compound established between 50 mL of water sample and 50 mL of headspace gas in 30 min. The method gave a percent relative standard deviation ( %RSD ) of 7.8 % for toluene, 7.8 % for ethylbenzene , 2.9 % for m-xylene, 4.7 % for o-xylene and 7.0 % for benzene in concentration range of 25 to 100 ppb.

McNally and Grob (28) applied headspace analysis to determine the solubility limit of halocarbons listed as the EPA priority pollutants. Each standard solution of increasing concentration was prepared in a 100 mL volumetric flask and allowed to equilibrate in a constant temperature at least 24 h. After that the solutions were pipetted to vials for headspace analysis to find out the signal of each concentration of the compounds. At the point where the solubility limit was reached the maximum value of the signal became independent of the amount of organic solute present in the liquid state and the graph of detector signal versus concentration of solute was no longer rised linearly but levelled off.

Lukavic, Mikulas and Kiss (20) determined seven chlorinated hydrocarbons i.e., 1,2-dichloroethane, trichloroethylene, tetrachloro ethylene, 1,1-dichloroethane, 1,1-dichloroethylene, 1,1,1,2-tetrachloroethane and 1,1,2-trichloroethane in waste water by headspace gas chromatography with 10 % 2-ethylhexyl sebacate + 2 % sebacic acid on chromaton N AW packed column and a flame ionization detector. The external standard method was applied for quantitative analysis in



the concentration range of 0.5 to 200 ppm.

Dietz and Singley (8) compared the headspace method with the purge and trap method which recommended by EPA for determination of volatile organics in drinking water, lake water and industrial water. The obtained results were equivalent but the chromatograms provided from the purge and trap method were of much poorer quality than those observed using headspace technique, e.g. peak tailing and detector base line noise. In addition, only 8 - 12 samples per day (8 h) could be analyzed using purge and trap method while 25 samples per day (8 h) were routinely examined by headspace method. Therefore the headspace technique was preferable to purge and trap method for routine sample analyses of volatile halocarbons in water samples.

Bassette (30) commended the headspace gas chromatographic analysis for measuring flavour in food including its use in qualitative and quantitative analyses and sources of errors and limitation of this method. It was necessary to be caution in an interpreting results of these analyses owing to the interaction of volatile components with lipids, protiens, acid or bases would affect the concentration of vapor markly in the headspace area.

Comparison of headspace analysis and liquid-liquid extraction methods were carried out for determination of trihalomethanes in drinking water as discussed by Onodera and Tabucanon (3). The sampling apparatus and procedure were very simple

and easy for both methods which were application for determination of the halomethane concentrations ranging 0.1 to 200  $\mu\text{g/L}$  but possible disadvantages for liquid - liquid extraction were its somewhat low sensitivity comparison with headspace analysis owing to the interferences i.e. non-volatile compounds and impurities were co-extracted into the extracting solvents and time consumption because the co-extraction non-volatile compounds required several minutes to be eluted from the column with late analysis. Hence, the sensitivity for chloroform and bromodichloromethane obtained by headspace technique were approximately 2 or 3 times higher than those obtained by liquid - liquid extraction method.

Johnson and co-worker (33) discussed the headspace method for the analysis of methane dissolved in sea-water by performing equilibration of the system at temperature of 25  $^{\circ}\text{C}$  in 50 mL serum bottles. The relative standard deviation of this analysis was from 0.3 to 2.6, the mean recovery was 92.7 % and there was no relationship between concentration and percent recovery over the concentration range tested ( 0.2 to 15  $\mu\text{mol /Kg}$  ).

Tsuchihashi, Nakajima and Nishikawa (35) investigated the analysis of stimulants in urine using headspace gas chromatographic system equipped with in-column sample trifluoroacetylation unit. A 5 mL aliquot of urine containing stimulants was pipetted into a 20 mL autosampler vial together with 3.5 g potassium carbonate. The vial was sealed and heated for 20 min at 80  $^{\circ}\text{C}$ ., then 0.8 mL of headspace gas and N-methylbis( tri - fluoroacetamide) gas were



injected simultaneously into gas chromatograph with a flame ionization detector. Calibration graphs prepared by the absolute calibration curve method showed good linearity over the concentration range of 0.04 to 50  $\mu\text{g/mL}$  for methamphetamine and amphetamine. The detection limits were 0.03  $\mu\text{g/mL}$  for both of these compounds.

McCown and Radenheimer (36) described the equilibrium headspace gas chromatographic method for the determination of volatile residues in vegetable oils and fats. The samples were prepared by weighting approximately 5.0 g of each sample into 40 mL vials and holds at 125  $^{\circ}\text{C}$  for 30 min. The recovery and relative standard deviation were over 98 % and less than 1 %, respectively and this method could be applied successfully to all of the analytes on the Federation of oils, seeds and fats.

Lawrence and Chadha (37) discussed the headspace technique for analysis of sulfite in foods. Minimum detectable levels of this method was about 1  $\mu\text{g/g}$ , based on a 15 g food samples for example, dried peaches, corn syrup, wine and garlic powder. However some foods e.g., canned shrimp and frozen shrimp caused the lower sulfite recovery due to sulfite was mixed with the foods prior to the analysis and resulted in the reaction of sulfite with the sample matrix to form irreversibly bound or oxidized products.

Keeley and Meriwether (38) studied the adsorption of benzene and toluene on poly(tetrafluoroethylene)(PTFE) during headspace

analysis. The adsorption of benzene and toluene on PTFE and glass covered magnetic stirring bars were determined in sodium chloride solutions of different ionic strengths from 0 to 4 at 25 °C in 125 mL septum bottles. The difference in the results was attributed to the adsorption of organic hydrocarbons on the PTFE and glass covered stirring bars.

Jones and co-worker (52) discussed the application of headspace gas chromatography to complex liquid samples. An automated headspace technique was easily applied to many complex industrial and natural samples. For example, a quantitative method for determination a variety of chemical process waste, industrial samples, and flavor and fragrance compounds and for the rapid approximation of total volatile hydrocarbon in storage tank sludge.

McNally and Grob (53) have written a review of the distinction of environmental application between static headspace and dynamic headspace which was known as purge and trap analysis. The advantages and disadvantages of the procedures of both techniques were discussed. Some compounds in air, water, waste water, industrial effluents, soil and sewage were also illustrated and determined by these two methods.

Kolb, Auer and Pospisil (21) analyzed volatile halogenated hydrocarbons in aqueous solution by headspace gas chromatography with SE-54 fused silica capillary column and an electron capture detector with detection limits below the parts per billion level. Calibration



of quantitative determination by the internal and external standard techniques and by the method of standard addition was discussed and compared with the multiple headspace extraction procedure, which was based on a repeated headspace extraction of the sample.

Roe and Stuart (39) used manual headspace method to analyze the six important volatile aromatics of gasoline, i.e. benzene, toluene, ethylbenzene and the three xylene isomers in ground water and soil samples. The method had proven to be a rapid and effective means of analyzing environmental samples. 20 samples per day ( 8 h ) were routinely examined by this headspace method and samples with a wide range of contamination from these volatile compounds ( about 1  $\mu\text{g/L}$  to at least 15000  $\mu\text{g/L}$  ) could be determined without dilution or other sample-handling techniques.

Croll and Summer (10) described a simple and rapid headspace with an electron capture gas chromatographic method for determination of trihalomethanes in water. Headspace vapours were withdrawn from the sample containers at ambient temperature and injected by means of a gas tight syringe with a valved needle, thus eliminating the contamination problems associated with established liquid-liquid extraction and purge and trap methods. Relative standard deviation of less than 2 % were observed for treated river water samples, and the results were comparable to those of an established liquid-liquid extraction method. The detection limit of chloroform, bromodichloromethane, dibromochloromethane and bromoform were 0.22, 0.01, 0.03 and 0.23  $\mu\text{g/L}$ , respectively and the

response was linear up to at least 100  $\mu\text{g/L}$ .

#### 1.4 The Purpose of the Study.

The headspace analysis technique was developed to analyze some volatile chlorinated hydrocarbons i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloro ethylene in water. The various parameters which affect the sensitivity would be studied and evaluated for the optimum condition of this technique. The parameters studied were :

1. The equilibration times of the sample i.e., 0, 10, 20, 30, 40, ... , etc. minutes.
2. The temperature for equilibrating sample i.e., 50<sup>o</sup>, 60<sup>o</sup>, 70<sup>o</sup> and 80<sup>o</sup> C.
3. The liquid to gas phase volume ratios i.e., 10:50, 20:40, 30:30, 40:20 and 50:10.
4. The headspace gas injection volumes i.e., 0.50, 1.00, 1.50 and 2.00 mL.
5. The salting out effect with sodium chloride, anhydrous sodium sulfate and calcium carbonate.

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 samples. The gas chromatograph equipped with flame ionization detector ( FID ) and electron capture detector ( ECD ) was used for the study.