



## CHAPTER I

### INTRODUCTION

The separation of organic priority pollutants in water and wastewater by means of extraction is employed to isolate the analytes into a water-immiscible solvent. Since quantitative recovery is stressed, multiple extractions with relatively large volumes of solvent are necessary. This exhaustive approach to the analysis is often the source of difficulties, e.g., emulsion, interferences, false positives and time-consumption. Therefore, a one step microextraction technique was developed for use in the analysis of water samples. Since, the microextraction technique is easy to perform, flexible, and requires no preconcentration step, minimal glassware and sample handling, it fulfills not only the practical requirements, but is also capability of giving reliable data.

The purpose of this investigation was to study

1. A microextraction technique and the effect of using the different sample-to-solvent ratios, e.g., 9:1, 5:5 and 2:8 on the percent recovery of an organic compound,
2. The effect of salts, e.g., sodium chloride and sodium sulfate on the percent recovery of each organic priority pollutant, and
3. The effect of various solvents, i.e., hexane, isooctane and cyclohexane on the percent recovery of organic priority pollutants.

Quantification of the data was performed by the gas chromatographic technique using an electron capture detector (ECD) and the internal standard method for the entire study.

## Historical



Some halogenated alkanes, e.g., chloroform and other volatile organohalides are considered to be a carcinogen and they are found in water sources in the U.S. (1-5), Japan (6) and many countries in Europe (7-8). These substances are priority pollutants and toxic, even though they may be in a small quantities, the concentration 2-4 ppb of the halogenated alkanes and alkenes e.g., methylene chloride, chloroform, carbontetrachloride etc. have a cancer risk of 1 to 100,000 (9).

It was reported that the potential carcinogen, chloroform, together with other trihalomethanes (THMs), e.g., dibromochloromethane, dichlorobromomethane, and bromoform were produced from the reaction of chlorine with organic precursors in raw waters (1-5). The other halogenated alkanes and alkenes arose as a result of synthetic chemical contamination from point source discharges and probably found in the industrial waste water or in the raw water sources (10).

Therefore, there is the need to develop a suitable method for determining the volatile organic compounds in the water and wastewater. Since, there are several techniques used in determining the halogenated organic compounds e.g., purge-and-trap (11-17), Grob closed-loop-stripping (18-19), headspace (20-22), resin adsorption/elution (23-26), direct aqueous injection (27) and liquid-liquid extraction (28-43).

### 1. Headspace Technique

Headspace technique involves a partitioning between the analyzed compounds in a water sample and the gaseous phase above the water. A quantity of the headspace over the water sample is drawn into a gastight syringe and is injected directly into a gas chromatograph.

### 2. Purge-and-Trap Technique

Purge-and-Trap is the technique in which the organic compounds are purged from the aqueous phase with a stream of inert gas e.g.,  $N_2$ , He, subsequently trapped in a column containing a porous polymer. The sorbed compounds are then thermally desorped from the column and analyzed by gas chromatograph.

### 3. Grob Closed-Loop-Stripping

The Grob closed-loop-stripping is also another technique used in analysis of the volatile organic compounds. The sample is purged and is trapped on a column containing an activated carbon, then the compounds are eluted from the activated carbon by carbon disulfide

### 4. Adsorption-Elution Technique

The adsorption-elution technique is performed by taking the water sample passing directly through the column with an adsorbent resin and eluting the sorbed compounds from the column by an organic solvent. Finally, the eluted solution is analyzed by gas

chromatograph. There are many kinds of adsorbents used in this technique i.e., carbopack B, graphite, carbon black, Porapak N etc.

#### 5. Direct Aqueous Injection

The simplest technique of analysis the organic priority pollutants in water is direct injection. However, this technique usually has high detection limit and in some case, it has not had a high sensitivity enough to analyze an organic compound in very low concentration.

#### 6. Liquid-Liquid Extraction

The liquid-liquid extraction is based on equilibrium of the organic compounds between aqueous phase and organic phase. It can be classified into two categories:

##### 6.1 Macroextraction

##### 6.2 Microextraction

6.1 Macroextraction usually uses 100.00-150.00 mL of organic solvent to extract 1000.00 mL of water sample. This technique can be used with an organic compounds which have high boiling points, however, it is not suitable for volatile compounds due to the loss of the compounds in the preconcentration step.

6.2 Microextraction technique uses a small amount of solvent 0.20-10.00 mL to extract 10.00-1000.00 mL of water. The microextraction requires no preconcentration step.

The microextraction was first reported by Rhoades and Millar (28) and it was used to determine the volatile organic

compounds in the fruit. Grob et al. (29) investigated the organic substances in water i.e., n-alkanes, aromatics and chlorinated hydrocarbons by using 0.50-1.00 mL pentane to extract 1000.00 mL of water. Henderson et al. (30) developed the method for analysis of halomethanes in ppb level using 5.00 mL pentane to extract 115.00 mL of water sample in 120.00 mL serum bottle capped with a PTFE-lined septum and an aluminium crimped over the bottle. The detection limit was 1 ppb. Mieure (31) determined chloroform, bromodichloromethane and chlorodibromomethane in water using methylcyclohexane as a solvent to extract the organohalide in the water, followed by determining by electron capture gas chromatograph. The 7.40 mL or 9.00 mL screwcap vial was used in an extraction and the various sample to solvent ratios i.e., 25:1, 5:1 and 1:1 were studied. The lower limit of detection was less than 1 ppb for each compound. Richard and Junk (32) determined halomethanes in water with liquid-liquid extraction. The extraction was made in 15.00 mL glass-stoppered and calibrated tubes or in the volumetric flasks. By using 1.00 mL of pentane to extract 10.00 mL of the water sample, less than 0.1 ppb of halomethanes were detected. Dressman et al. (33) conducted the study on the accuracy of the three methods developed by Henderson et al., Mieure and Richard et al. and purge-and-trap methods. The results obtained from the study were compared for the quantitative accuracy. Murray (34) developed an extraction flask to use in microextraction technique for analysis of the trace amount of the organic compounds in the water. The 980.00 mL of water was extracted by 0.20 mL of hexane in the flask. The solvent layer was held in the capillary tube which placed in the center portion

and about 0.05 mL of the organic solvent was drawn and analyzed by gas chromatograph. In addition, there were also the comparison between microextraction and macroextraction methods which were used 10.00 mL of solvent to extract 1000.00 mL of water. Thrun et al. (35) studied various effects on extraction efficiencies when using microextraction technique to extract benzene, toluene, ethylbenzene and o-xylene from water into pentane e.g., the effect of sample-to-solvent ratios 20:1 and 100:1, salting out with sodium sulfate and the presence of other organic substances (acetonitrile) in the matrix. Trussell et al. (36) selected Henderson et al. technique to optimize routine trihalomethanes analysis. The aluminium crimp top was replaced with a twist cap which bore down on the septum to provide a positive seal and the capillary gas chromatography was used in analysis of the trihalomethanes. Rhodes (37) verified that microextraction was highly effective for using in analysis of the volatile organic pollutants in the industrial wastewaters. The waste water samples (10.00-100.00 mL) were extracted in volumetric flasks with 0.20-1.00 mL of solvents. The percent recoveries of the organic compounds in microextraction were comparable to the results of the macroextraction. Glaze et al. (38) described second and third generation liquid-liquid extraction for routine determination of trihalomethanes and other volatile organic compounds in water by gas chromatograph with electron capture or flame ionization detector. In both techniques pH and ionic strength of the water were adjusted prior the extraction. The sample to pentane ratio was 20:1 for the second generation method and 120:0.5 for the third one. The detection limits of halogenated compounds analyzed by GC/ECD were

0.01-2.20 ppb and 20.00-27.00 ppb by GC/FID. The median R.S.D. (%) value was 7.00-14.00% in most case. Junk et.al. (39) also used this microextraction technique to test the recovery of many different organic compounds from water by using sample-to-solvent ratios of 100:1 and 500:1. The studied compounds were halocarbons, herbicides, insecticides and aromatic compounds in variety of natural and wastewaters. The pentane or hexane was used as a solvent and a 100.00 mL extraction vessel with 4 mm i.d. neck was used as an extractor. Reunanen and Kroneld (40) used microextraction technique for quantitative determination of volatile halocarbons in raw and drinking waters, human serum and urine. The samples were extracted with pentane or petroleum ether and analyzed by gas chromatography with electron capture detector. The sample-to-solvent ratios were 20:1 and 100:1. The reproducibility and accuracy of duplicate analysis were good. Mehrzad et al. (41) described the rapid, simple method for determination of trihalomethanes in water. The procedure was consisted of the extraction of trihalomethanes from 44.00 mL of aqueous sample with 5.00 mL of pentane in vials with teflon-face silicone rubber septa and sealed by aluminum foil, the analysis was carried out by gas chromatograph, using a Hall electrolytic conductivity detector. The detection limit was ca. 0.10 ppb with a coefficient of variation  $\pm 2.00\%$ . Nicholson et al.(42) analyzed trihalomethanes in water by using methylcyclohexane as solvent and short capillary column gas chromatography with electron capture detector. The extraction efficiencies ranged from  $77\pm 2\%$  -  $80\pm 2\%$  for all compounds excepted  $57\pm 1\%$  for chloroform. Thielen et. al. (43) applied



microextraction and capillary column gas chromatography techniques to plant discharge streams for repetitive wastewater discharge permit analyses.

## Theory

### Phase Rule (44-45)

Liquid-liquid extraction is based on the distribution of a solute between two immiscible solvents. One phase is usually an aqueous phase and the other is an organic phase. A solute which is soluble in both phases would distribute between the two phases in a definite proportion and therefore, Gibbs' phase rule can be used to explain and to predict the behavior of a multiphase system of all phase distributions and also elucidate the equilibrium state obtained.

Gibbs' phase rule,

$$P + V = C + 2 \quad (1)$$

where P is the number of phases

V is the degree of freedom

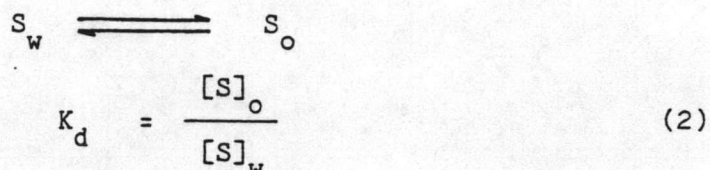
C is the number of components

In the particular solvent extraction, there are two essentially immiscible solvents and one solute distributed between them so that  $P = 2$  and  $C = 3$ . At constant temperature and pressure, the Gibbs' phase rule predicts a degree of freedom of unity. This means that, if the concentration of the solute in one phase is chosen, the solute concentration in the other phase is fixed. This definite relation between the solute concentrations in each of the solvent phase is quantitatively described in the distribution law.

### Distribution Law (45)

Distribution law first stated in 1872 by Berthelot and

Jungfleish (46) and elaborated by Nernst (47) in 1891, the distribution law states that a solute would distribute between two essentially immiscible solvents in such a manner that, at equilibrium, the ratio of the concentrations of the solute in the two phases at a particular temperature would be a constant provided the solute has the same molecular weight in each phase. For a solute, S, distributes between aqueous phase and organic phase.



where  $K_d$  is the distribution coefficient, a constant independent of total solute concentration.

$[S]_o$  is the concentration of the solute in the organic phase.

$[S]_w$  is the concentration of the solute in the aqueous phase.

The above expression is valid only for an ideal systems as can be seen from a thermodynamic derivation of the law.

#### Thermodynamic Derivation of Distribution Law (48)

A thermodynamic explanation of the conditions existing in each of the phase at equilibrium will be useful in understanding the nature of the approximations involved in the distribution law.

The change in free energy in a system is expressed by the differential

$$dF = \left( \frac{\partial F}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left( \frac{\partial F}{\partial P} \right)_{T, n_1, n_2, \dots} dP + \left( \frac{\partial F}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} dn_1 + \left( \frac{\partial F}{\partial n_2} \right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \quad (3)$$

Since, by definition

$$\left( \frac{\partial F}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} = \text{partial molar free energy} = \mu_1 \quad (4)$$

= chemical potential

$$dF = \left( \frac{\partial F}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left( \frac{\partial F}{\partial P} \right)_{T, n_1, n_2, \dots} dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots \quad (5)$$

At constant temperature and pressure,

$$dF = \mu_1 dn_1 + \mu_2 dn_2 \quad (6)$$

Since there is no change in the total amount of material involved in the partitioning phenomenon, the system is thermodynamically closed. One of the conditions of equilibrium for a closed system at constant temperature and pressure is that

$$dF = 0 \quad (7)$$

Therefore,  $\mu_1 dn_1 + \mu_2 dn_2 = 0 \quad (8)$

or  $\sum \mu dn = 0 \quad \text{at equilibrium} \quad (9)$

This condition applies to the entire closed system. If a small quantity of component 1 is moved within the system from phase I to phase II then at equilibrium.

$$-\mu_{1,I} dn_1 + \mu_{1,II} dn_2 = 0 \quad (10)$$

$$\mu_{1,I} = \mu_{1,II} \quad (11)$$

That is, the chemical potential of a component distributed between two phases that are in equilibrium is the same in both phases. The chemical potential of any solute in solution can be

written as

$$\mu = \mu^{\circ} + RT \ln a \quad (12)$$

where  $a$  is the activity of the solute in a solution.  $\mu^{\circ}$  is the chemical potential of the solute in a specific reference state.  $\mu^{\circ}$  is a constant, independent of the composition but dependent on the temperature and pressure of the system.

The chemical potential of a substance distributed between two phases in equilibrium can be expressed as

$$\mu_{1,I} = \mu_{1,I}^{\circ} + RT \ln a_{1,I} \quad (13)$$

$$\mu_{1,II} = \mu_{1,II}^{\circ} + RT \ln a_{1,II} \quad (14)$$

in phase I and II respectively.

Since at equilibrium  $\mu_{1,I} = \mu_{1,II}$  and  $\mu_1^{\circ}$  is a constant, the expression reduces to

$$\frac{a_{1,I}}{a_{1,II}} = P \quad (15)$$

$a_{1,II} = \text{partition coefficient}$

For dilute solutions the equation (15) becomes the original form, equation (2), that is

$$K_d = \frac{[S]_{1,I}}{[S]_{1,II}} \quad (16)$$

This expression holds true for dilute solutions and ideal behavior.

#### Distribution Ratio (45)

In the extraction, there are chemical interactions of the distributing species such as dimerization, complexing formation,

adduct formation etc., with the other components in each phase, it can affect the concentration of the distributing species. The overall or stoichiometric distribution of the components of interest between the phases is concerned. It becomes necessary to introduce a more practical quantity to describe the extraction, and it is called the distribution ratio,  $D$ . This is a stoichiometric ratio including all species of the same component in the respective phases.

$$D = \frac{\text{Total concentration of the solute in organic phase}}{\text{Total concentration of the solute in aqueous phase}} \quad (17)$$

If the concentrations in the extraction are ideal, i.e., the species are not involved in the reactions in either phase,  $D$  would reduce to  $K_d$ .

#### Percentage Extraction (37, 45)

The practical interest in describing the extraction is in the calculation of the percent recovery (%E). This can be derived from  $K_d$ ,

$$K_d = \frac{[S]_o}{[S]_w} \quad (18)$$

The total amount of solute in the system can be expressed as the sum of the amounts of solute in each phase.

$$C_s = [S]_o V_o + [S]_w V_w \quad (19)$$

where  $C_s$  is the total amount of solute in the system.



$[S]_o, [S]_w$  are the concentration of solute in organic phase and in aqueous phase, respectively.

$V_o, V_w$  are the volume of organic solvent and water, respectively.

According to the Nernst distribution law

$$[S]_o = K_d [S]_w \quad (20)$$

substituting  $K_d [S]_w$  for  $[S]_o$  in equation (19) gives

$$C_s = K_d [S]_w V_o + [S]_w V_w \quad (21)$$

The amount of the extracted in the organic solvent,  $C_o$ , is the product of the concentration of the solute in organic solvent and the volume of the organic phase. That means,

$$C_o = [S]_o V_o \quad (22)$$

substituting  $K_d [S]_w$  for  $S_o$  in equation (22) yields

$$C_o = K_d [S]_w V_o \quad (23)$$

Thus, from equation (23) and (21), the percent recovery (%E) can be written as

$$\%E = \frac{K_d [S]_w V_o}{K_d [S]_w V_o + [S]_w V_w} \times 100 \quad (24)$$

which simplifies to

$$\%E = \frac{100K_d}{K_d + \frac{V_w}{V_o}} \quad (25)$$

#### Salting Out (44-45, 49-51)

The salting out is the addition of inorganic salts e.g.  $Na_2SO_4$ ,  $NaCl$  to the aqueous phase to increase the distribution ratio of the substances in favor of the extracting phase.

In general, the addition of a soluble salt to an aqueous solution of organic compounds decreases the solubility of the organic compounds as shown in the linear equation (49)

$$\log \frac{S}{S_0} = C - K_s u \quad (26)$$

where  $K_s$  is the salting-out constant whose value depends on the organic compound and on the nature of the salt (50) but it is independent on temperature and pH.

$S_0, S$  is the solubility in a solution of the organic compound in pure solvent and in a solution of the salt, respectively.

$u$  is the ionic strength of the solution.

$C$  is the constant.

The salting out effect may be explained in part by the pronounced effect of the salt that is added on the activity of the distributing species. The water is probably bound as a shell of oriented water dipole around the ion, and thus becomes unavailable as "Free solvent". Finally, it is noteworthy that the dielectric constant of the aqueous phase decreases with increasing salt concentration and the result is the enhancement of extraction of the solutes in organic solvent.

The requirements of the salts used in the extraction

1. the salt must not interfere in the analysis
2. the large salting-out power is desired.

The anions and cations can be arranged in two series according to their salting-out powers toward most organic compounds.



These series are  $\text{NH}_4^+ > \text{Na}^+ > \text{K}^+ > \text{Mg}^{+2} > \text{Li}^+ > \text{H}^+$   
 and  $\text{PO}_4^{-3} > \text{SO}_4^{-2} > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$

3. the inorganic salt must have a high solubility

### Choice of Solvent

The selection of a specific solvent for use in a given separation is one of a difficult decision. The first problem encountered in choosing a solvent for extraction is its selectivity which refers to its ability to extract one component of a solution in preference to another. Even though the phase diagrams and distribution coefficients can be used to determine the selectivity of the solvent, there are not many either of them in literatures. However, the following factors and solvent properties can be used to consider the choice of solvent for a liquid-liquid extraction.

#### a) Miscibility of the solvents

According to the concept that like substances are miscible, the polar solvent should be chosen for the extraction of the polar solute and vice versa. The solubility parameter of Hildebrand and polarity parameter of Rohrsneider (51) can help for choosing some suitable solvents for the given solutes.

#### b) Physical properties of the solvent

(1) The density of the two phases must be different so that they will separate rapidly. Very small density differences are not the only causes for slow separation of the phases. Frequently surface tension, colloidal effects, and the viscosity play an important role.

(2) Low viscosity is important for the utilization of small density differences. In general the smaller the viscosity of the solvent is, the more quickly the separation occurs.

(3) The surface tension is important for the phase transport. Differences in the surface tension between phases which are due to the dissolution of a substance from a surface of one phase are usually favorable. They produce eruptions with break through the surface skin and contribute markedly to rapid substance exchange.

(4) Solvents which form emulsions easily are to be avoided. Emulsions are frequently produced by the substance to be extracted, especially if they are surface active such as proteins or long chain fatty acids. In alkaline systems this behavior occurs more frequently than in acid systems. The addition of neutral salts or change in the pH value sometimes prevent this. When hydrocarbons or high-molecular-weight ethers are used as solvents, small additions of alcohol can be used to break emulsions.

(5) The boiling point is one of the important physical properties of the solvent pair. The suitable boiling point of the solvent depends on the next step after the extraction step. The volatile solvent should be chosen if the evaporation step is required to concentrate the solute in the solvent. However, in other case, the low boiling point of the solvent may cause the wrong solute concentration due to the volatility of the solvent.

(6) Toxicity and Flammability. When using toxic or easily flammable solvents, the proper precaution must be taken, especially if large quantities are used.

c) Chemical properties of solvents

The solvent should not undergo irreversible chemical reaction with the substances to be separated.

d) Economy

The cost of the solvent does not play a significant role in single extraction. However it will be significant if a large amount of solvent is used and the high purity grade is required.

