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Solvent sublation of Toluene from aqueous phase

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ABSTRACT

SOLVENT SUBLATION OF TOLUENE FROM AQUEOUS MEDIA

by
Mei Chen

Solvent sublation, a surface chemical technique, was used to remove toluene from aqueous solution into a layer of paraffin oil.

Analytical methods for GC determination of toluene in both gas and aqueous phase were set up. The comparison of solvent sublation and conventional air stripping on toluene removal was carried out. It was found that solvent sublation provides significant improvement over air stripping in removing toluene from water, and reduces toluene emission to the atmosphere. The toluene emissions reduction by solvent sublation are 30%-70% under different conditions. The effects of air flowrates and thickness of organic layer were studied. Increased air flowrate enhanced the efficiency of toluene removal from water. It took less than 1 hour to remove 90% of the toluene from water at a high flowrate (60, 94 ml/min). However, it was also found that increased air flowrate (from 32 ml/min to 94 ml/min) increased the toluene emission to the air (from 29% to 66%). Toluene removal appeared independent of thickness of organic layer. In contrast, more organic solvent could reduce toluene emission to the air. The toluene emission reduction was about 60% when the thickness of organic layer was 20mm. Added surfactants (sodium lauryl sulfate and hexadecyltrimethylammonium bromide) and organic solvent (ethanol) can also improve the efficiency of toluene removal, since they reduce the surface tension of the solution and consequently reduce air bubble size.

Our study on toluene emission reduction by solvent sublation is the first systematic investigation in this area.

SOLVENT SUBLATION
OF TOLUENE FROM AQUEOUS PHASE

by
Mei Chen

A Thesis
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in Partial Fulfillment of the Requirements for the Degree of
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Department of Chemical Engineering,
Chemistry and Environmental Science

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APPROVAL PAGE

SOLVENT SUBLATION OF TOLUENE FROM AQUEOUS PHASE

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This thesis is dedicated to my parents.

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CHAPTER 1

INTRODUCTION

Volatile organic compounds (VOC) are a major class of air pollutants, which includes pure hydrocarbons, partially oxidized hydrocarbons, as well as organics containing chlorine, sulfur, nitrogen or other atoms in the molecule. VOC emissions are often the result of industrial operation such as combustion processes and solvent evaporation. In the atmosphere, VOCs react with NO_x, to form ozone (O_3) and peroxyacetyl nitrate (PAN) which are oxidizing agents. These oxidants are severe eye, nose and throat irritants, and can also cause vegetation damage. (1)

The federal legislative efforts on air pollution began with the Air Pollution Control Act of 1955. In the following years, several pieces of legislation were passed by the Congress. The Clean Air Act of 1970 is widely recognized as a powerful environmental legislation. One of the major objectives of the Act was to attain clean air by 1975. As a result, new standards and timetables were established. The ambient air quality standards define "levels of air quality which the administrator judges are necessary, with an adequate margin of safety, to protect the public health" or "to protect public welfare from any known or anticipated adverse effects of a pollutant". The Clean Air Act Amendment of 1977 has many modifications and additions to the 1970 Act (1). In 1990, Congress amended the Clean Air Act in significant respects (for example, by revamping the system of hazardous air pollution regulation and by addressing new air pollution problems such as acid deposition). Under 1990 amendments, 189 substances will be regulated, including both hazardous organics and metals. Prior to 1990, EPA had 33 substances which included ozone, SO_2, CO and NO_x. (2).

The quality of surface, ground and drinking water continues to be a major public health concern. The Clean Water ACT of 1987 was amended to take care of unfinished business - tightening the focus on toxic dischargers, forcing action on toxics oriented water quality standards, attempting to resolve long-standing problems with the effort to regulate storm water runoff and to strengthen the enforcement mechanisms. The Clean Water Act listed Primary Toxic Pollutants, including benzene, Dichlorophenol, toluene and trichloroethylene (2, 3).

In the water treatment industry, air stripping has long been recognized as an efficient and economical method for removal of VOCs from waste water (4). However, it has the following disadvantages (5):

1) the organic compounds are released to the atmosphere.

2) the compounds removed by air stripping are redissolved into the storage water.

3) only volatile and hydrophobic compounds can be effectively removed from water by air stripping.

Stringent air pollution regulations make it difficult to apply air stripping efficiently. Charcoal and other sorbents are used to remove the stripped VOCs from the effluent stream, but this increases both the cost and complexity of the system. Moreover, for highly volatile organics, the stripping is usually quite efficient, but the less volatile compounds are only partially removed.

The facts mentioned above have motivated our interest in another separation technique, the so-called solvent sublation (also called flotoextraction). This technique improves upon the efficiency of air stripping, while simultaneously reducing the air pollution resulting from stripping. During the solvent sublation process, hydrophobic compounds are adsorbed onto bubble surfaces or inside the bubble and are transported to the top of solvent sublation column, where they dissolve in a layer of immiscible, non-volatile organic solvent, such as mineral oil, octanol, or anisole (6).

Although many publications have mentioned that solvent sublation reduces the emissions of VOC to the atmosphere, there have been no systematic studies which included analytical determinations of organic pollutants in both the aqueous phase and the air phase. Our objectives in conducting these experiments were to:

(a) compare the efficiencies of solvent sublation and air stripping techniques in removing VOC from the aqueous phase.

(b) estimate the extent of VOC emission reduction in solvent sublation process in comparison to air stripping.

(c) ascertain the effects of parameters like air flowrate, bubble size, and organic layer thickness.

(d) understand the effects of certain co-solutes on the removal efficiency of organic pollutants.

Toluene was chosen as a test compound, because it is an important component of many industrial solvents and fuels, and it is also a "priority pollutant" on the list of Chemical Industry Institute of Toxicology (7) as well as on the Environmental Protection Agency (EPA) list (8). The exposure limits for toluene in the work place is regulated by OSHA at 200ppm. The minimum contaminant level goal (MCLG) for toluene in drinking water under the Safe Drinking Water ACT of 1974 is 2.0mg/L (3). Moreover, toluene's Henry's law constant - the most important parameter for air stripping and solvent sublation processes, is close to that of other important volatile hydrocarbons and chlorinated pollutants like benzene, xylenes, trichloroethylene, etc.. Therefore, the study of solvent sublation of toluene could be treated as an example of the removal of volatile hydrocarbons and chlorinated pollutants.

CHAPTER 2

BACKGROUND

2.1 Literature Review

Adsorptive bubble separation techniques have found wide applications in removing and concentrating hydrophobic materials from waste water (4,6). These techniques are based on differences in surface activity. Materials, which may be molecular, colloidal, or macro particulate in size, are selectively adsorbed or attached at the surfaces of bubbles rising through the liquid, and are thereby concentrated or separated. A substance which is not surface active itself can often be made effectively surface active through union with or adherence to a surface active collector. The substance so removed is termed the colligend. (4)

Most of the processes mentioned above involve the creation of a large amount of foam. However, two processes, named "bubble fractionation" and "solvent sublation" involve the creation of little or no foam at all (9). Bubble fractionation is the transfer of material within a liquid by bubble adsorption or attachment, followed by deposition at the top of the liquid as the bubble exits the solution (4). Solvent sublation involves the use of an immiscible organic solvent floated on the aqueous phase to capture the materials brought to the surface by air bubbles (4,6,10).

In the 1960s, Sebba originated solvent sublation mainly for removal of inorganic ions, but he noted that ionizable dyes and indicators could also be readily and selectively removed by adjustment of conditions and use of suitable surfactants (10).

Lemlich has edited a comprehensive book named "Adsorptive Bubble Separation Techniques" (7). In the book, Karger has written a review of solvent sublation as far as the removal of ionic compounds was concerned. Caragay, Karger, and Lee (11) in the 1960s investigated the solvent sublation process for separation of two dyes, methyl orange (MO) and rhodamine B (RB), using hexadecyltrimethyl ammonium bromide (HTMAB) as cationic collector and 2-octanol as immiscible organic layer. The pH of the solution was adjusted so that MO was anionic and RB zwitterionic. Consequently, MO was rapidly removed from aqueous phase with HTMAB. Simultaneously, the rate of RB removal was suppressed by the added HTMAB, which successfully competed with RB for adsorption sites on the bubble surface. In addition, Karger and coworkers examined the solvent sublation of methylorange and $FeCl_4^-$ ions (12) with cationic collectors. For removal of inorganic ions and dyes by solvent sublation, polar compounds like 2-octanol and anisole were used as organic layer.

Renewed interest in solvent sublation process was sparked in the beginning of the 1980s for its advantages on removal of dissolved hydrophobic organics (13). Removal of organics emulsified in water was also demonstrated (14). It was also reported that a layer of motor fuel enhanced removal of emulsified organics from water by induced air flotation (14). Less soluble and inexpensive paraffin oil and other nonvolatile hydrocarbons instead of octanol were proposed as organic layer for removal of hydrophobic compounds (14,15). On the other hand, mathematical models have been proposed by various investigators (13,16, 17, 18).

Wilson and co-workers (17) carried out the solvent sublation of 1,1,1-trichloroethane (TCE) and chloroform into 1-octanol. A mathematical model was proposed , which included the effects of finite rate of solute mass transfer from the aqueous into vapor phase. Results were calculated for removal of TCE into 1-octanol. Experimental data on solvent sublation of TCE are in good agreement with the model. Wilson also indicated that small bubbles and a long column provided large bubble surface to volume ratios and long bubble contact times, both of which favor increased mass transfer.

Kun-Yauh Shih, Wei-Der Han and Shang-Da Huang (19) investigated the removal of hexachlorobutadiene and 2,4,6-trichlorophenol into paraffin oil by solvent sublation.

The effects of added salt, ethanol and surfactant were studied. Over 99% of hexachlorobutadiene (initial concentration 100ppb) can be removed in 10 min. The improvement of removal rate by solvent sublation was observed in comparison with air stripping. The presence of salt and ethanol increased the rate of separation of hexachlorobutadiene. About 64% of 2,4,6-trichlorophenol was removed from a solution containing 50ppm 2,4,6-trichlorophenol at pH 1.84 in one hour. Cationic surfactant, hexadecyltrimethylammonium bromide (HTMAB) improved the rate of removal of 2,4,6-trichlorophenol.

Jin-Yin Huang and Shang-Da Huang (20) examined the removal of Acid Red 114, an anionic dye from aqueous phase by solvent sublation of Acid Red-hexadecyltrimethylammonium complex into paraffin oil. The effects of concentration of surfactant, pH, neutral salts and ethanol were studied. Different concentrations of HTMAB (cationic surfactant) were added to the aqueous solution. It was found that 1:1 mole ratio of surfactant to dye gave the fastest rate of separation and the lowest residual dye concentration. The results at different pH in solution showed that for pH between 4.0 to 4.5 the rate of removal of dye was the highest. The experiments on adding $NaNO_3$ indicated that the presence of $NaNO_3$ at less than 0.1M did not affect the process, but the separation efficiency decreased significantly when $NaNO_3$ concentration was greater than 0.5M. Increasing ethanol concentration decreased the separation efficiency. This might be due to an increasing solubility of the Acid Red-HTMAB complex by the alcoholic solution. Another explanation was that alcohol might interfere with the formation of Acid Red-HTMAB complex.

Solvent sublation for the removal of hydrophobic chlorinated compounds was carried out by Valsaraj, Porter, Liljenfeldt and Springer (5). The comparison of solvent sublation and conventional fine bubble aeration was investigated. The effects of the nature of the compounds, the bubble size, the flowrate, the nature and thickness of organic solvent, as well as co-solutes were studied. It was found that solvent sublation using fine bubbles is a marked improvement over conventional fine bubble aeration. The nature of the compounds had effects on removal efficiency. Mono-, di-, and tri-chlorobenzenes have been tested, and results showed that solvent sublation is more effective for relatively non-polar compounds of high hydrophobic character, low aqueous solubility and low vapor pressure. Tall column and fine bubbles were essential for the success of the process. Increased flowrate enhanced the efficiency of the process somewhat, but it also caused large bubbles in the column, which decreased the efficiency of sublation. As a result, choosing a suitable flowrate was very important in solvent sublation. Valsaraj and co-workers investigated the effect of the nature and thickness of the layer, and found that the volume of the organic layer has little effect on solvent sublation when the organic volume is larger than a critical value. The organic solvent chosen for solvent sublation should have low aqueous-solvent interfacial tension, very low aqueous solubility, but should have a affinity for toxic contaminants. It should also be non-toxic, non-volatile and inexpensive. Adding small amounts of organic co-solutes would improve the rate of removal while larger concentration would decrease the removal rate.

The Solvent sublation of a number of chlorinated organics and two nitrophenols was demonstrated at bench scale in batch apparatus by Valsaraj and Wilson (15). A thoery for the prediction of the behavior of chlorinated organic hydrocarbons in solvent sublation was proposed and tested. A method was developed for estimating the boundary layer thickness of the rising bubbles which was needed to estimate mass transfer rates in solvent sublation.

Studies on pentachlorophenol (PCP) removal from acidic solutions by both solvent extraction and solvent sublation were carried out by Valsaraj and Springer (18). In comparison with solvent extraction, solvent sublation has the advantage of minimal contact of the solvent phase with the aqueous section, since it is a rate-controlled process, it may give removal efficiency exceeding that of solvent extraction. Valsaraj and co-workers also found that both solvent sublation and solvent extraction of PCP are more effective at low pH values. PCP is used as a bactericide, fungicide for the preservation of wood and wood products, so Valsaraj tried the solvent sublation on an actual waste sample from a wood preserving industry. The results gave lower removal in comparison with laboratory studies, which might be due to interferences from the suspended solid present with aqueous phase.

Later, Valsaraj and co-workers (21) extended their studies on continuous countercurrent solvent sublation and bubble fractionation of hydrophobic organics. The compounds used in their experiments included pentachlorophenol (PCP), 1,2,4-trichlorobenzene (TCB), 2,3,6-trichloroanisole (TCA) and 2,4,6-trichlorophenol (TCP). The experiments were conducted with the aqueous and air phases in continuous countercurrent modes, and organic solvent as a stagnant layer. The results showed that continuous countercurrent solvent sublation was a technically feasible method of removing hydrophobic organics. It is found that the removal efficiency was a function of the ratio of air flowrate (Q_a) and influent feed rate (Q_w). Increased Q_w tended to decrease the removal. Valsaraj explained that increased Q_w not only leads to increased axial dispersion in the column, it also decreased the bubble-water contact time, both of which tend to decrease the removal rate and the steady-state efficiency.

In recent years, mathematical models were developed by many investigators. Valsaraj and Thibodeaux (16) proposed a complete model which incorporates all known mechanisms for transfer of solutes between aqueous and organic solvent phases in continuous countercurrent solvent sublation. They chose neutral pentachlorophenol (PCP) molecules and ionic PCP + HTMAB complex as model compounds. Later, Valsaraj, Lu, Thibodeaux (9) continued their investigations on mathematical model on PCP, 2,4,6-trichlorophenol and naphthalene. The mathematical predictions were in good agreement with experimental data, while using a steady state "stagewise" model along with the determination of key hydrodynamic parameters for the bubble column such as bubble radius and number of equilibrium stages.

Previous work had focused on the removal of contaminants from the aqueous phase, with air flowrates, properties of the organic solvent and added co-solutes having effect on efficiency of removal. Although it was clear that solvent sublation does not only improve removal efficiency from the aqueous phase but also reduce the air contamination caused by air stripping, there were no systematic studies on the effects of solvent sublation on the gas phase. The stringent regulation of air emissions have led more people to become interested in the studies of the emission reduction by solvent sublation process.

2.2 Basic Principles of Solvent Sublation

2.2.1 The Comparison of Air Stripping, Solvent Extraction and Solvent Sublation

Solvent sublation is a separation technique in which volatile or nonvolatile surface-active compounds are transported by air bubbles to the top of sublation column and are captured by an immiscible organic solvent floating on top of the aqueous phase (4, 10, 13). Ionic compounds can be complexed with surfactant ions of opposite charge and the surface-active ion-surfactant complex can be levitated by air bubbles (4,11).

Solvent sublation combines the effectiveness of air stripping and solvent extraction, and adds more advantages over either of the two processes (21). Solvent sublation is more efficient than air stripping since it is also capable of removing nonvolatile organic compounds. The volatile compounds will dissolve in the overlying organic solvent instead of being emitted to the exhausted air as in the air stripping process. On the other hand, this overlying layer will also prevent the compounds from redissolving into the waste water. In comparison with solvent extraction, solvent sublation offers two advantages - first, the degree of redissolution of organic compounds in aqueous phase during the solvent sublation process is less than that of the solvent extraction process. Secondly, solvent sublation is a rate-controlled process, while solvent extraction is a equilibrium controlled process. This makes solvent sublation a more effective operation than solvent extraction. Figure 1 shows the different mechanisms for air stripping, solvent extraction and solvent sublation. This can help us understand the various transport mechanisms between the aqueous and organic phases, which makes the solvent sublation superior to the other two processes.

2.2.2 The Mechanism of Solvent Sublation

Basically, there are two different and simultaneous transport mechanisms in solvent sublation (16, Figure 1):

1. The transport of compounds by the air bubbles.

The organic compounds are either absorbed on the surfaces of the air bubbles or present as vapor inside the bubbles. The mechanism depends on the air flowrate (Q_a), the bubble radius (r), the mass transfer coefficient of the solute to the bubble in the aqueous phase (K_w), the combination of Henry's constant (H_c) and the absorption constant for the solute at the air/water interface of the bubble (K_a).

According to Valsaraj and coworker's studies (21), ($H_c + 3K_a/r$) can be considered an "effective" partition constant for the solute between the air bubble and aqueous phase. The larger this values The higher the capacity of the hydrophobic compounds to be associated with the air bubbles. Henry' constant (H_c) is one of the most important parameters that effect the solvent sublation. The higher the H_c the more hydrophobic and volatile the compound is (5). When the compounds are hydrophobic in the aqueous phase, they tend to have high activity coefficients, because this prevents them from competing with the strong hydrogen bonding forces between water molecules. Therefore, these compounds tend to prefer the air/water interface of the rising bubbles rather than the aqueous phase. Valsaraj and co-workers (16) indicated that H_c determined the vapor-phase solute concentration within the bubble while K_a determined that on the surface of

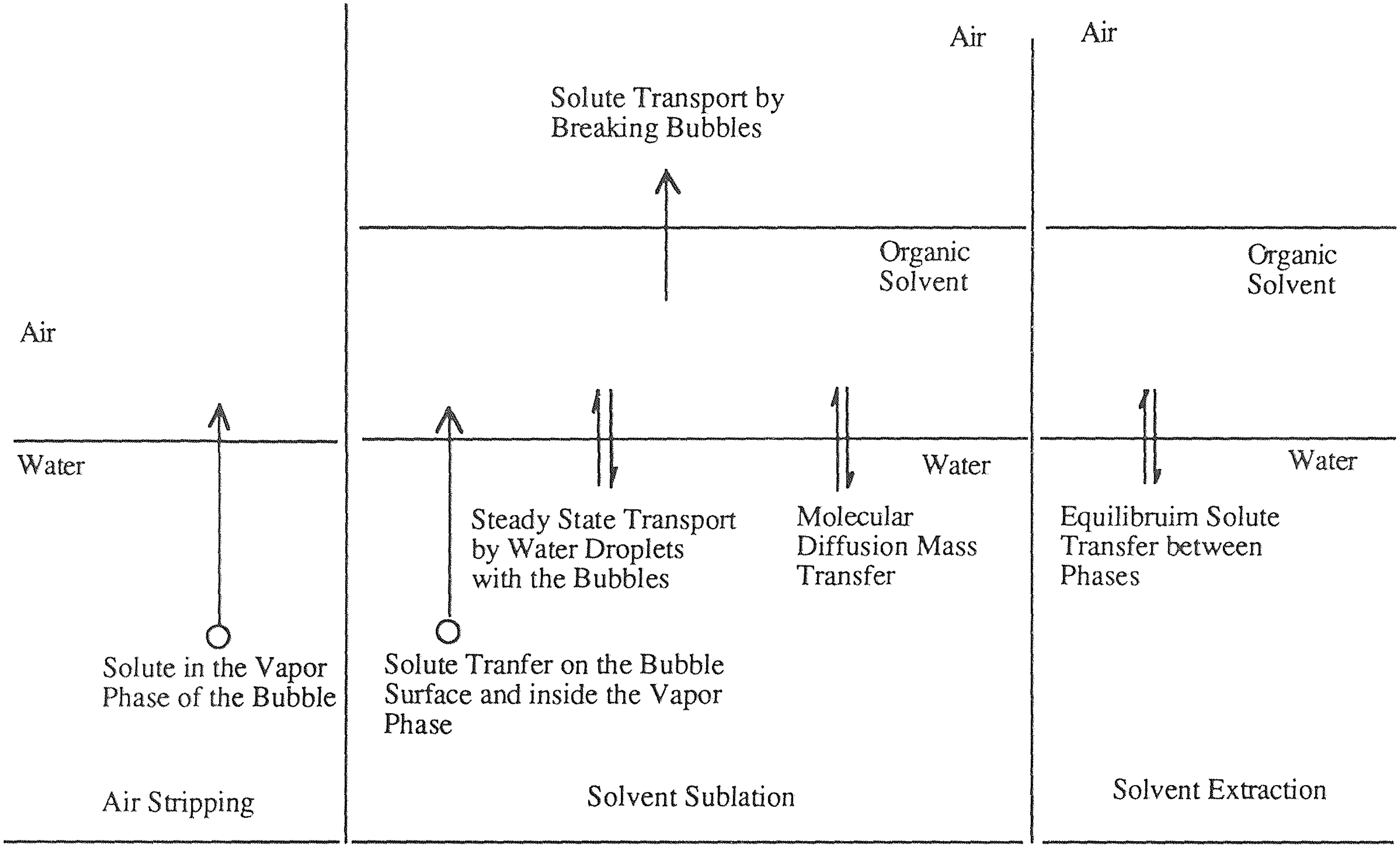


Figure 1 Mechanisms of Solute Transport in Air Stripping, Solvent Sublation, and Solvent Extraction.

bubble. Increasing H_c or K_a increased the amount of hydrophobic compounds carried by the bubble and hence improved the sublation efficiency.

2. A molecular diffusion process dependent on the solute concentration gradient between the organic solvent and aqueous phases (21).

This mechanism can be characterized by a mass transfer coefficient (k_l), which depends on the turbulence at the water solvent interface, as well as the solvent/water partition coefficient (K_{ow}) for the particular solute. If K_l and K_{ow} are very high, then the maximum efficiency which can be obtained in solvent sublation is the same as solvent extraction, but the amount of organic solvent dissolved in the aqueous phase is less in solvent sublation than in solvent extraction. When K_l and K_{ow} are small, increased efficiency can be achieved by increasing air flowrate (Q_a) or decreasing bubble radius in solvent sublation than in solvent extraction.

2.2.3 The Effects of Some Parameters

1. The nature of removed substance.

Solvent sublation is more effective for relatively non-polar compounds of high hydrophobic character, low aqueous solubility and low vapor pressure (9).

2. Flowrate (Q_a) and bubble radius (r).

Higher flow rate enhances the removal of compounds from the aqueous phase, but it also increases the diameter of the bubbles, which leads to increased bubble velocities and shortened bubble/liquid contact time in the column, hence decreased sublation efficiency (5). Moreover, at very high flowrate, the overlying organic solvent may be disrupted and partially emulsified into the water phase. Therefore, the key to increasing the efficiency of solvent sublation is to keep the bubble size small without reducing the air flow rate.

3. The nature and thickness of the organic solvent.

The organic solvent used as a layer in solvent sublation must be relatively nonvolatile and insoluble in water, and have little tendency to emulsify in water. If the solvent sublation technique is applied in industry, the cost and disposition of the organic solvent must also be considered.

The thickness of the layer is another parameter which may effect the sublation efficiency. Increasing the thickness of the layer may increase the efficiency of the process up to a certain point, after which there is no further improvement, because an increase in the volume of layer reduces the water/oil ratio and lessens the concentrating effect of the extraction.

4. Surfactants

As mentioned before, the hydrophobicity of the compound is an important parameter in solvent sublation. Any other co-solute which influences its hydrophobicity would also affect the separation efficiency (5).

The presence of surfactants at the air-water interface can reduce the diffusion constant of solutes through the surface of the air bubble (5). However, surfactants tend to reduce the surface tension of the aqueous solution drastically, which decreases the size of the bubbles generated at the sparger. As a result, the population of small bubbles increases, providing a larger interfacial area per unit volume of air, which apparently more than offsets the effects of decreased mass transfer coefficient, and so increases the overall transfer rate (22). Moreover, with the presence of surfactants, the interfacial tension at water-oil interface is also reduced, this helps the bubbles to traverse the interface easily without coalescence. On the other hand, too high concentration will have a negative effect on solvent sublation. Firstly, the high concentration of surfactant can form an emulsion of organic solvent with water, the water is contaminated by the organic solvent. Secondly, at high surfactant concentration, a large foam would be formed on top of the column, which may cause problems.

5. Ethanol

Valsaraj and coworkers in 1986 studied (5) the influence of various concentrations of ethanol upon the removal rates of TCB. At low mole fractions (< 0.04) enhanced removal rates were observed whereas at mole fractions 0.04 and higher the removal rates start to decrease, the effect becoming quite predominant at 0.10 mole fraction. The reason for this is that at low mole fraction the addition of ethanol changes the bubble properties considerably. The number of very small bubbles are much larger than when ethanol was absent, due to the fact that added ethanol prevents the bubbles from growing to large sizes by lowering the surface tension of water. These smaller bubbles provide a very large surface area per unit volume of air which contributes to enhanced mass transfer from liquid phase to the bubbles. In contrast, at high mole fraction (> 0.04) added ethanol tends to disrupt the water structure considerably and make aqueous phase more comfortable for organics, i.e. the phase behavior of ethanol-water mixtures is more organic-like. This make the organic compounds more soluble in aqueous phase and hence makes it more difficult to remove them by solvent sublation.

6. Sodium chloride

The presence of sodium chloride increases the removal rates of organics (5). This is due to the so-called "salting out" effect. Adding salts to the aqueous phase decreases the aqueous solubility of hydrophobic organic compounds. The effect is due to the "tying up" of the water molecules in the hydration shells of the ions and thereby reducing the number of the "free" water molecules available for solubilizing the hydrophobic in solution. Therefore, the removal of the hydrophobic compound on the air-water interface of the rising bubbles also increases.

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 Design of Equipment

A laboratory bench-scale solvent sublation apparatus was set up for studying the removal of volatile compound from water. Figure 2 shows the sketch of the solvent sublation apparatus. The glass column used in the experiment is supplied by Fisher Scientific Inc. with height of 70cm and inner diameter of 40mm. Two tubes are inserted in a large rubber stopper sealing the top of column. One tubing is used for vent gas, the other one is used to allow the stripping air to pass through to the gas chromatograph. Another rubber stopper is arranged at 15cm from the bottom, where a needle is inserted to the center of the column to allow liquid to be collected. A fine glass porous frit supplied by Fisher is fitted at the bottom. The flow of compressed air from a cylinder is measured by an air rotameter (Scott Specialty Gases). The flowmeter was calibrated by a soap film flow meter and a stopwatch.

3.2 Design of Experiment

3.2.1 Choice of Testing Compound

Toluene was chosen as a test compound for two reasons: first, it is one of the important components of many industrial solvents and fuels, and it is also a "priority pollutant" on the list of the Environmental Protection Agency (7). Second, it is a volatile, hydrophobic organic compound having low aqueous solubility. These make it a suitable compound for solvent sublation and air stripping. Table 1 lists the major properties of toluene.

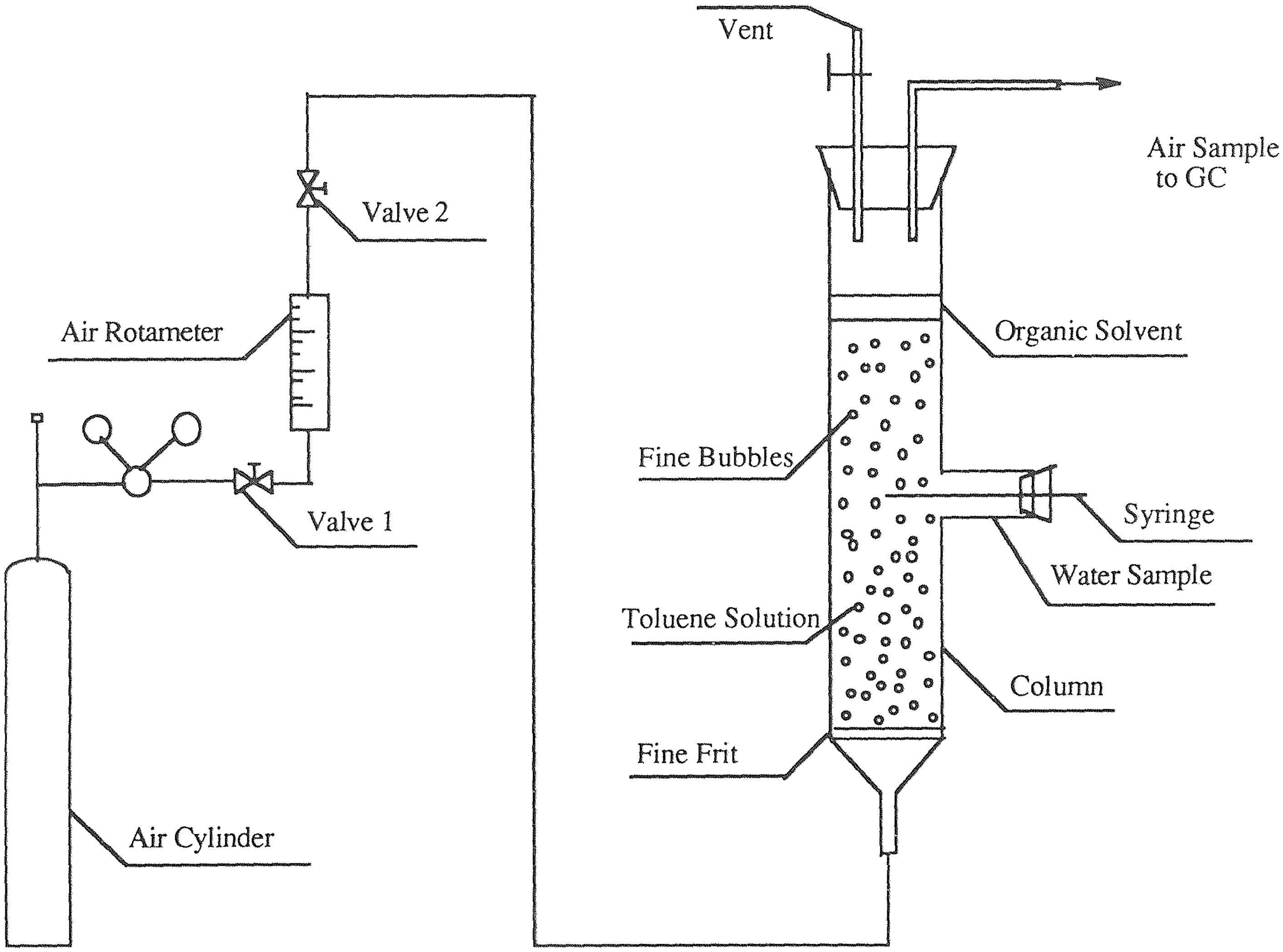


Figure 2 Sketch of the Solvent Sublation Apparatus.

Table 1 Characteristics of Toluene

Properties	Value
Molecular weight	92.15*
Density (g ml^{-1}) at 20°C	0.8669
Vapor Pressure (mmHg) at 31.8°C	40
Aqueous Solubility (mg l^{-1})	515**
Boiling Point (°C)	110.6
Melting Point (°C)	-95
Henry's Constant (dimentionless) at 25°C	0.25***
Henry's Constant (atm m^3 $Mole^{-1}$ K^{-1})	0.0061**
Exposure Limits (ppm) by OSHA	200*

Sources:

* Pradyot Patnaik, *A Comprehensive Guide to the Hazardous Properties of Chemical Substances.*, New York: Van Nostrand Reinhold, 1992. (8)

** James. W. Patters, *Industrial Waste Water Treatment Technology*. Salem, NH: Butterworths, 1985. (23)

*** Xiao Y. Lu, K. T. Valsaraj, and L. J. Thibodeaux, " Studies in Batch and Continuous Solvent Sublation. IV. Continuous Counter current Solvent Sublation and Bubble Fractionation of Hydrophobic Organic from Aqueous Solution", *Sep. Sci. & Tech.*, 26 (7), pp. 977-989, 1991. (21)

Usually different Henry's law constants are given by different investigators because they use different methods to measure it.

Others from David R. Lide, *CRC Handbook of Chemistry*. Boca Raton, Ann Arbor, Boston: CRC Press, 1991-1992. (24)

3.2.2 Experimental Procedure

1. Preparation of toluene solution

A 1000ml-volumetric flask was filled with 600ml distilled water, and 60ul toluene was injected to the flask. The flask was shaken about 3 minutes and the solution was immediately transferred into the column. The concentration of toluene solution was 100ppm.

2. The experiment was carried out as follows:

1) The glass column was rinsed with distilled water.

2) Filled with 600ml distilled water. Valve 1,2 (Figure 2) were opened, and the flowrate was adjusted to the desired value.

3) Valve 1,2 were closed, the distilled water was drained off and the column was filled with toluene solution.

4) The required volume of organic solvent was added. (For air stripping, this step was not required)

The volume of solvent was calculated by the equation below:

$$Volume\ of\ Solvent\ (ml) = \pi \cdot r^2 \cdot L$$

Where

r : inner radius of column, 20mm

L: thickness of the solvent, mm

5) Valve 1,2 were opened. The timer was started when first aqueous sample was collected. Gaseous sample was analyzed 5 minutes later.

6) The aqueous samples were collected every 15 minutes and the gaseous samples were injected into the GC column every 15 minutes. The experiment was stopped after about 80 minutes.

7) After the experiment was over, the solution was drained into waste bottle.

8) The glass column was washed with detergent, and rinsed with distilled water.

3. Standard Input Parameters

Table 2 shows the parameters used in experiments.

Table 2 Standard Input Parameters

Parameter	Value
Aqueous Column Height	45cm
Column Radius	2cm
Bubble Diameter*	0.2-0.7mm
Organic Layer	Paraffin oil
Organic Layer Height	5-20mm
Air Flow Rate	32-94ml min^{-1}
Initial solute concentration	100ppm
Temperature	Room temp. (20-22 ^{o}C)
Column Run Duration	90min

* bubble diameters were roughly estimated by video camera technique.

3.3 Analytical Apparatus and Methods

3.3.1 Aqueous Phase Analysis

1. Without co-solutes.

The concentrations of toluene solution were measured by a Varian 3700 gas chromatograph, using flame ionization detector (FID). Samples were directly injected to the column supplied by Supelco, Inc., which was a 1/8 inch in diameter by 3 feet long stainless steel column packed with 80/100 mesh carbopack B coated with 1% SP1000.

Table 3 presents the GC operating conditions. Figure 3 shows the typical peak resolution and retention time of toluene.

Table 3 GC Operating Conditions for Aqueous Phase Analysis (without co-solutes)

Parameters	Value
Detector Temperature	290^{o}C
Injection Temperature	200^{o}C
Oven Temperature	170^{o}C
Helium (Carrier Gas)	30ml/min
Air	300ml/min
Hydrogen	30ml/min

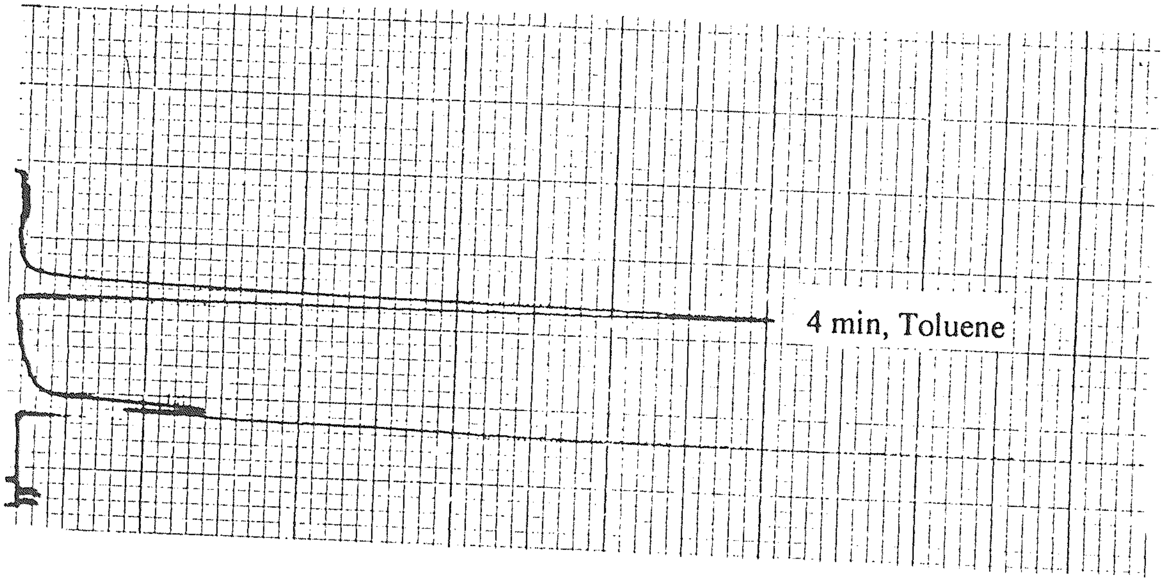


Figure 3 GC Chromatogram of Aqueous Phase Analysis (without co-solutes).

Calibration curve was obtained with different concentration of toluene from 0-100ppm and it was found that the peak areas were proportional to concentration of toluene solutions.

2. With co-solutes.

1) Toluene solution with surfactant

2.0ml of aqueous sample was collected in a 3.7ml vial, extracted into 1.0μl ethyl ether, and 1.0μl ethyl ether solution was injected into GC (FID). Figure 4 shows the typical peak resolution and retention times of ethyl ether and toluene.

2)Toluene solution with ethanol

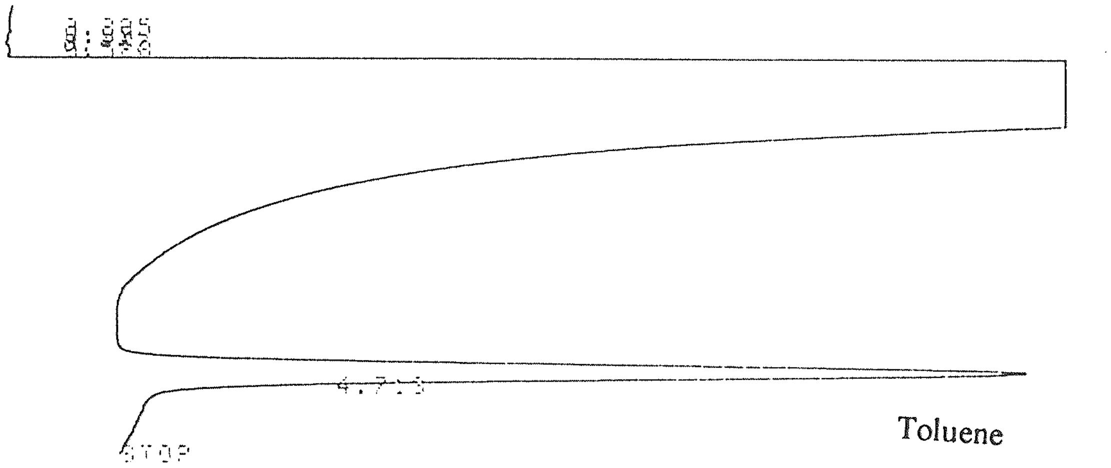
1.0μl sample was directly injected into GC (FID). Figure 5 shows the typical peak resolution and retention times of ethanol and toluene.

3) GC operating conditions

The concentrations of solutions were measured by a Varian 3300 gas chromatograph, using flame ionization detector (FID). The components were separated on 1/8 inch in diameter by 6 feet long stainless steel column packed with 80/100 mesh super P coated with 25% OV-101. Table 4 presents the GC operating conditions.

Table 4 GC Operating Conditions for Aqueous Phase Analysis (with co-solutes)

Parameters	Value
Detector Temperature	250°C
Injection Temperature	190°C
Oven Temperature:	
With Surfactant	80°C (initial)
	100°C (final)
With Ethanol	110°C
Nitrogen (carrier gas)	30ml/min
Air	300ml/min



```
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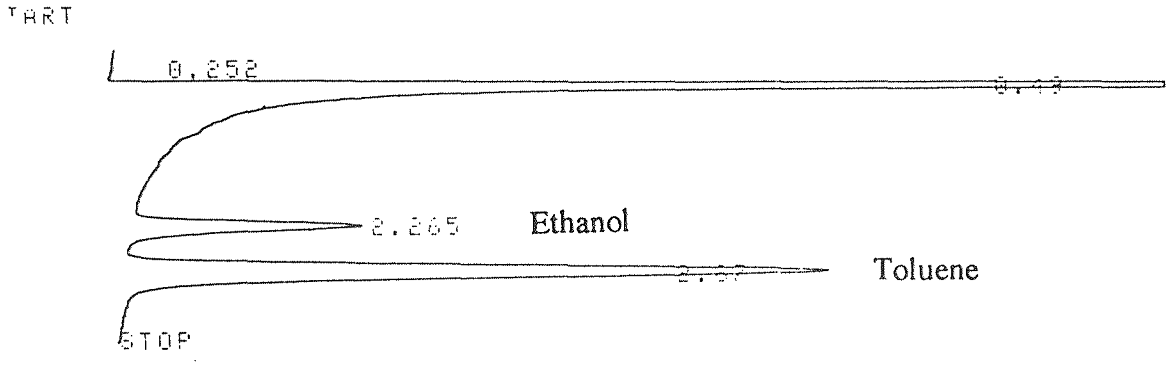
PLE NO    0                             METHOD        41
ORT NO    494

O       TIME       AREA   MK   IDNO      CONC        NAME

1      0.35        1075                      0.0023
2      0.447       1006                      0.0021
3      0.528       3723                      0.0079
4      0.94    20132408    E                42.7089
5      0.97    25460674  SVE                54.0122
6      4.713    1539826  T                   3.2666
               ---------            -------------
      TOTAL    47138708                 100
```

Figure 4 GC Chromatogram of Aqueous Phase Analysis (added surfactants).



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ORT NO    593

D       TIME       AREA   MK   IDNO      CONC        NAME

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2       2.265     262782 T                  4.2589
3       2.87      969385 T                 15.711
                ---------            -------------
       TOTAL     6170119                 100
```

Figure 5 GC Chromatogram of Aqueous Phase Analysis (added ethanol).

Calibration curve was obtained with different concentration of toluene solutions (0-100ppm) after extraction by ethyl ether. The curve shows that peak areas are proportional to concentrations of toluene solutions.

3.3.2 Gas Phase Analysis

1. Trap and injection system

Figure 6 shows the trap and injection system for gas analysis. This system consists of two six-port valves, a 60/80 mesh glass bead cryogenically cooled trap, a vacuum pump and a ballast tank.

The procedure of trap and injection process is given below (Figure 6):

1) Switch six-port valve 1 to solid-line position (analysis position). 2ml/min helium should always pass through capillary column to maintain the column quality.

2) Put the glass microbead trap into a Dewar flask which contains iso-propyl alcohol frozen to a slush with liquid nitrogen (-186^{o}C). Cool the trap for about 5 minutes.

3) Turn on the pump. Evacuate the 135ml ballast tank to below 1mmHg pressure.

4) Switch six-port valve 2. to solid-line position (trap position). Allow the gas sample to pass through the glass microbead trap into the ballast tank, where the pressure is monitored by Wallace and Tiernan high accuracy pressure gauge (Model 61D-1A-0030).

5) When the ballast tank pressure reaches to 2 psig, switch valve 2. to dotted-line position (injection position).

6) Remove the Dewar flask from the trap, heat the trap to about 95^{o}C with a beaker of hot water. Raise the GC oven temperature to 120^{o}C. The 2ml/min helium will pass through the trap, and carry the toluene to the GC column.

2. The calculation of volume of air sample injected is given by:

$$V_s = \frac{\Delta P \cdot V_r}{P_s}$$

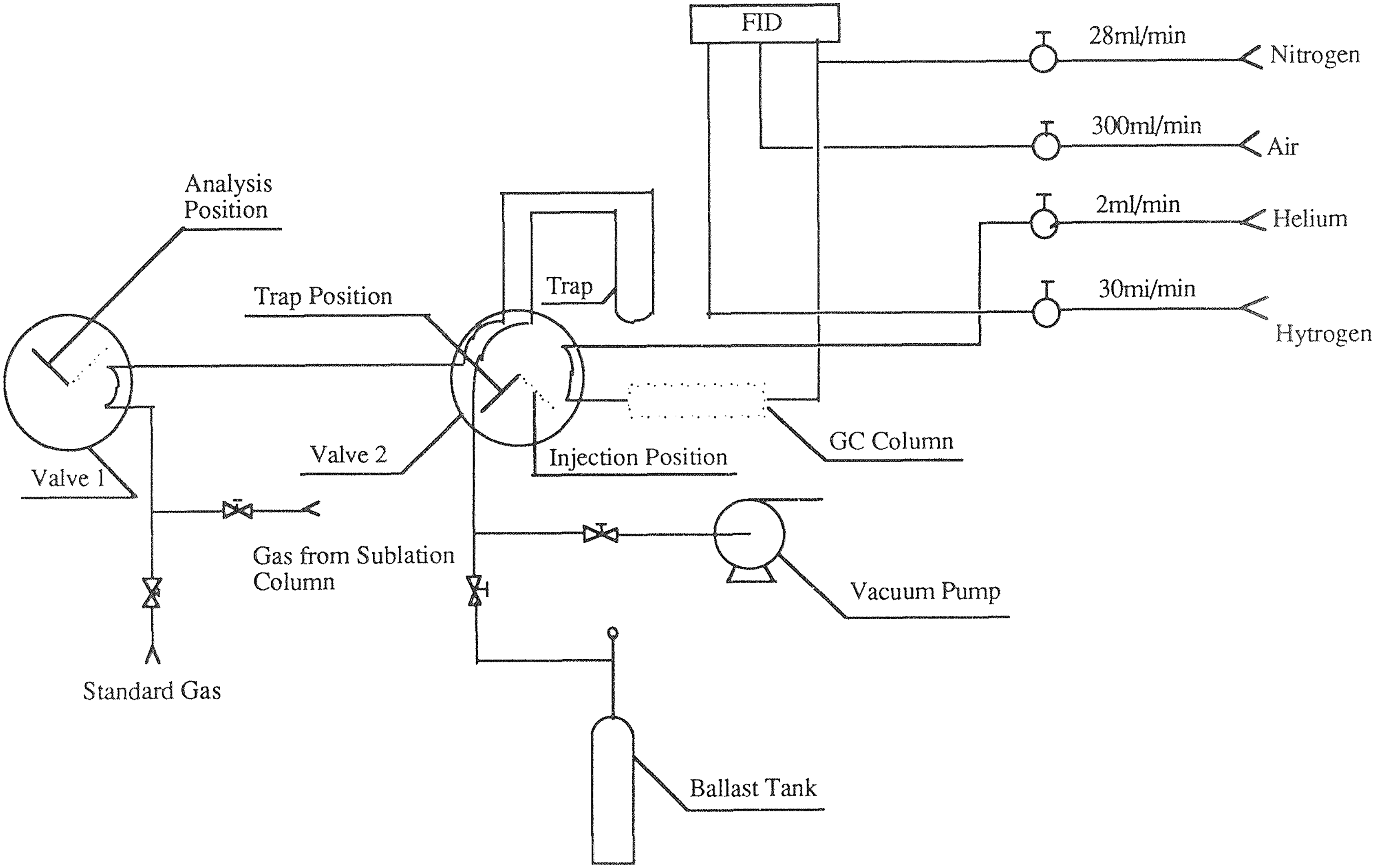


Figure 6 Trap and Injection System for Gas Phase Analysis.

Where

V_S = Volume of air sample injected at 1 atm (liter)

ΔP = Pressure difference measured by high accuracy gauge (psi)

V_r = Volume of vacuum ballast tank (135ml)

P_S= Standard pressure (14.7psi)

In this experiment, the pressure difference was 2 psig, so the volume of air sample was about 0.02 liter.

3. GC operating conditions.

The air samples were measured by a Varian 3700 gas chromatograph, using flame ionization detector (FID). A 15meters long, 0.54mm in diameter crosslinked methyl fused silica column (Alltech Associates Inc.) with 1.2 micron film thickness of SE-30 was used for analyzing toluene. Table 5 shows the GC conditions for analysis of air sample. Figure 7 shows the typical peak resolution and retention time of toluene in gas phase.

Table 5 GC Operating Conditions for Gas Phase

Parameters	Value
Detector temperature	290°C
Oven temperature	130°C
Helium (carrier gas)	2ml/min
Air	300ml/min
Hydrogen	30ml/min
Nitrogen (make-up gas)	28ml/min

4. Standard gas for calibration

Figure 8 is the sketch of the preparation of standard gas. A 6 liter canister was used as a container of standard gas, and the required toluene concentration was 500ppm (26).

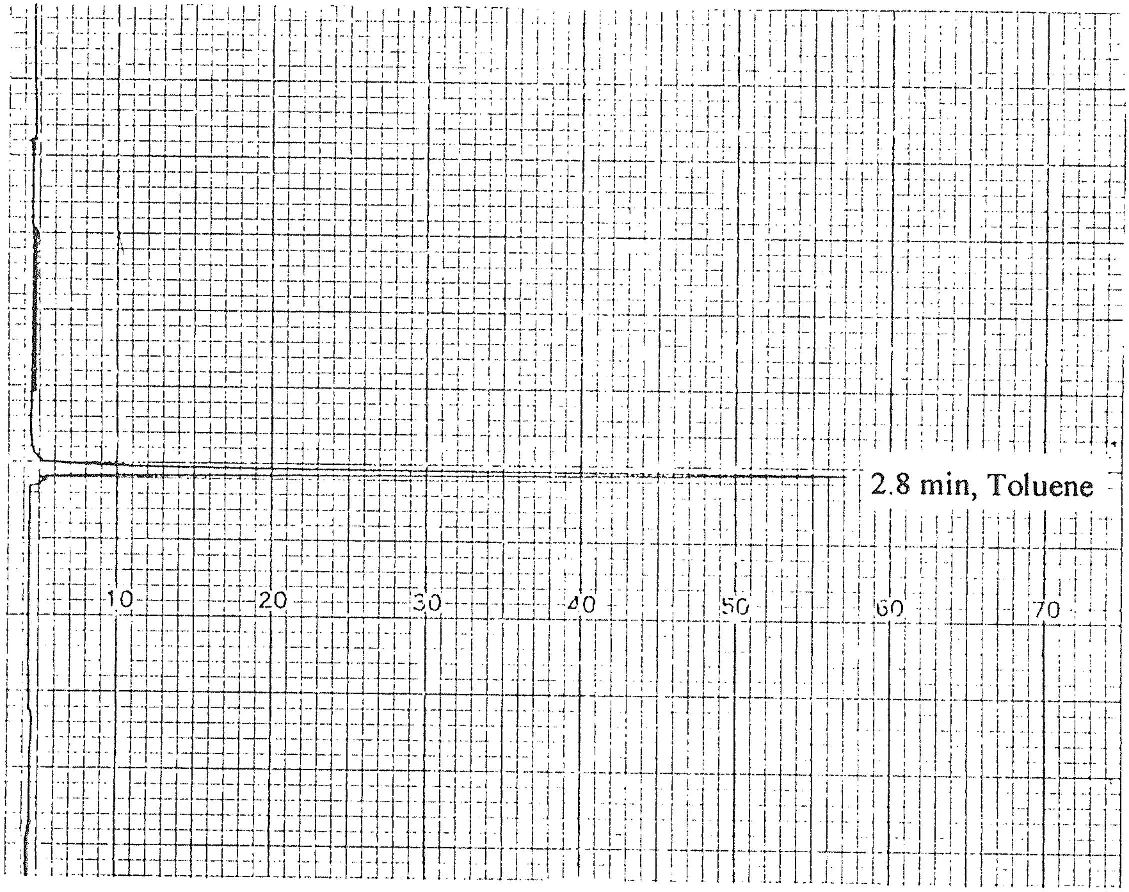


Figure 7 GC Chromatogram of Gas Phase Analysis.

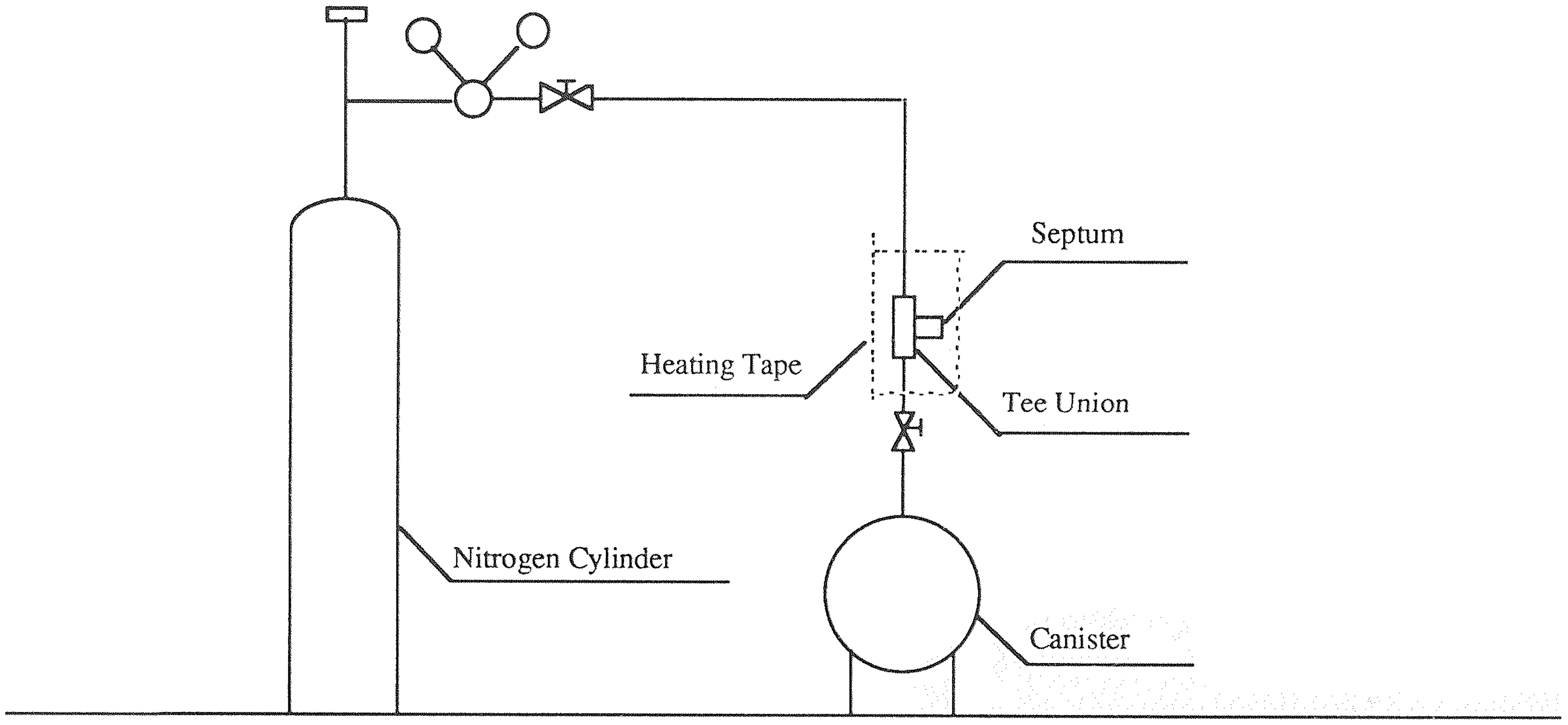


Figure 8 Standard Gas Preparation Apparatus.

1) Canister cleaning

The canister was evacuated to -20psig using a pump and then filled with nitrogen. This step was repeated twice.

2) Preparation of the standard gas

The cleaned canister was again evacuated to -20psig, and connected to a nitrogen cylinder (Figure 8) by a Tee union with one branch covered with a septum. The Tee union was heated by a heating tape, and then a certain amount of toluene was injected through the septum by a syringe. The toluene was evaporated at high temperature. After that, the valve of nitrogen cylinder was opened and the pressure of the output gas was adjusted to 40psig (gauge). The nitrogen was allowed to pass through the Tee union, which would sweep the toluene vapor from the Tee union into the canister. After 30 minutes, the equilibrium between the canister and the nitrogen cylinder was reached, and then the valves of both canister and nitrogen cylinder were closed, the canister was removed.

3).Calculation of the volume of toluene injected is given by:

$$V = \frac{C \cdot V_c \cdot M \cdot P_c}{24.46 \cdot P_1 \cdot D} \cdot 10^{-6}$$

Where

C = Concentration of standard gas, ppm

D = Density of toluene, 0.8669g ml^{-1}

24.46 = Gas constant at $20^{o}C$

V = Volume of toluene injected, μl

V_C = Volume of canister, 6 liter

P_C = Pressure inside the canister, 54.7psig

P_1 = Standard pressure, 14.7psig

4) 500ppm of toluene standard gas was prepared. The canister of standard gas was connected to the three-way ball valve (Figure 6) and the standard gas was allowed to pass

using the same trap and injection system as in the case of gaseous samples from the solvent sublation column. The calibration curve was obtained by passing different amount of standard gas (1psig, 2psig, and 4psig).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 The Effect of Air Flowrate

Solvent sublation and air stripping of toluene from aqueous medium were investigated at different air flowrates (32, 60, 94 ml min^{-1}). It was found that the rate of toluene removal from water increased with increasing air flowrate for both air stripping and solvent sublation (Thickness of layer was 10mm), and the runs followed first-order kinetics. The first order kinetics is given by the equation:

$$\frac{dC}{dt} = K \cdot C$$

Integrating we get

$$\ln\left(\frac{C_0}{C}\right) = -K \cdot t$$

Where

C_O = initial concentration of toluene solution, ppm

C = toluene concentration at t time, ppm

t = time from the run started, min

K = rate constant, min^{-1}

The effect of air flowrate on toluene removal from water is shown in figure 9,10 which are plotted as $\ln(C_O/C)$ vs t. The slope of the line is the rate constant of each run. The larger the K value the more efficient the removal. Table 6 lists the different rate constants of different flowrates for both air stripping and solvent sublation. Figure 11 shows the effect of air flowrate on rate constant.

The increasing flowrate would increase the removal rate because more bubbles are generated which provide more interfacial area between bubble and solution. It is observed

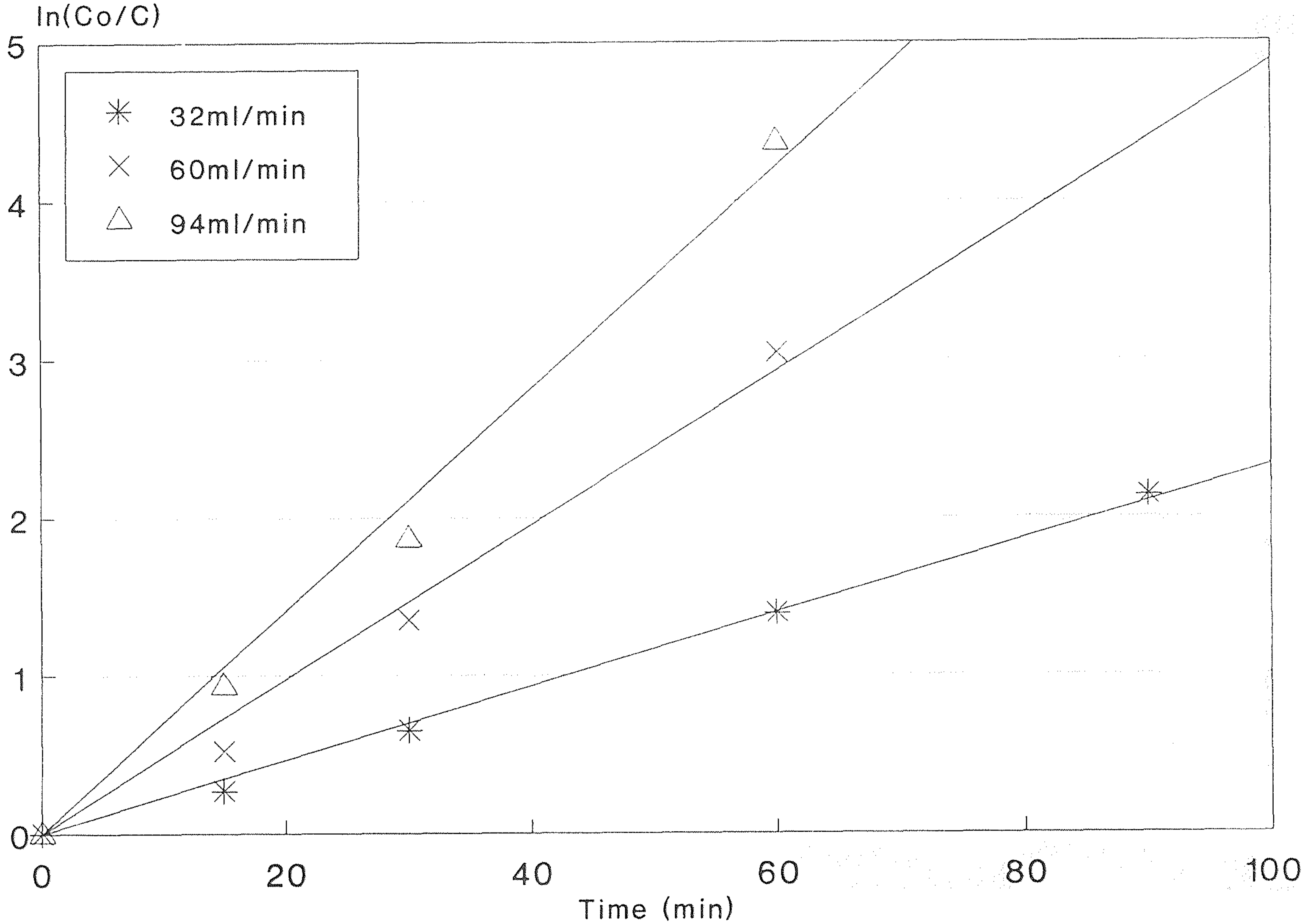


Figure 9 The Effects of Air Flowrates on Toluene Removal from Water by Solvent Sublation.

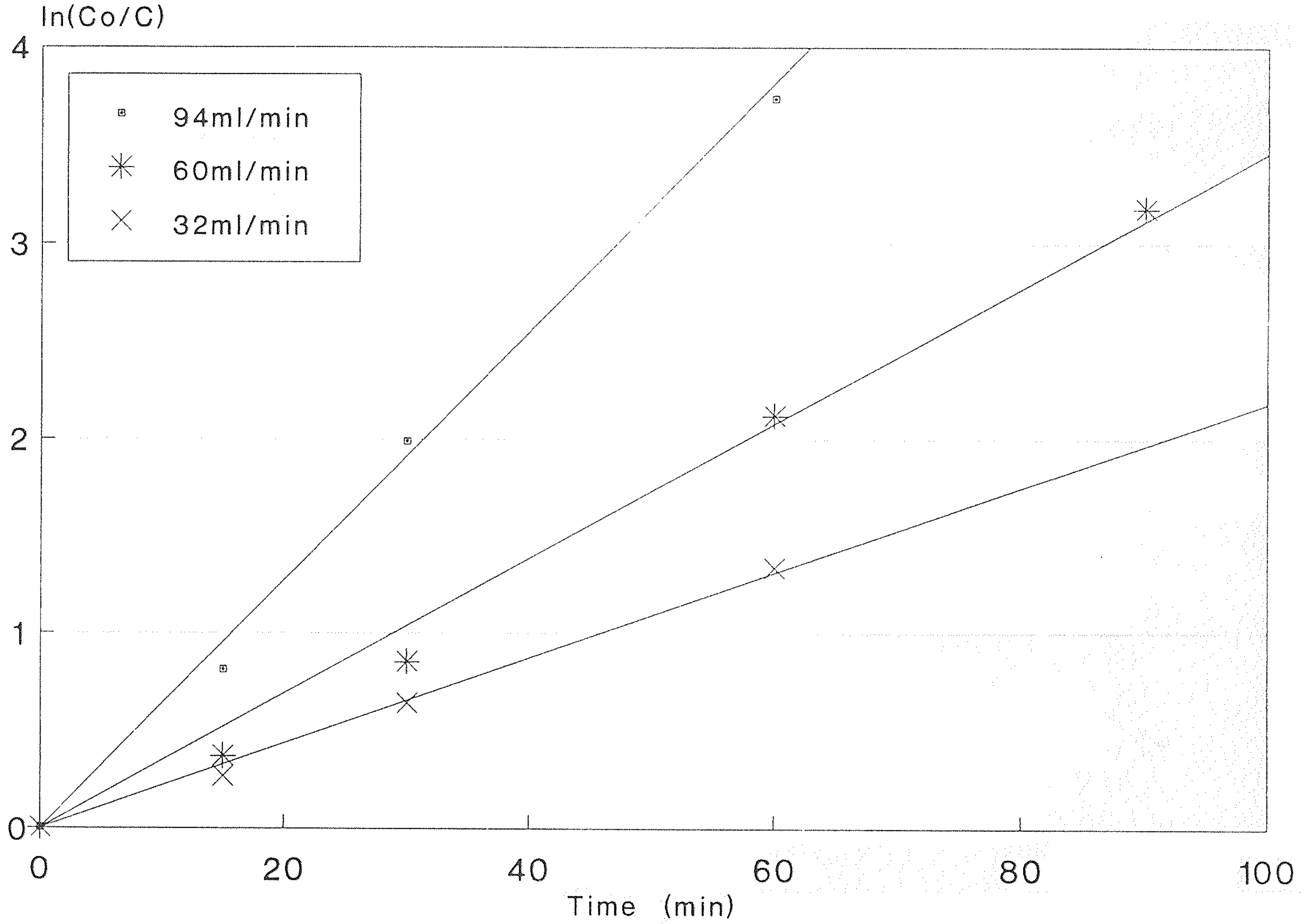


Figure 10 The Effects of Air Flowrates on Toluene Removal from Water by Air Stripping.

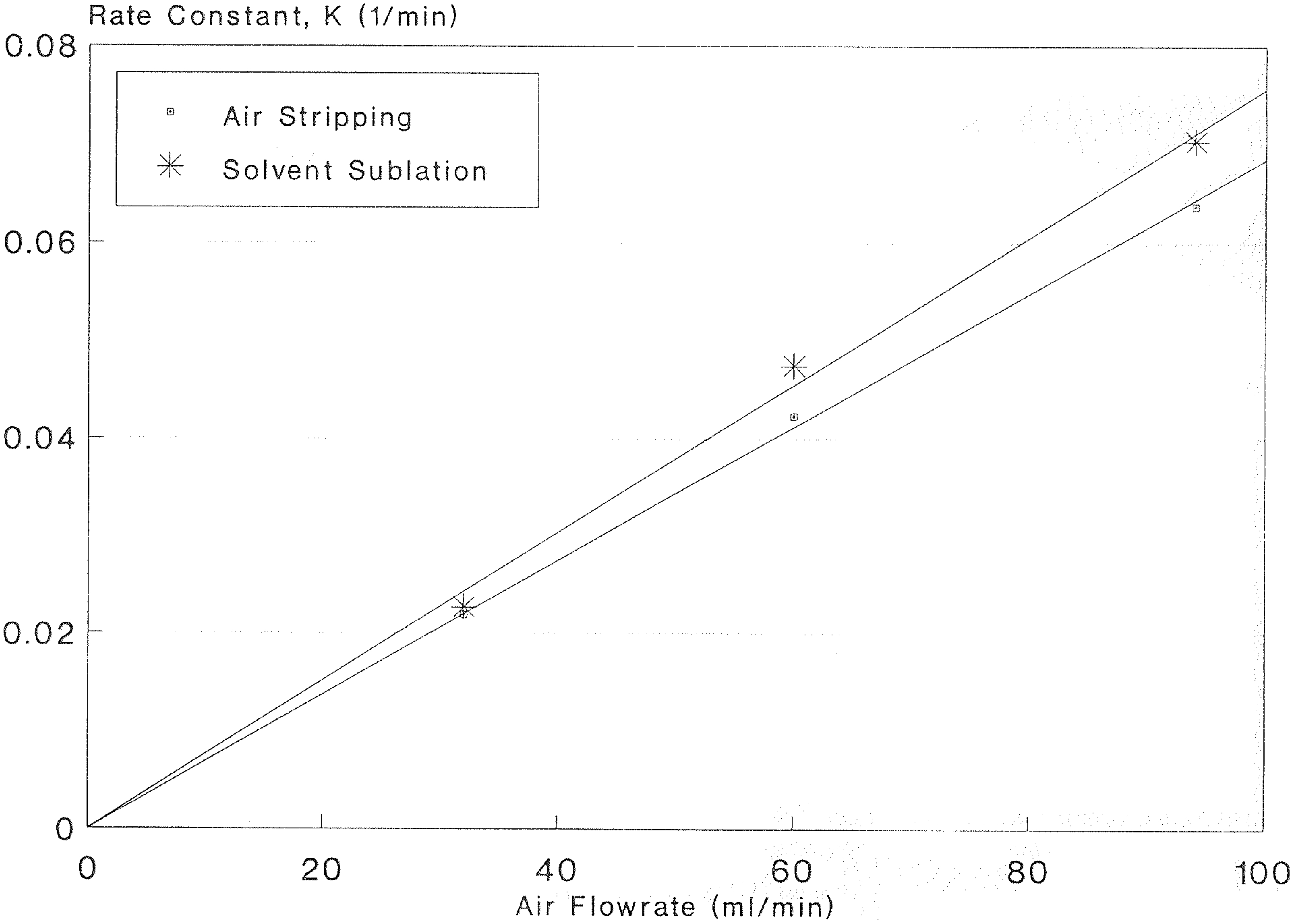


Figure 11 The Effects of Air Flowrates on Rate Constant.

in Figure 11 that the increase in removal of toluene from aqueous phase is almost proportional to the increase in the air flowrate under 94ml min^{-1}. But it was found by Valsaraj and co-workers (8) that if the flowrate was increased to a certain point, the removal rate was not proportional to flowrate anymore. This is probably due to the increase in mean bubble radius as the flowrate increased, which decreased the interfacial area per unit volume of air (8,25). Moreover, large bubbles have less residence time in the solution and higher rise velocities (5). Therefore, the proper way to increase the efficiency of removal is to keep bubble size small without reducing the flowrate (5).

Table 6 Rate Constants of Different Flowrate *

	Rate Constant, K, min^{-1}		
	32ml/min	60ml/min	94ml/min
Air stripping	0.0218	0.0422	0.0637
Solvent Sublation	0.026	0.0474	0.0703

* Thickness of Organic Layer: 10mm

The effect of air flowrate on toluene emission to the air was also examined. Figure 12, Table 7 show the change of toluene concentration in the air at different times for air striping. It was found that at higher flowrate the initial concentration of toluene in air was higher, but it dropped very fast compared to that of lower flowrates. The same type of result was also obtained in the solvent sublation (Figure 13, Table 7). The reason for this is that at higher flowrate the toluene removal rate constant is higher than that of lower flowrate, thus more toluene is emitted to the air at the beginning of high-flowrate run.

The comparison of air stripping and solvent sublation at different flowrates was carried out. It was observed that in case of solvent sublation much less toluene was emitted to the air than in air stripping. This is due to the paraffin oil floated on top of the column which dissolved most of the toluene stripped by air. The layer also prevents the toluene from regenerating to the aqueous phase. Figure 14 shows the comparison of

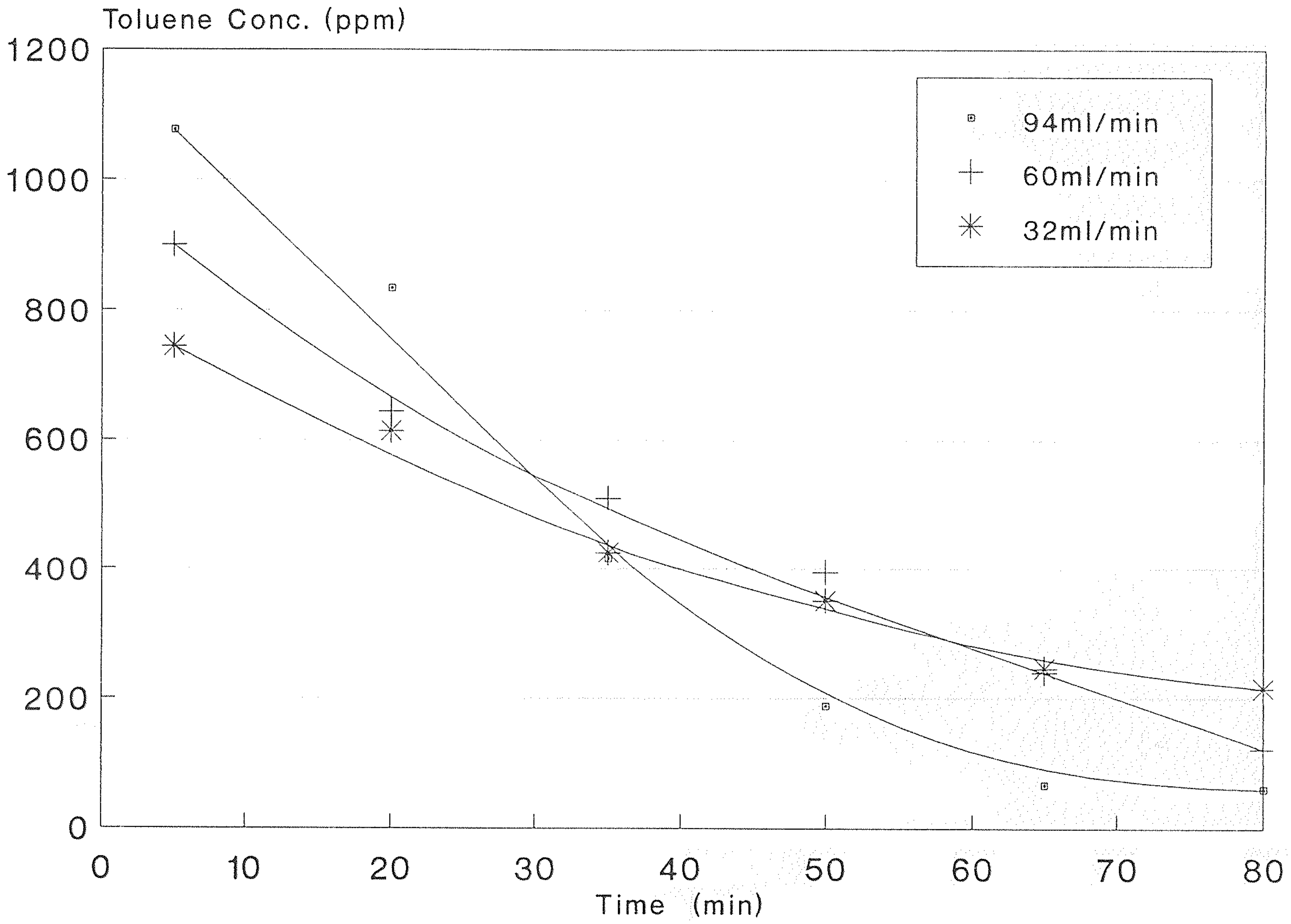


Figure 12 The Effects of Air Flowrates on Toluene Emission to the Air by Air Stripping.

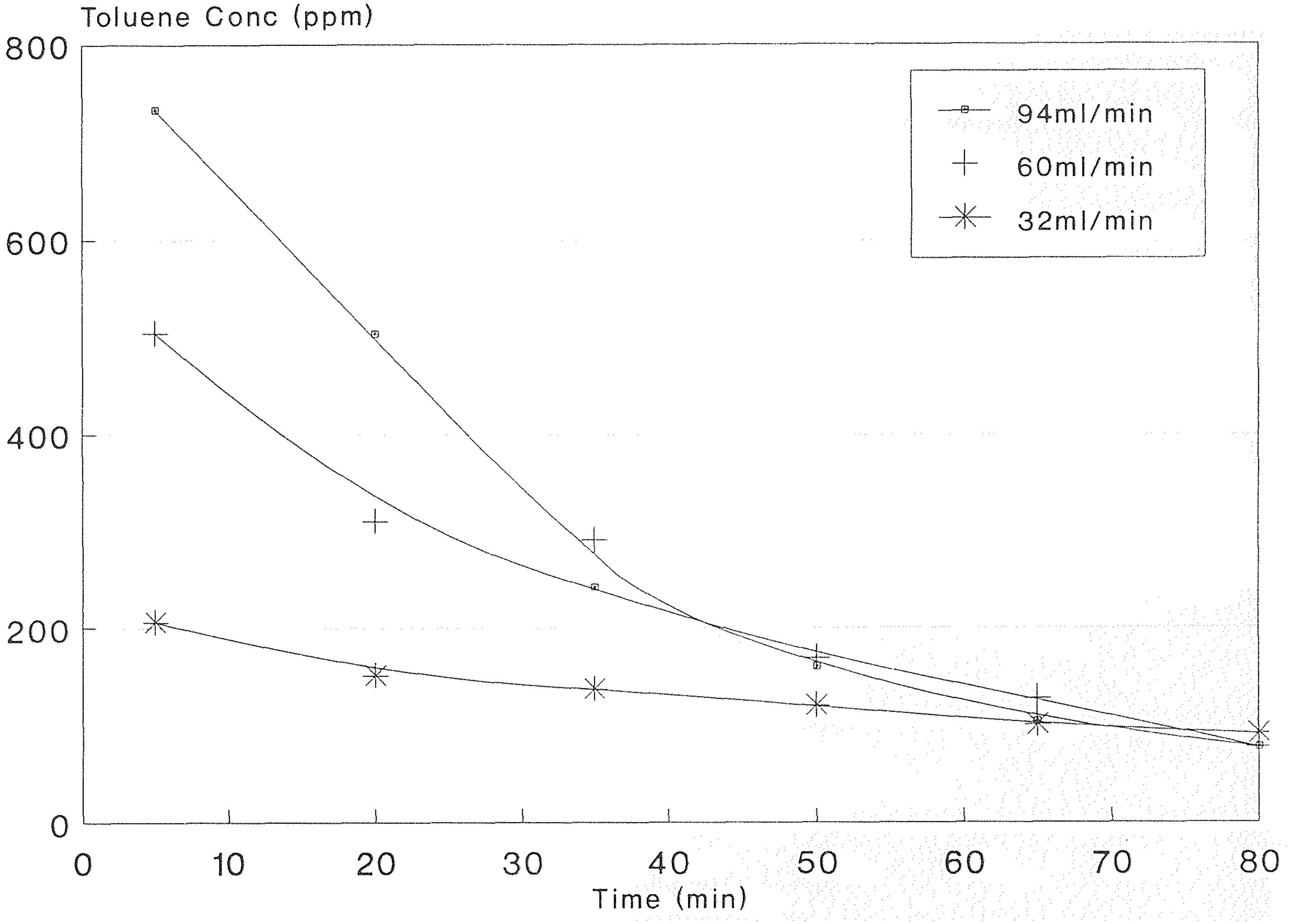


Figure 13 The Effects of Air Flowrates on Toluene Emission to the Air by Solvent Sublation.

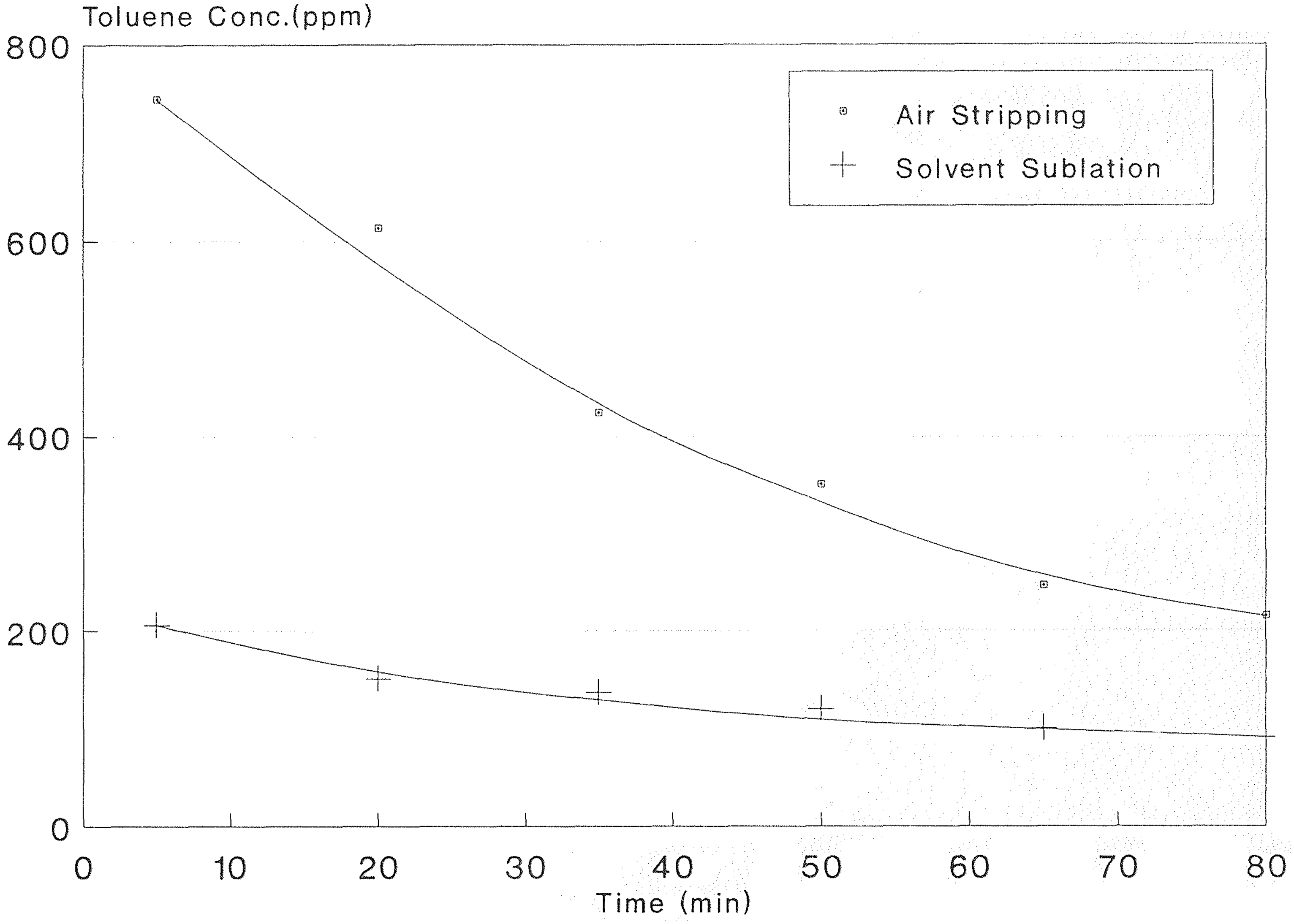


Figure 14 The Comparison of Air Stripping and Solvent Sublation on Toluene Emission to the Air.

air stripping and solvent sublation at flowrate of 32ml min^{-1}.Toluene emissions could be expressed by the areas under each curve, which can be calculated by numerical integration of the curve. The emission reductions of toluene in air at different air flowrates by solvent sublation for 80min are listed in Table 8 and Figure 15. It shows the emission reduction is higher at low flowrate than that of high flowrate, because at low flowrate the bubble rise velocity is low and the residence time for bubble to travel through the layer is long, thus more toluene is extracted to the oil.

Table 7 The Effect of Air Flowrate on Toluene Emission to Air by Solvent Sublation *

		Toluene Conc. in Air, ppm					
Flowrate (ml/min)	Time (min)	5	20	35	50	65	80
94	Air Stripping	1076	833	415	187	66	60
60	Air Stripping	900	644	508	394	240	122
32	Air Stripping	744	613	424	415	246	215
94	Solvent Sublation	733	503	241	160	103	71
60	Solvent Sublation	504	310	291	169	127	77
30	Solvent Sublation	206	151	137	120	101	91

* Thickness of Organic Layer: 10mm

Table 8 Emission Reduction by Solvent Sublation at Different Air Flowrates

Air Flowrate, ml/min	32	60	94
Emission Reduction, %	71	49	34

* Thickness of Organic Layer: 10mm

Table 9 shows the ratios of volume of air passed through the column and volume of water in the column at different air flowrates by both air stripping and solvent sublation when the removal rate is 90%. It is found that less air is needed by solvent sublation to remove 90% of toluene from aqueous phase. Therefore, solvent sublation is more efficient than air stripping.

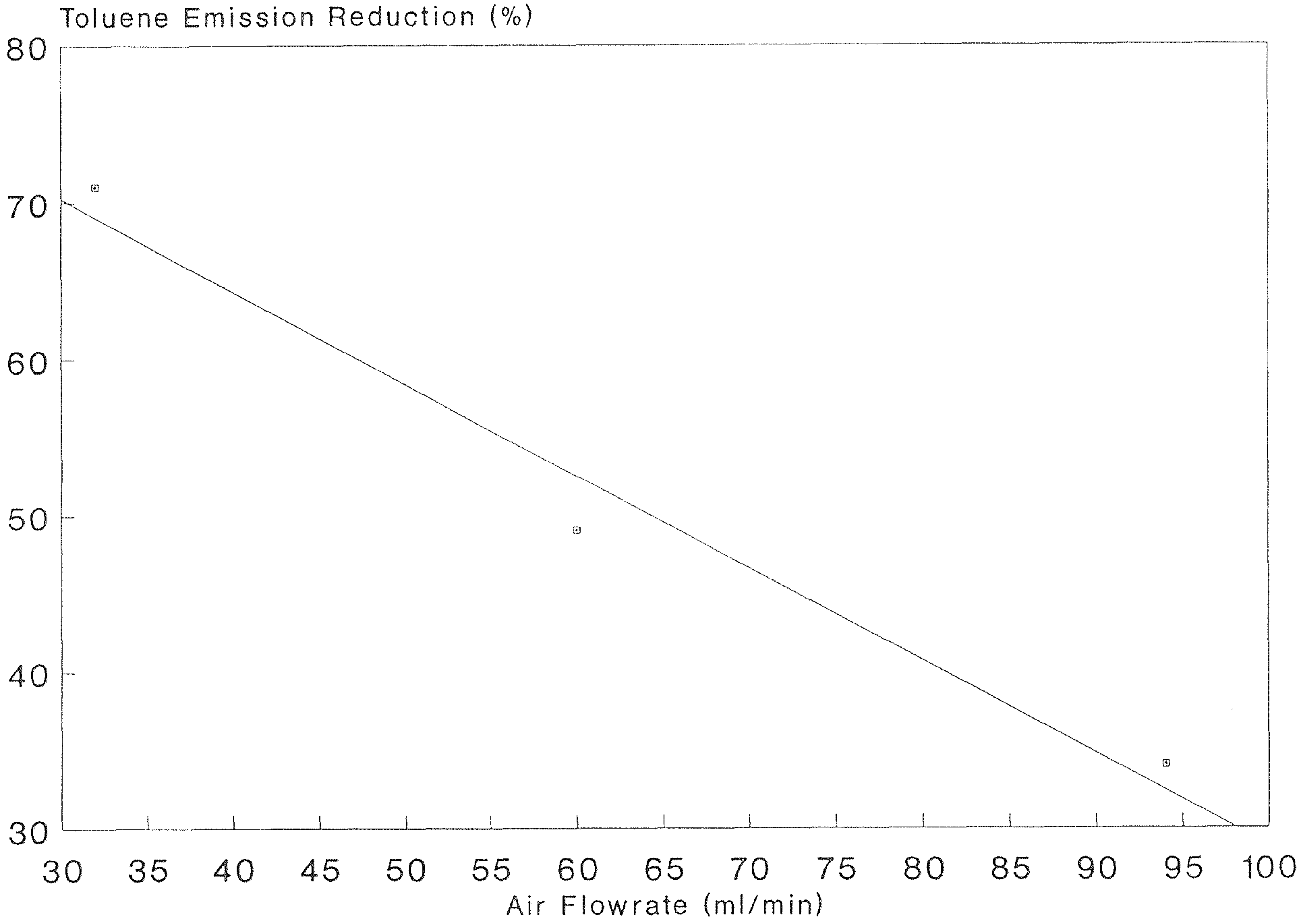


Figure 15 The Effects of Air Flowrates on Toluene Emission Reduction by Solvent Sublation.

Table 9 The Comparison of Air/Water Ratios by Air Stripping and Solvent Sublation at Different Air Flowrates. *

Air Flowrates, ml/min	Air/Water Ratio (ml/ml)	
	Air Stripping	Solvent Sublation
32	5.6	5.4
60	5.4	4.8
94	5.6	5.2

* The toluene removal rates are 90%
Thickness of Organic layer: 10mm

4.2 The Effect of Thickness of Organic Layer

The effect of thickness of organic layer on solvent sublation was investigated. In comparison with air stripping, solvent sublation improved the removal efficiency, because the organic layer captured the toluene carried by the bubbles and prevented the toluene from redissolving into the aqueous phase, but no marked improvement was observed on toluene removal from water using different thickness of layer varying from 10mm to 20mm at flowrate 60 ml/min (Figure 16). Table 10 gives the rate constant of different thicknesses of layer and Figure 17 shows the effect of the thickness of layer on rate constant. It is found that a layer up to 10mm thick increased the efficiency of removal somewhat, but much thicker layer (› 10mm) does not give a marked improvement at flowrate of 60 ml/min. The reason for this may be as stated by Valsaraj et. al. (5):

1. The mass-transfer mostly occurs from bubbles crossing the aqueous-solvent interface and not from molecular diffusion of solute. As a result, the amount of toluene removal depends on the amount of air crossing the interface, not on the volume of organic layer.
2. If the organic layer is too thin, the oil-water interface may be disrupted and the process would lose its efficiency, reverse mass transfer of solute from the organic layer to the aqueous phase would occur. At this time, thickness of layer would have an effect on the removal efficiency.

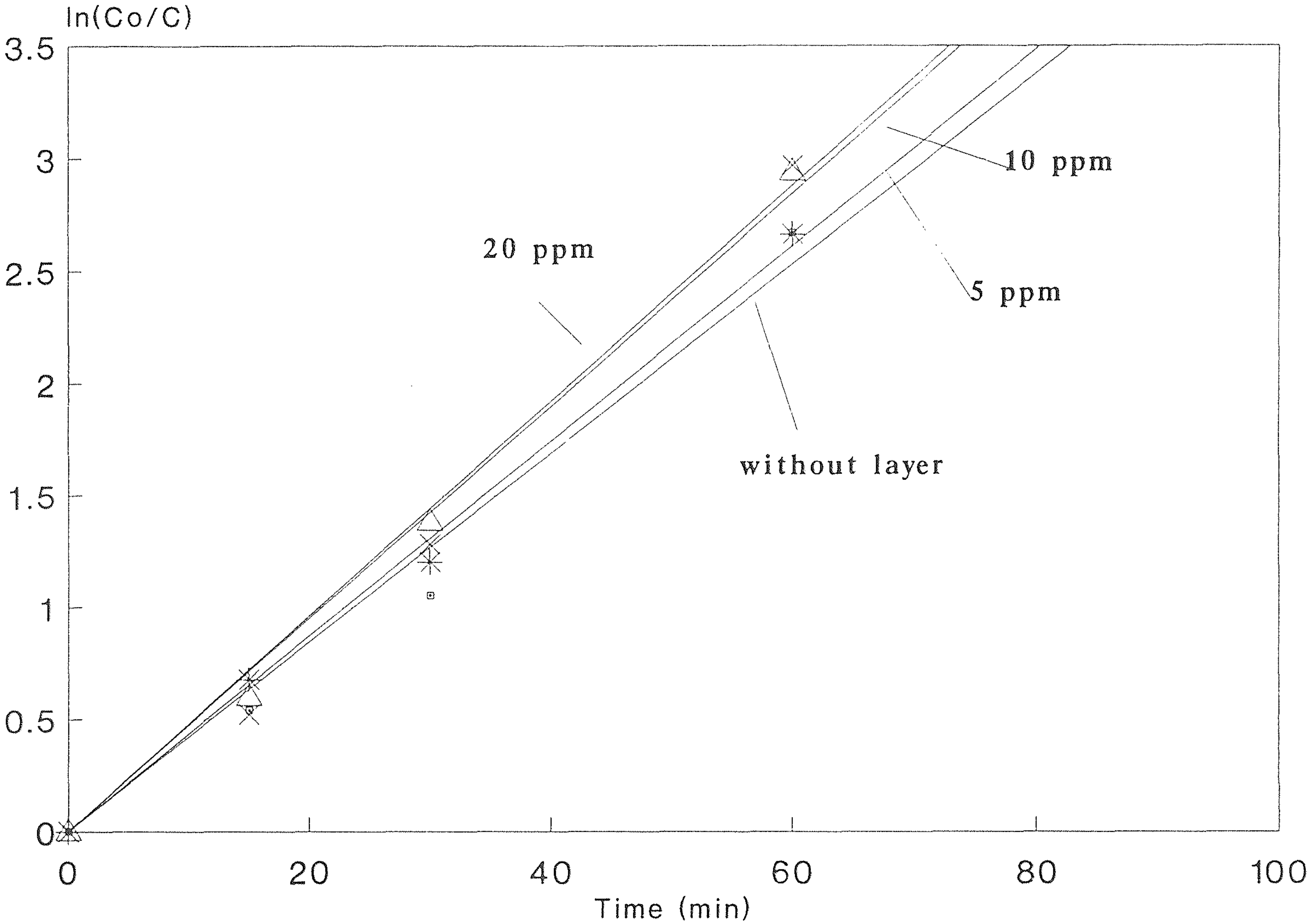


Figure 16 The Effects of Thickness of Organic Layer on Toluene Removal from Water.

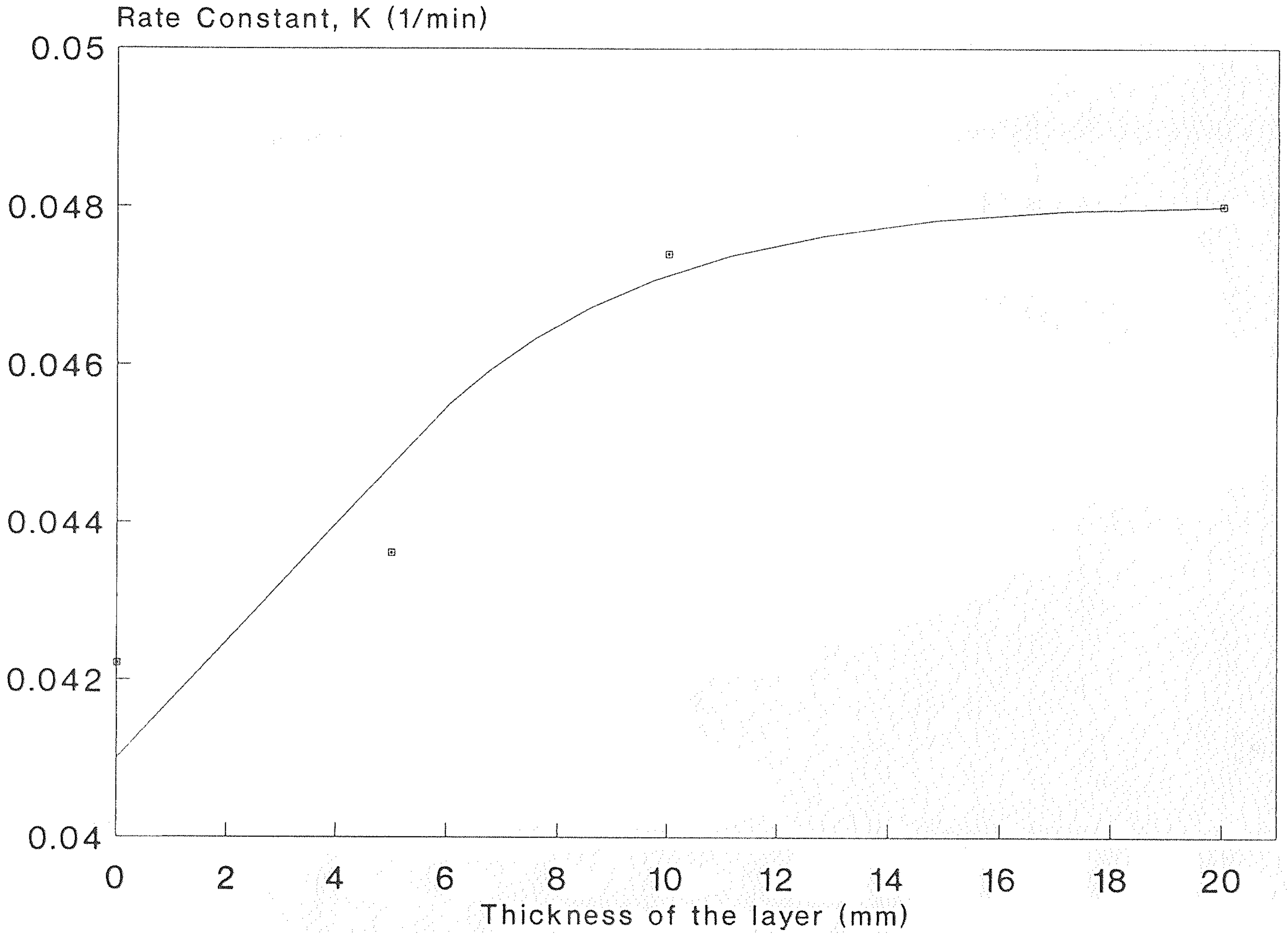


Figure 17 The Effects of Thickness of Organic Layer on Rate Constant.

Table 10 Rate Constants of Different Thickness of Layer *

Thickness of Organic Layer (mm)	Rate Constant, K (min^{-1})
0	0.0422
5	0.0436
10	0.0474
20	0.0480

*Air Flowrate: 60ml min^{-1}

On the other hand, thickness of organic layer has more effect on toluene emission to atmosphere that on their removal from water (Figure 18, Table 11). As mentioned before (5), hydrophobic compounds which are volatile (like toluene) or partly volatile will be carried by bubbles simultaneously in the vapor phase within the bubbles and also on the surface of the bubbles. When the bubble transits the aqueous column and moves through the organic layer, the toluene on the bubble surface is stripped into the organic phase. At the same time, equilibrium between the vapor (inside the bubble) is being established, the volatile materials in the interior of the bubble may also partition into the organic layer. If the organic layer remains non-agitated, the mass transfer from the organic layer to the atmosphere is a very slow process. If the flowrate is not too low, and the organic layer is only 5mm thick, as the bubble passes through the organic layer, it does not have enough time to establish the equilibrium between the vapor phase inside the bubble and the organic layer. As a result , the toluene is emitted to the atmosphere as the bubble exits the layer. If the layer is thicker (20mm), the bubble has more residence time which is required for the toluene inside the bubble to be partitioned into the organic layer. Table 12 and Figure 19 give the emission reductions for different thicknesses of layer.

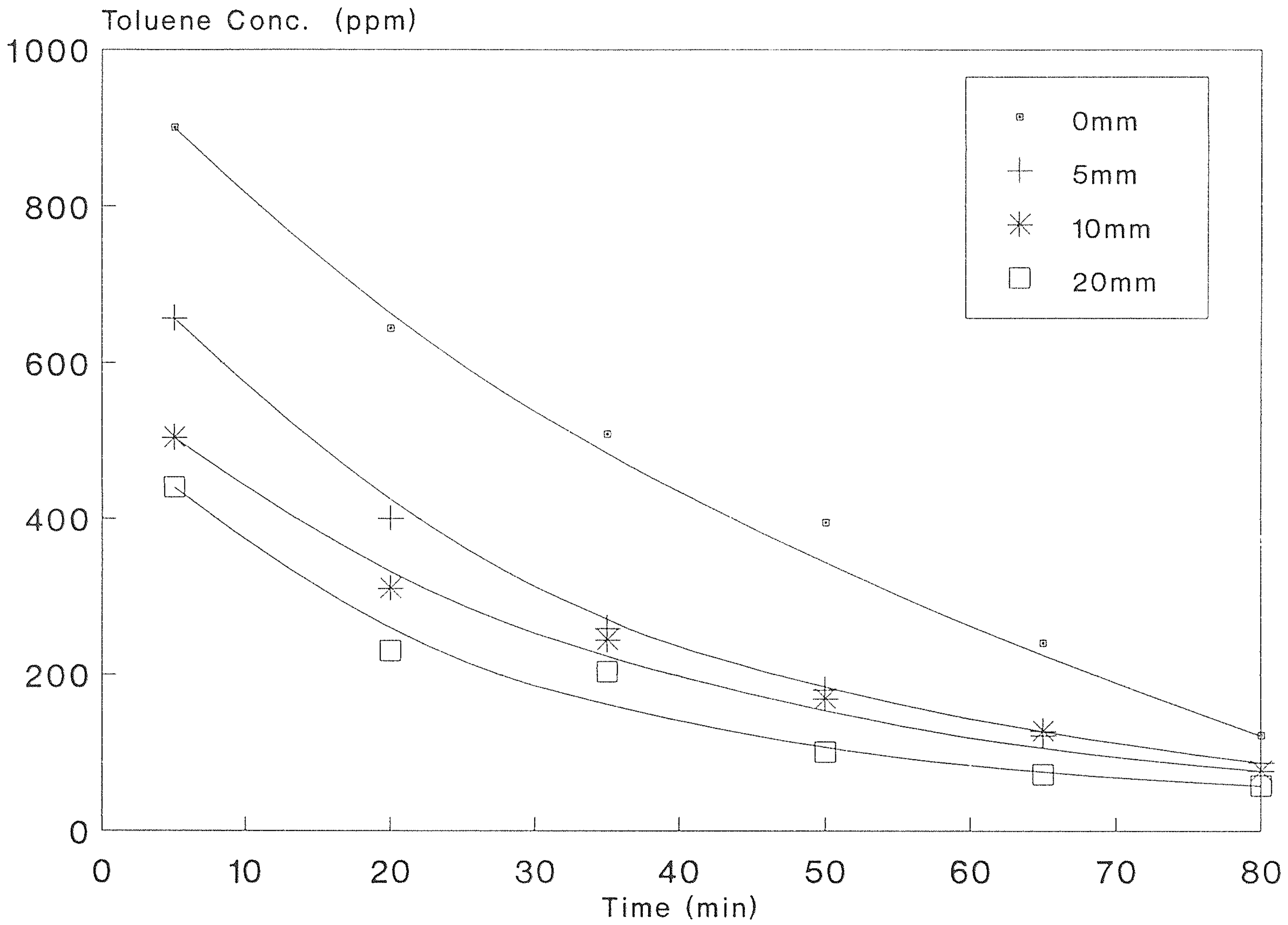


Figure 18 The Effects of Thickness of Organic Layer on Toluene Emission to the Air.

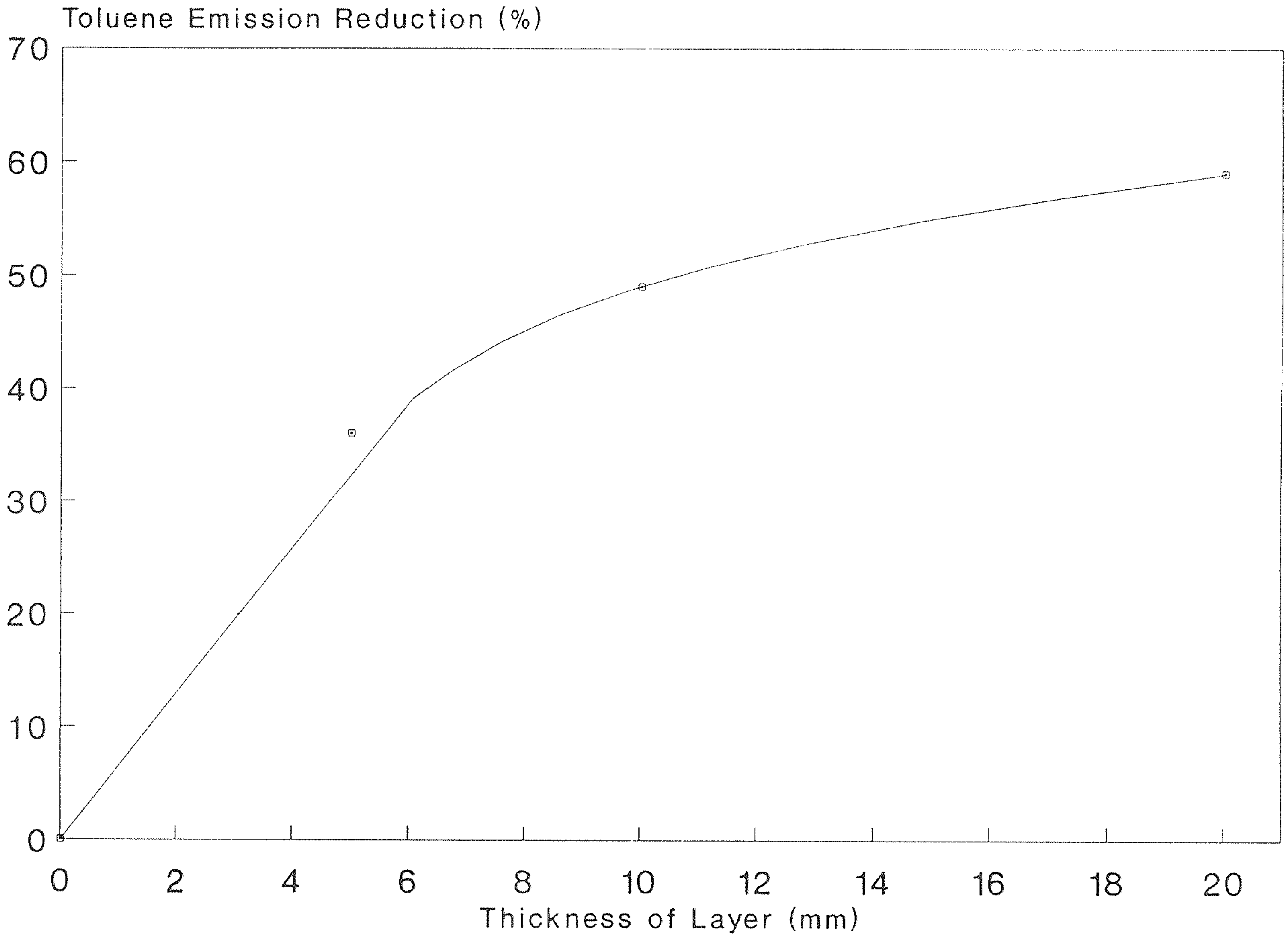


Figure 19 The Effects of Thickness of Organic Layer on Toluene Emission Reduction by Solvent Sublation.

Table 11 The Effect of Thickness of Layer on Toluene Emission*

Thickness of the layer,		Toluene Conc. in Air,					
mm	Time (min)	5	20	35	50	65	80
0		900	644	508	394	241	122
5		657	400	259	180	122	87
10		504	310	291	169	127	77
20		440	230	203	101	72	58

* Air Flowrate: 60ml min^{-1}

Table 12 Emission Reduction by Solvent Sublation of Different Thickness of Layer *

Thickness of Layer ,mm	5	10	20
Emission Reduction, %	36	49	59

* Air Flowrate: 60ml min^{-1}

4.3 The Effect of Co-solutes

4.3.1 Surfactants

1. Anionic surfactant (sodium lauryl sulfate)

Sodium lauryl sulfate (SLS) was chosen as a anionic surfactant on removal of toluene from water. The air flowrate was 60 ml/min, the thickness of organic layer was 10mm. Figure 20 shows that no improvement was obtained by adding 10 ppm SLS to the sublation process. The presence of surfactant in the solution leads to two contradictory effects on the air - water interface. Firstly, the ionic surfactant was adsorbed on the surface of bubble and provided a electrical barrier for bubbles to coalesce, which reduced the extent of diffusion of the hydrophobic across the boundary layer of bubble. Secondly, the surfactant also reduced the surface tension of the liquid which leads to decrease the bubble size (9). However, the surfactant reduces the surface tension of the aqueous solution mostly depending upon its concentration (5). A typical surface tension - concentration curve is shown in Figure 21. It can be seen surfactant concentration less than a certain value does not significantly reduce the surface tension, and thus could not

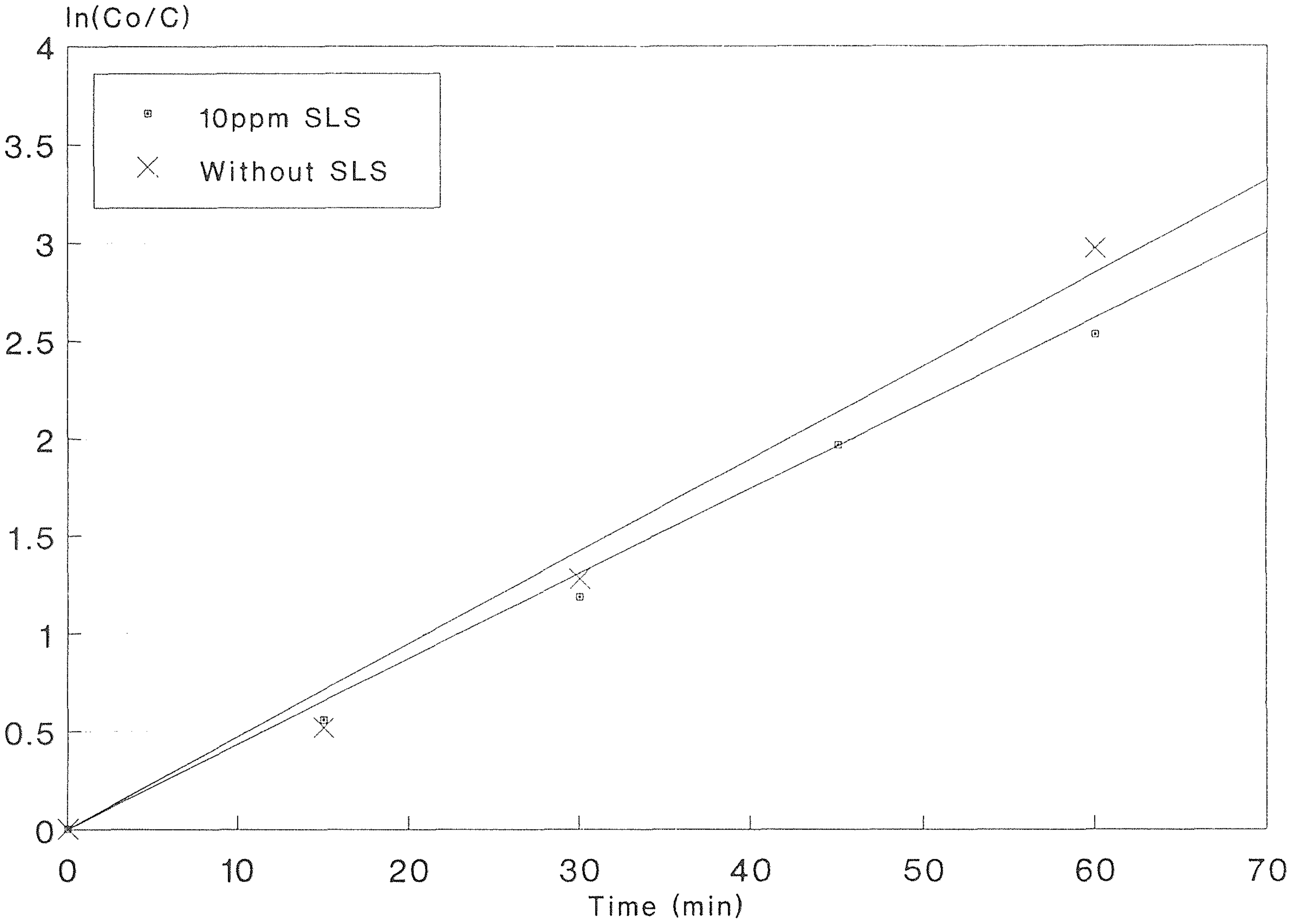


Figure 20 The Effects of SLS on Toluene Removal from Water.

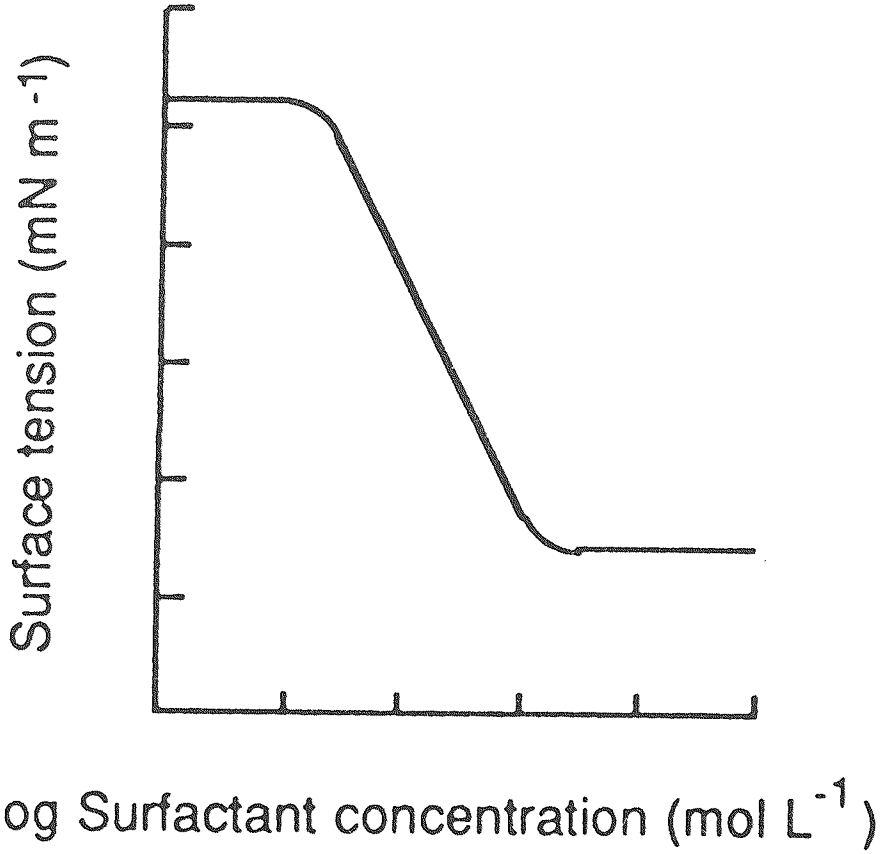


Figure 21 Schematic Illustration of a "typical" Surface Tension - Concentration Curve for an Aqueous Surfactant Solution.

drastically improve the sublation efficiency (27). The concentration of SLS chosen for our experiment is 10ppm, which may be too low to increase the sublation efficiency, but higher concentration of SLS in aqueous phase would cause much foam on top of the sublation column which give problems for analyzing the gas phase. Moreover, too high concentration of SLS would lead emulsion of oil layer and aqueous phase. Future work will be done to solve these problems.

The effect of SLS on toluene emission was also studied, Table 13 and Figure 22 show the results. The toluene emission reduction was 28% when SLS concentration was 10ppm. It was found that toluene emission reduction was much less than without SLS, the reason may be that SLS changed the surface property of bubble and made the toluene which was either on surface of the bubble or inside the bubble difficult to dissolve in the layer.

Table 13 The Effect of SLS on Toluene Emission to Air *

Conc. of SLS	Flowrate		Toluene Conc. in Air, ppm					
ppm	ml/min	Time, min	5	20	35	50	65	80
10	60	Air Stripping	1002	701	523	290	190	106
10	60	Solvent Sublation	852	466	358	146	98	54

* Thickness of Organic Layer: 10mm

4. Cationic surfactant

The efficiency of toluene removal was slightly improved by adding cationic surfactant hexadecyltrimethylammonium bromide (HTMAB) at the concentrations of 5 and 10ppm (Figure 23). The air Flowrate was 32 ml/min, and thickness of layer was 10mm. Table 13 list the rate constants at different concentration of HTMAB. Figure 24, Table 14 shows the effect of HTMAB on removal rate constants, increased concentration of HTMAB increased toluene removal rate. As mentioned before, surfactant could reduce the surface tension of the aqueous solution, thus decreasing the bubble size and increasing

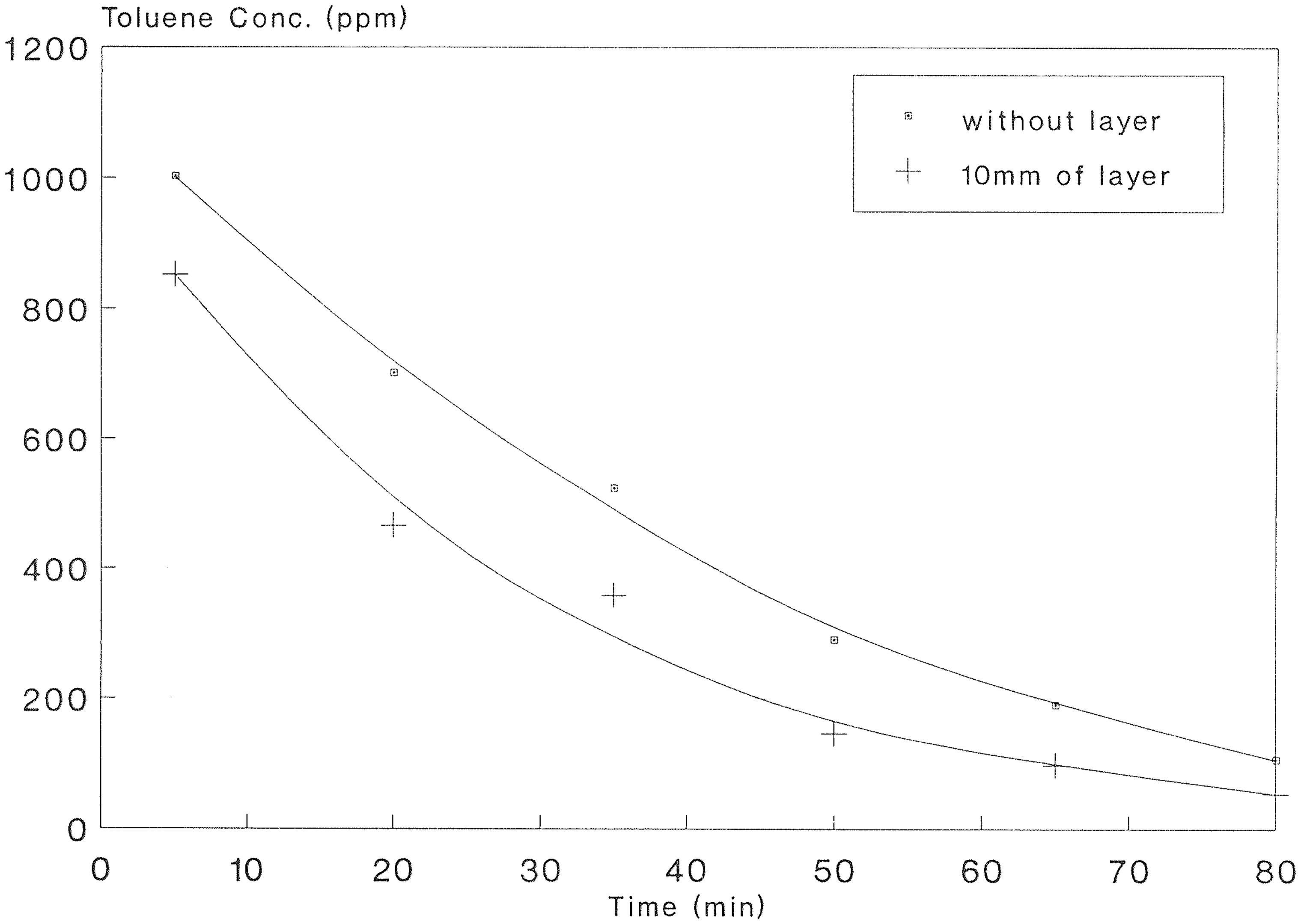


Figure 22 The Effects of SLS on Toluene Emission to the Air.

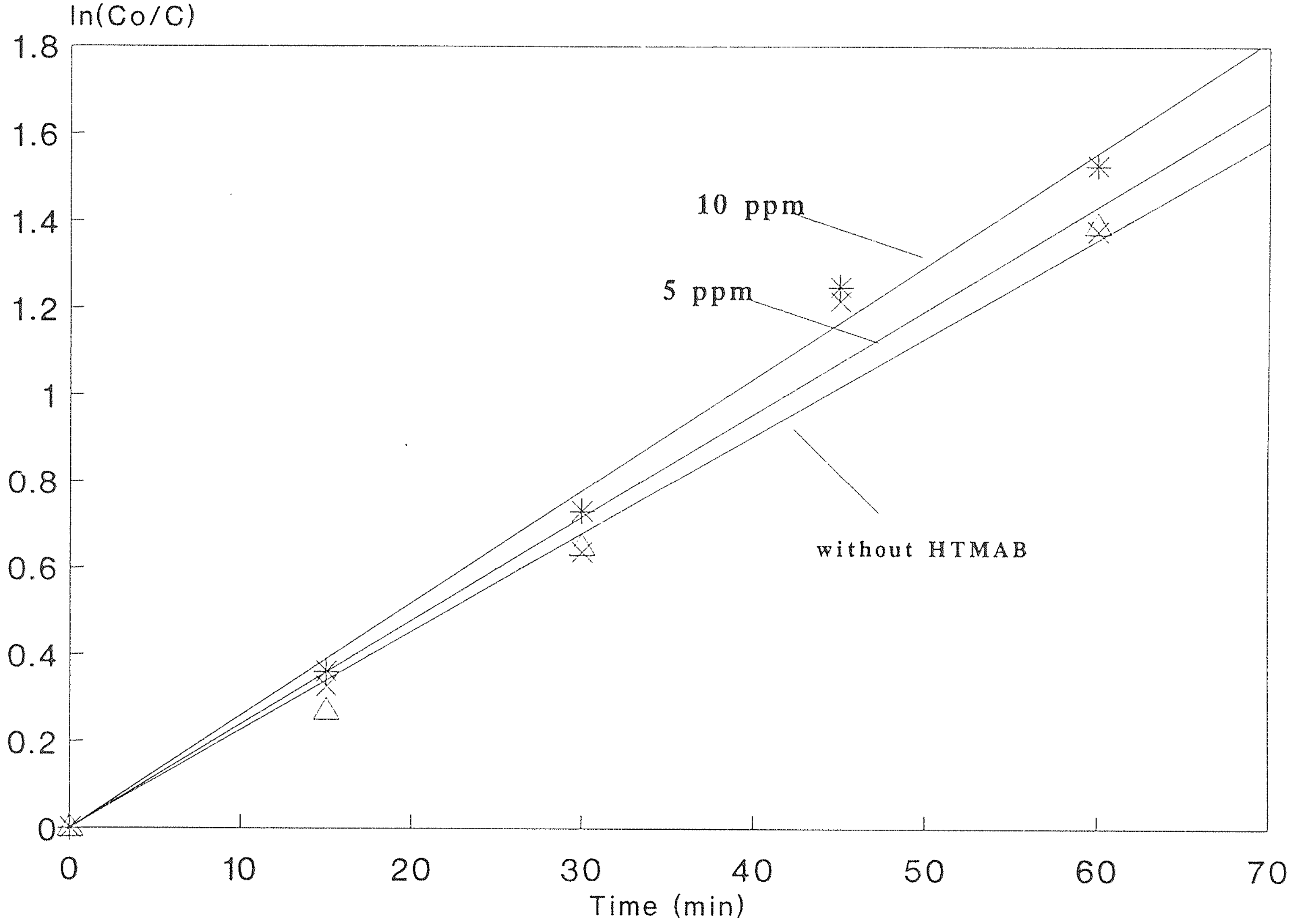


Figure 23 The Effects of HTMAB Concentration on Toluene Removal from Water.

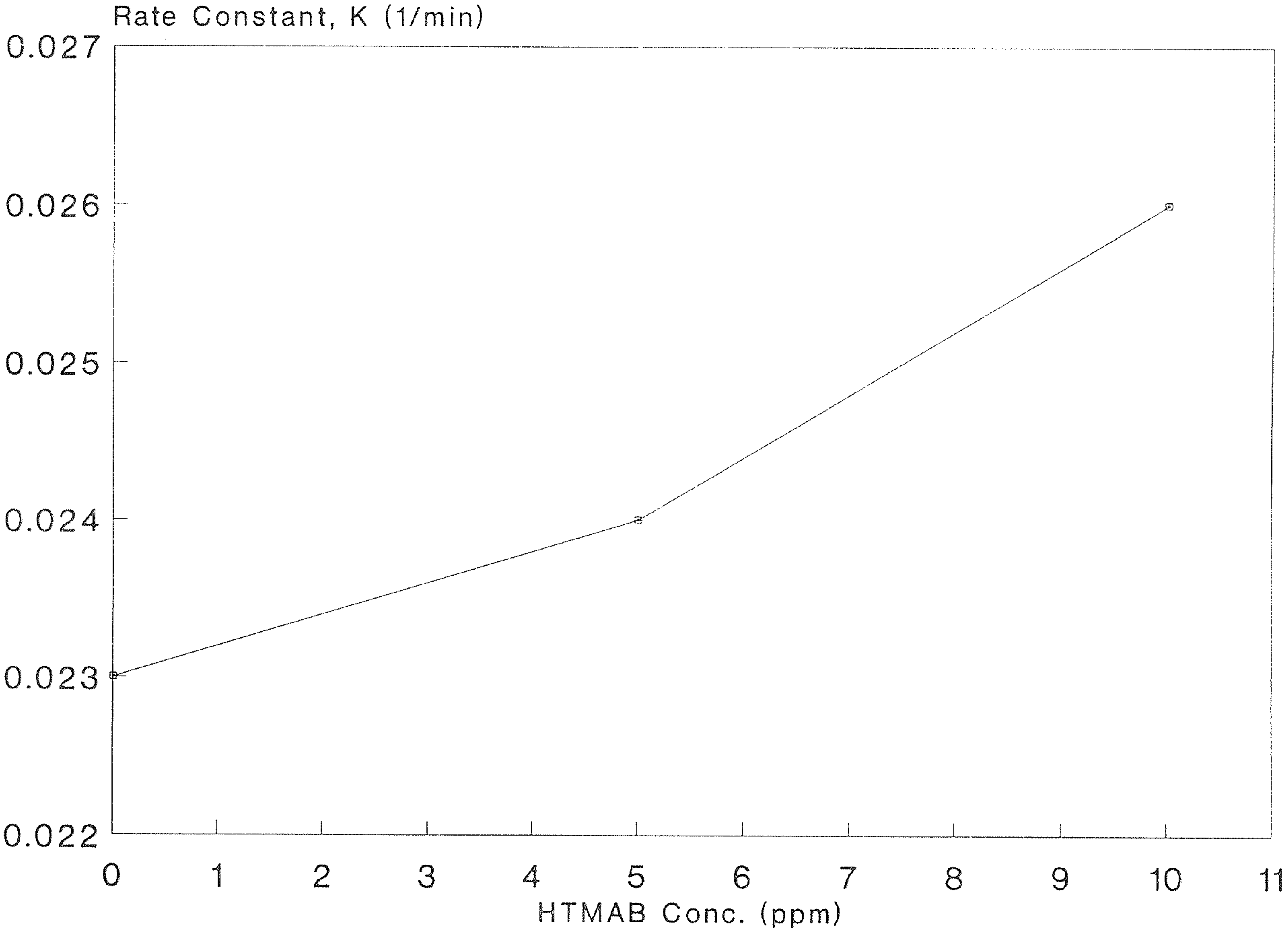


Figure 24 The Effects of HTMAB Concentration on Rate Constant.

the interfacial area per volume of air. Because of the limitation of gas phase analysis (large foam caused by the presence of surfactant), we could not increase the HTMAB concentration further, so no significant improvement was observed by adding HTMAB. In comparison with anionic surfactant SLS, HTMAB is somewhat more efficient (there was almost no improvement by adding 10ppm SLS). This may be due to the fact that HTMAB is more surface active than SLS (the hydrophobic chain length of HTMAB is longer) (8).

Table 14 The Effect of HTMAB on Removal Rate Constant *

Concentration of HTMAB, ppm	Rate Constant, K (1/min)
0	0.0226
5	0.0239
10	0.0259

* Air Flowrate: 32ml min^{-1}, Thickness of Organic Layer: 10mm

HTMAB also has an effect on toluene emission to the air in solvent sublation process. Figure 25, Table 15 shows the effect of HTMAB on gas phase. The initial concentration of toluene in air was lower than that without HTMAB. It gradually increased and reached to a maximum at 20 to 30 minutes. This is because the formation of foam on top of the sublation column. The toluene carried out by the air bubbles was adsorbed in the foam, and held for a while and then emitted to the air because the foam saturated in the layer. Comparing 5ppm HTMAB and 10ppm HTMAB, it was found that at HTMAB concentration of 5ppm the maximum toluene concentration was reached earlier than that of 10ppm HTMAB due to larger amount of foam forming at higher HTMAB concentration. In the presence of HTMAB, the toluene emission reduction is some what less than that without HTMAB. The comparison of the toluene removal reduction is showed in Table 16. Figure 26 shows the solvent sublation process from toluene removal from the aqueous phase to the toluene emission to the air at the presence

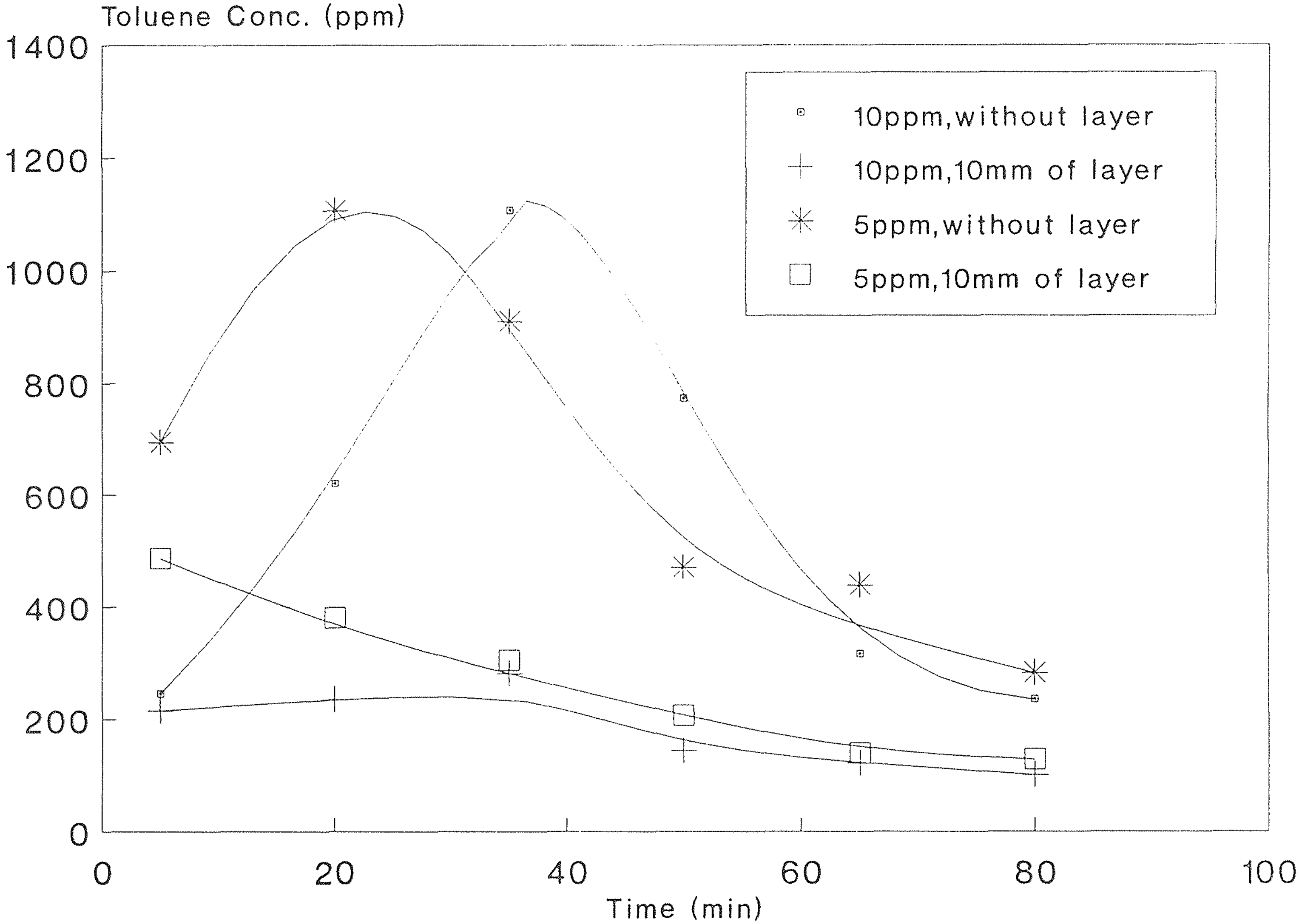
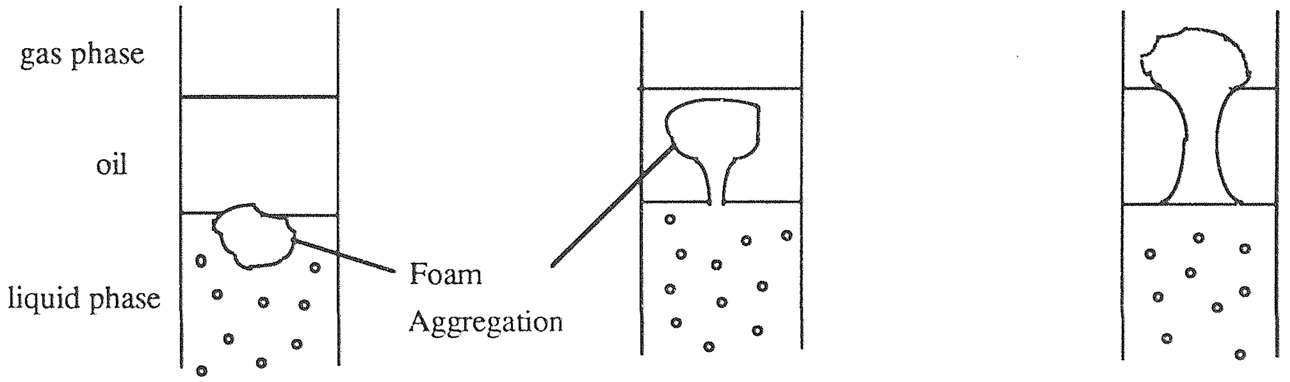


Figure 25 The Effects of HTMAB Concentration on Toluene Emission to the Air.



under the organic layer

in the organic layer

out of the organic layer

Figure 26 The Process of Toluene Emission from the Aqueous Phase to the Air in the Presence of HTMAB of HTMAB. It was observed that foam formed under the organic layer, and coalesced into masses of bubbles, which passed through the organic layer. The foam prevented the bubble which adsorbed toluene on its surface or inside itself from contacting with the organic layer. As a result, more toluene was emitted to the air.

Table 15 The Effect of HTMAB Concentration on Toluene Emission to Air *

Conc. of HTMAB		Toluene Conc. in Air, ppm					
ppm	Time, min	5	20	35	50	65	80
5	Air Stripping	695	1107	910	469	438	282
5	Solvent Sublation	486	380	304	206	139	128
10	Air Stripping	244	620	1107	772	315	234
10	Solvent Sublation	215	234	281	144	121	101

* Air Flowrate: 32ml min^{-1}
Thickness of Organic Layer: 10mm

Table 16 The Comparison of Emission Reduction (with and without HTMAB)*

Concentration of HTMAB, ppm	0	5	10
Emission Reduction, %	71	55	67

* Air Flowrate: 32ml min^{-1}
Thickness of Organic Layer: 10mm

4.3.2 Ethanol

The effect of ethanol on the toluene removal was investigated. It was found that certain amount of ethanol could improve removal efficiency (Figure 27). Table 17 gives the rate constants obtained by our research. The concentration of ethanol in toluene solution for our experiment was 0.1% (Vol.%), which was selected because it was found by Valsaraj and coworkers (5) that ethanol concentration between 0.01-4% can enhance the removal rate of organics. The presence of toluene lowers the surface tension of solution and prevents the bubbles from growing large. The smaller bubbles provide a large interfacial

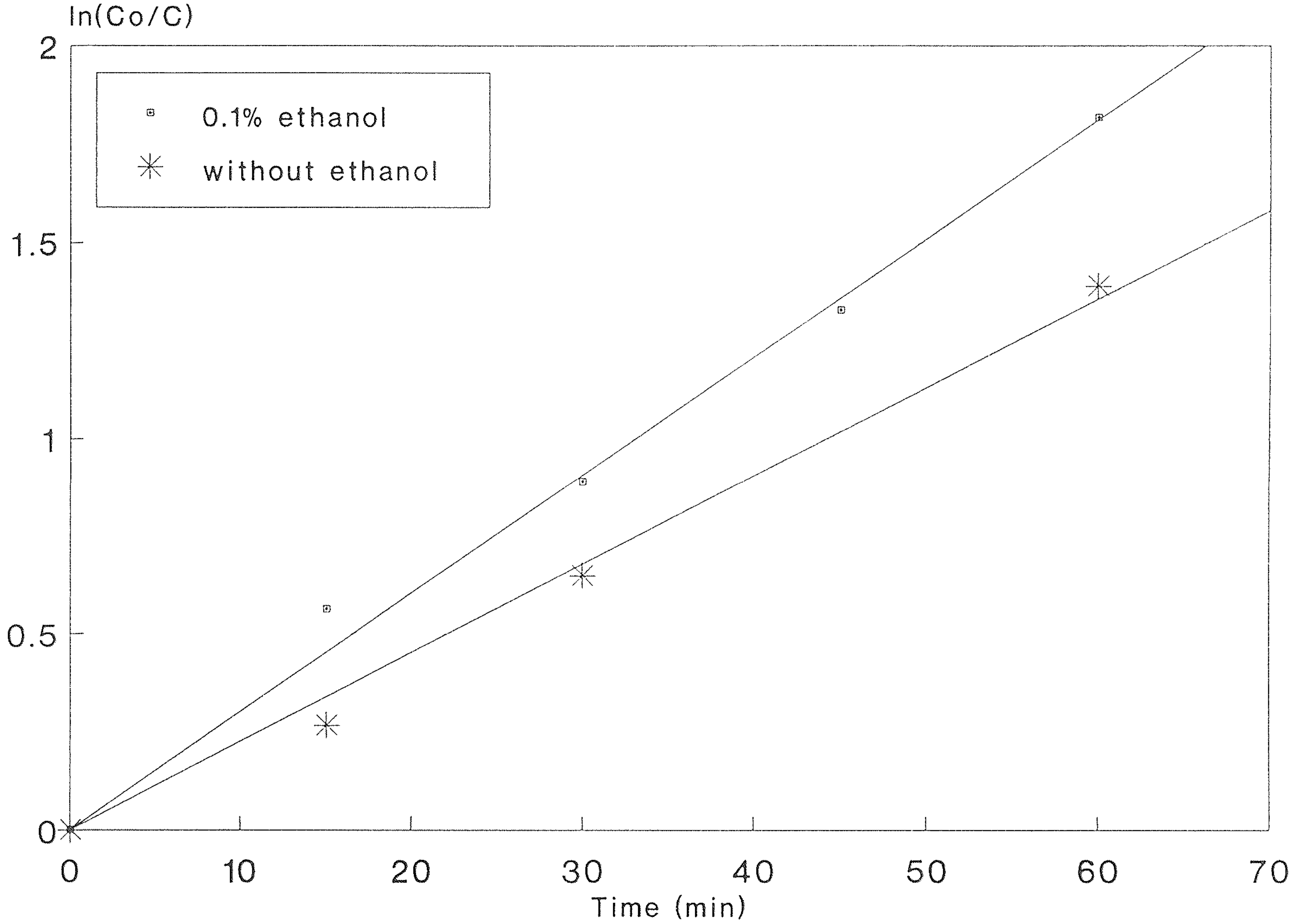


Figure 27 The Effects of Ethanol on Toluene Removal from Water.

area per unit volume of air, which finally enhances mass transfer from the liquid phase to bubbles and also increases the residence time within the aqueous phase.

Table 17 The Effect of Adding Ethanol on Rate Constant *

	Rate Constant , min^{-1}
without Ethanol, with layer (10mm)	0.0226
0.1% Ethanol, without layer	0.0260
0.1% Ethanol, with layer (10mm)	0.0302

* Air Flowrate: 32ml min^{-1}

Ethanol also has effect on toluene emission. It is found that more toluene is emitted to the air during the solvent sublation process. This may be due to the formation of foam under the organic layer, which coalesced with the bubble and prevented it from contact with the organic layer. Figure 28, Table 18 show the effect of ethanol on toluene emission for both air stripping and solvent sublation. The emission reduction of toluene with 0.1% ethanol by solvent sublation was less in comparison with that without ethanol (Table 19). As a result, the presence of ethanol could improve the toluene removal efficiency effectively, but at the same time it increased the toluene emission.

Table 18 The Effect of Ethanol on Toluene Emission to Air *

		Toluene Conc. in Air ,ppm					
0.1% Ethanol	Time, min	5	20	35	50	65	80
Air Stripping		1167	1178	695	441	335	218
Solvent Sublation		349	387	429	206	144	122

* Air Flowrate : 32ml min^{-1}
Thickness of Organic Layer : 10mm

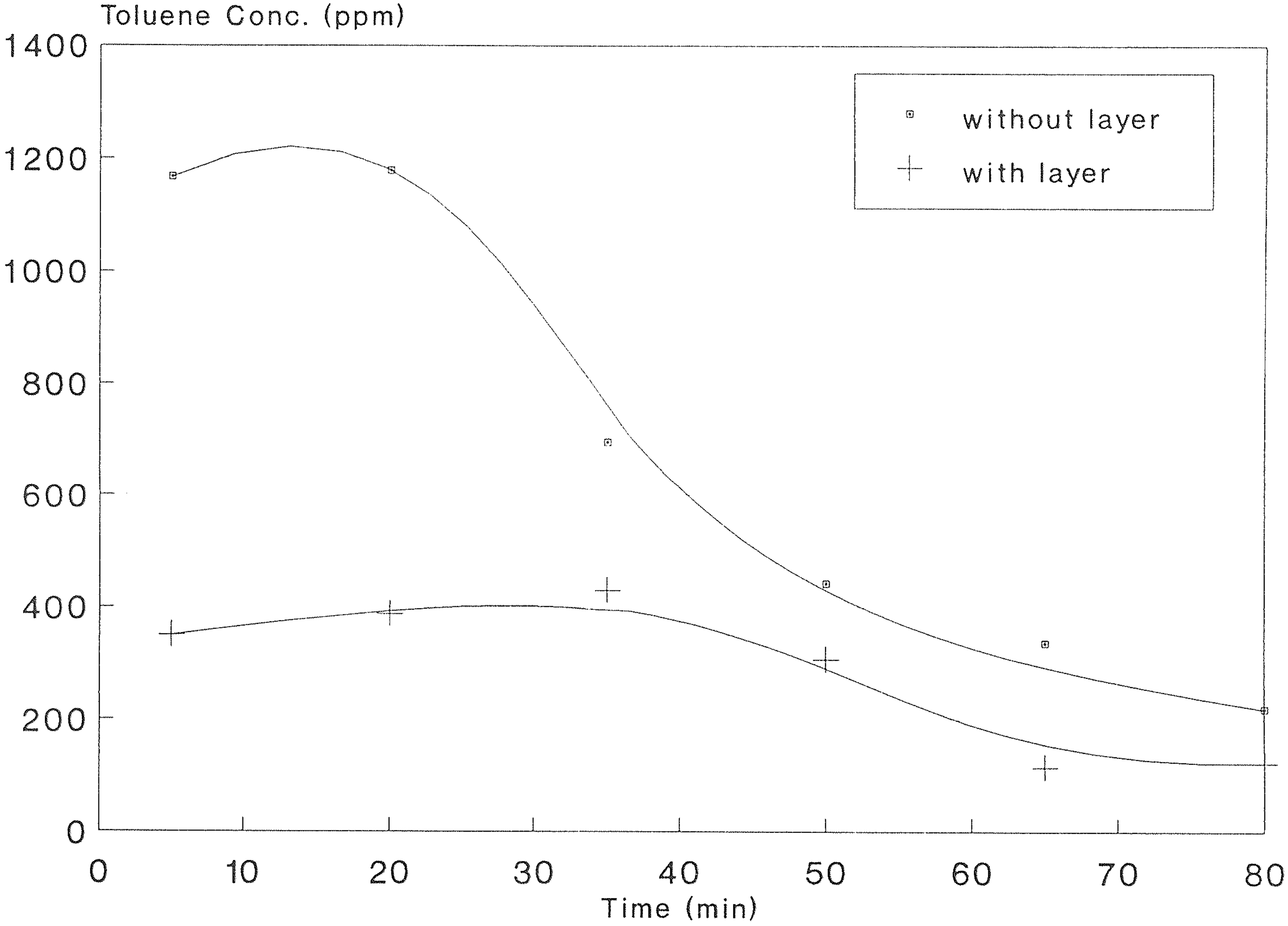


Figure 28 The Effects of Ethanol on Toluene Emission to the Air.

Table 19 The Effect of Ethanol on Toluene Emission Reduction *

Concentration of Ethanol, Vol%	0	0.1
Emission Reduction, %	71	59

* Air Flowrate: 32ml min^{-1}
Thickness of organic layer in solvent sublation: 10mm

Adding surfactants (SLS and HTMAB) did not show significant improvement on toluene removal from water as it was found by other investigators. This may be due to the different conditions like equipment and temperature.

CHAPTER 5

CONCLUSIONS

From our bench-scale studies of air stripping and solvent sublation for removal of toluene from aqueous phase we conclude that:

1. Solvent sublation gives marked improvement over air stripping both on removal of toluene from water and reducing its emission to the atmosphere. Toluene is transported in the absorbed phase and in the vapor phase of fine bubbles to the top of the sublation column and is finally dissolved in the organic solvent floating on top of the aqueous phase.
2. Less air passing through the column is needed for removing 90% of toluene from aqueous phase by solvent sublation than by air stripping.
3. Increased air flowrates enhance the efficiency of toluene removal from water linearly up to a flowrate of 94 ml/min.
4. Increased the air flowrates (32ml/min to 94ml/min) increases the toluene emission (39% to 66%) to the air in the process of solvent sublation.
5. Certain thickness of organic solvent (< 10mm) could improve the toluene removal somewhat, but more organic solvent would not give further improvement, because solvent sublation is a rate controlled process rather than an equilibrium controlled process.
6. The thickness of the organic layer has more effect on toluene emission to the atmosphere than on its removal from the aqueous phase. The thicker the layer, the less toluene will be emitted to the air. This is due to the fact that the toluene transported by the bubbles is dissolved in the organic solvent, and the thicker the layer the more residence time for the bubbles in the layer, thus more toluene is dissolved in the organic layer.

7. Small amounts of surfactants (e.g. sodium lauryl sulfate, hexadecyltriammonium bromide) would improve the toluene removal efficiency because surfactants reduce the surface tension of aqueous solution and thus decrease the bubble size. The efficiency of toluene removal mostly depends on the amounts of surfactant added to the aqueous phase. At higher concentration, surfactants improve the toluene removal, but at the same time it would form much foam on top of the column and give technical problems for gas analysis. HTMAB as a cationic surfactant is more effective on toluene removal compared to SLS (anionic surfactant) because it is more surface active.

8. Organic co-solute (e.g. 0.1% ethanol) added to the aqueous phase will improve the separation effectively, because ethanol reduces the surface tension of aqueous phase.

9. Toluene emission reduction in solvent sublation process in comparison with air stripping with investigated co-solutes (surfactants and ethanol) is somewhat less than that without them. This is due to the fact that the foam forms under the organic layer, which coalesces the bubbles and prevents the toluene in the bubbles from dissolving into the organic layer.

WORKS CITED

1. Cooper, C. D., and F. C. Alley. 1986. *Air Pollution Control: a Design Approach.* Boston, MA: PWS Engineering.

2. Arbuckle, J. G. et al. 1993. *Environmental Law Handbook.* Rockville, MD: Government Institutes, Inc..

3. Calabrese, E. J., C. E. Gilbert, and H. Pastides. 1990. *Safe Drinking Water ACT-Amendments, Regulations and Standards.* Chelsea, MI: Lewis Publishers.

4. Lemlich, R. 1972. *Adsorption Bubble Separation Techniques.* NY: Academic Press.

5. Valsaraj, K. T., J. L. Porter, and E. K. Liljenfeldt. "Solvent Sublation for the Removal of Hydrophobic Chlorinated Compounds from Aqueous Solutions." *Wat. Res.* 20(1986) : 1161-1175.

6. Clarke, A. N., and D. J. Wilson. "Separation by Flotation." *Separation and Purification Methods*, 7(1978): 55-78

7. Hackman, E. E. 1978. *Toxic Organic Chemicals - Destruction and Waste Treatment.* Park Ridge, NJ: Notes Data Corporation.

8. Patnaik, P. 1992. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances.* NY: Van Nostrand Reinhold.

9. Valsaraj, K. T., X. Y. Lu, and L. J. Thibodeaux. " Continuous Countercurrent Solvent Sublation for the Removal of Hydrophobic Organics from Water." *Wat. Res.* 25(1991): 1061-1072.

10. Sebba, F. 1962. *Ion Flotation.* NY: Elsevier.

11. Karger, B. L., A. B. Caragay, and S. B. Lee. "Studies in Solvent Sublation, Extraction of Methyl Orange and Rhodamine B." *Sep. Sci. Technol.* 2(1967): 39-64.

12. Spargo, P. E., T.A. Pinfold. "Studies in the Mechanism of Sublate Removal by Solvent Sublation." *Sep. Sci. Technol.* 5(1970): 619-635.

13. Clarke, A. N., and D. J. Wilson. 1983. *Foam Flotation - Theory and Applications.* NY: Mercel Dekker.

14. Ososkov, V.K., N. N. Ovsyannikova, and M. A. Kornelli. "Application of the Floating Layer for Tensification Emulsified Oil Separation by Flotation. "*Khimiya i Techn. Vody.* 3(1981): 430-433.

15. Valsaraj, K. T. and D. J. Wilson. "Removal of Refractory of Organics by Aeration. IV. Solvent Sublation of Chlorinated Organics and Nitrophenols." *Colloids and Surfaces*, 8(1983): 203-224

16. Valsaraj, K. T., and L. J. Thibodeaux. "Studies in Batch and Continuous Solvent Sublation. I. A Complete Model and Mechanism of Sublation of Neutral and Ionic Species from Aqueous Solution." *Sep. Sci. Technol.* 26 (1991): 37-58.

17. Lionel, T., D. J. Wilson, and D. E. Pearson. "Removal of Refractory Organics from Water By Aeration. I. Methyl Chloroform." *Sep. Sci. Technol.* 16(1981): 907-935.

18. Valsaraj K. T., and C. Springer. "Removal of Traces of Pentachlorophenol from Aqueous Acidic Solutions by Solvent Extraction and Solvent Sublation." *Sep. Sci. Technol.* 21(1986): 789-807.

19. Shih, Kun-Yauh, Wei-Der Han, and Shang-Da Huang. "Solvent Sublation of Hexachlorobutadiene and 2,4,6-Trichlorophenol." *Sep. Sci. Technol.* 25(1991): 477-487.

20. Huang, Jin-Yin, and Shang-Da Huang. "Solvent Sublation and Adsorbing Colloid Flotation of Acid Red." *Sep. Sci. Technol.* 26(1991): 59-71.

21. Lu, X. Y., K. T. Valsaraj, and L. J. Thibodeaux. "Studies in Batch and Continuous Solvent Sublation. IV. Continuous Countercurrent Solvent Sublation and Bubble Fractionation of Hydrophobic Organics from Aqueous Solutions." *Sep. Sci. Technol.* 26(1991): 977-989.

22. Eckenfelder, W. W. 1966. *Industrial Water Pollution Control.* NY: McGraw-Hill.

23. Patters, J. W. 1985. *Industrial Waste Water Treatment Technology.* Salem, NH: Butterworths.

24. Lide, D. R. 1991-1992. *CRC Handbook of Chemistry.* Ann Arbor, MI: CRC Press.

25. Chiu, Hui-Ling, and Shang-Da Huang. "Adsorptive Bubble Separation of Heptachlor and Hydroxychlordene." *Sep. Sci. Technol.* 26(1991): 73-83.

26. Hsu, J. P., G. Miller, and V.Moran. "Analytical Method for Determination of Trace Organics in Gas Samples Collected by Canister." *Journal of Chromatographic Science.* 29(1991): 569-582.

27. Myers, D. 1991. *Surfaces, Interfaces and Colloids Principles and Applications.* NY: VCH Publishers, Inc.