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METHODS DEVELOPMENT FOR DETERMINATION OF TRACE POLAR VOLATILE ORGANICS IN ENVIRONMENTAL SAMPLES

by

Qingchu Peng

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology
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Title of Thesis: METHODS DEVELOPMENT FOR DETERMINATION OF TRACE POLAR VOLATILE ORGANICS IN ENVIRONMENTAL SAMPLES

Name of Candidate: QINGCHU PENG
Master of Science in Chemistry, 1991

Thesis and Abstract Approved: _____ _____

Dr. Barbara B. Kebbekus — Date
Professor
Chemistry Department

_____ _____

Dr. George Lei — Date
Associate Professor
Chemistry Department

_____ _____

Dr. Somenath Mitra — Date
Assistant Professor
Chemistry Department

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VITA

Name: Qingchu Peng

Permanent address:

Degree and date to be conferred: MS CHEM, 1991

Date of birth:

Place of birth:

Collegiate institutions attended	Dates	Degree	Date of Degree
Sichuan University	1978-1982	B.S.	January 1982
Nanjing University	1982-1984	M.S.	December 1984
New Jersey Institute of Technology	1989-1991	M.S.	May 1991

Major: Chemistry

ABSTRACT

Title of Thesis: METHODS DEVELOPMENT FOR DETERMINATION OF TRACE POLAR VOLATILE ORGANICS IN ENVIRONMENTAL SAMPLES

Name of Candidate:

Qingchu Peng
Master of Science
Chemistry Department, 1991

Thesis directed by:

Dr. Barbara B. Kebbekus
Professor
Department of Chemistry, Chemical Engineering
and Environmental Science

The determination of trace levels of organic compounds in water samples is well developed for the less polar compounds, but the polar compounds are more difficult. The development of reliable and reproducible methods for such compounds as volatile alcohols and ketones is necessary if environmental monitoring is to be extended to these compounds.

The purge-and-trap method is frequently used for determination of volatiles in water samples. The method has problems when hydrophylic substances are being analyzed, since these are less easy to purge from the solution and more difficult to trap and desorb quantitatively. The high amount of water carried over into the trap from prolonged purging or higher purge temperature adds to the difficulty in injecting a sharp plug of analyte onto the high resolution gas chromatographic

column.

This study focused on the definition of conditions for accurate purge and trap analysis of various types of water samples for the polar compounds. Standards and spiked samples have been tested under varying conditions to determine the best conditions for quantitative transfer of compounds to the GC column. The optimum operation parameters have been obtained. The recovery of the target polar compounds is between 75 – 114% in various types of aqueous matrices. The precision of the method is less than 15% for determination of trace polar compounds. The method detection limit ranged from 0.5 – 5 ppb. The results obtained by using the method to analyze the target polar compounds in water samples are satisfied.

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Chapter 1

Introduction

Owing to industrial pollution, increasing amounts of harmful organic compounds are entering the environmental systems. It is estimated that there exist a total of *ca.* 4×10^6 organic compounds, of which 40,000-50,000 are used in the industry and are potential environmental pollutants[1,2]. Over 1,300 individual chemical compounds have been identified in water samples of various origins, which constitute of only 10-20% of the total dissolved organic compounds(DOC)[3]. According to other evaluations[4–6], water and other wastes may be polluted with over 2,000 organic compounds. A report on drinking water and health issued by the U. S. National Academy of Sciences[7] concluded that 90% of volatile and semivolatile organic compounds and only 5-10% of nonvolatile organic compounds in drinking water have been identified and quantified. As volatile and semivolatile compounds represent only ca. 10% of total organic material in drinking water, *ca.* 90% of the material remains to be identified. An even smaller percentage of organic material in natural waters has been iden-

tified because natural waters have not been analysed as thoroughly as drinking water. The range of concentration of organic constituents in various types of water spans more than four orders of magnitude, as shown in Table 1.1[8].

TOC in water exists in a number of forms and phases. They are classified as purgeable organic carbon(POC), dissolved nonpurgeable organic carbon(NPOC) and suspended organic carbon(SOC). Typical POC and NPOC values in various types of water are summarized in Table 1.2[9].

1.1 Analysis Methods for VOCs in Aqueous Samples

Samples of water of various origin can be subjected to chromatographic analysis using two basic procedures. First, by direct injection analysis(DIA) of the polluted water and second, by isolation and/or preconcentration of the organic contaminants from the water prior to analysis.

The method involving direct injection of contaminated water into a gas chromatograph [10–24] causes difficulties associated with the presence of water in the chromatograph, which in numerous instances makes the application of this method impossible. Its sensitivity is generally low(usually *ca.* 1 mg/l).

The investigation of water contamination with such low concentrations of compounds is a complex problem which can only be solved by

Table 1.1 Representative Concentrations of Organic Carbon in Various Types of Water

Water type	TOC (mg/l)	DOC (mg/l)	POC (mg/l)
Ground water	0.7	0.7	-
Sea water	1.1	1.0	0.1
Drinking water	2.0	-	-
Surface water (lakes)	7.7	7.0	0.7
Surface water (rivers)	8.0	5.0	3.0
Untreated domestic sewage	200	80	120

Table 1.2 Typical POC and NPOC Values in Various Types of Water

Water type	POC (ug/l)	NPOC (mg/l)	(mg/l)
River water	<2	2--6	-
Well water	<2	0.1--2	0.1
Lake water	<2	0.3--3	-
Drinking water	1--15	0.3--3	
GAC effluent	<2	0.05--0.3	0.7
Deionized water	<2	0.03--0.2	
Distilled water	<2	0.05--0.3	3.0
Reverse osmosis	<2	0.05--0.3	120

using isolation and preconcentration procedures prior to the analysis. The reasons for these two procedures are to transfer the analytes to a matrix that is more suitable for GC analysis(e.g., an organic solvent or gas instead of an aqueous phase), and to increase the concentration level of the analytes in the final sample which can sometimes be achieved in a single stage.

1.2 Isolation/Preconcentration of VOCs in Aqueous Samples

The techniques used for the isolation and/or preconcentration of volatile and semivolatile organics contained in an aqueous phase can be divided into the following basic groups[25]: liquid-liquid extraction, gas extraction; sorption from water, permeation techniques, and other methods.

An overview of proposed U. S. EPA methods for the isolation and determination of priority pollutants in water by GC and GC-MS has been published[26]. Analytical methods have been proposed for 114 organic compounds on the priority pollutants list[27]. Reviews and comparisons of different isolation/preconcentration techniques have also been published in numerous papers[8,23,24,28–33]. Fundamental principles of separation methods have also been presented[34].

Headspace analysis provides an indirect method for determination of volatile organic compounds[35–38]. The vapor phase above the sample and not the sample matrix itself is taken for analysis. Analy-

sis of a sample is in the thermodynamic equilibrium with its headspace in a closed thermostated vessel is referred to as static headspace analysis. When a carrier gas is passed over the sample and the volatiles are accumulated in a cryogenic or sorbent trap prior to analysis, the method is called dynamic headspace analysis. If the carrier gas is introduced below the surface of the sample and passes through the sample in the form of a stream of small bubbles which strip the volatile organics that are accumulated in a sorbent trap, the method is referred to as dynamic headspace, purge-and-trap, gas-phase sparging or gas-phase stripping. The headspace sampling methods are used predominantly for the determination of trace concentrations of volatile substances in samples which are difficult to handle by conventional chromatographic means. Examples include dilute solutions where the matrix would obscure the components of interest, damage the column or require excessively long analysis times owing to late elution of peaks. Inorganic or high- molecular-weight polymers which cannot be volatilized or solubilized under normal conditions and inhomogeneous mixtures such as blood, sewage and colloids which require extensive sample clean-up prior to analysis are also analyzed by this technique. The advantage of the headspace analysis is that the problems associated with the sample-matrix are eliminated. The sensitivity of the headspace method can be increased in some instances by adjusting the pH, salting-out or raising the temperature of the sample. The main disadvantage of quantitative headspace analysis is the need for

careful calibration.

A unique feature of the static headspace method is that the information obtained from the experiment, the chromatographic peak area of a substance in the gas phase, is an indirect measure of the concentration of that same substance in the original sample. The liquid- and gas-phase concentration are related to each other by the partition coefficient which is matrix dependent and remains unknown for most analyses; it must, therefore, be accounted for by calibrating the sampling system.

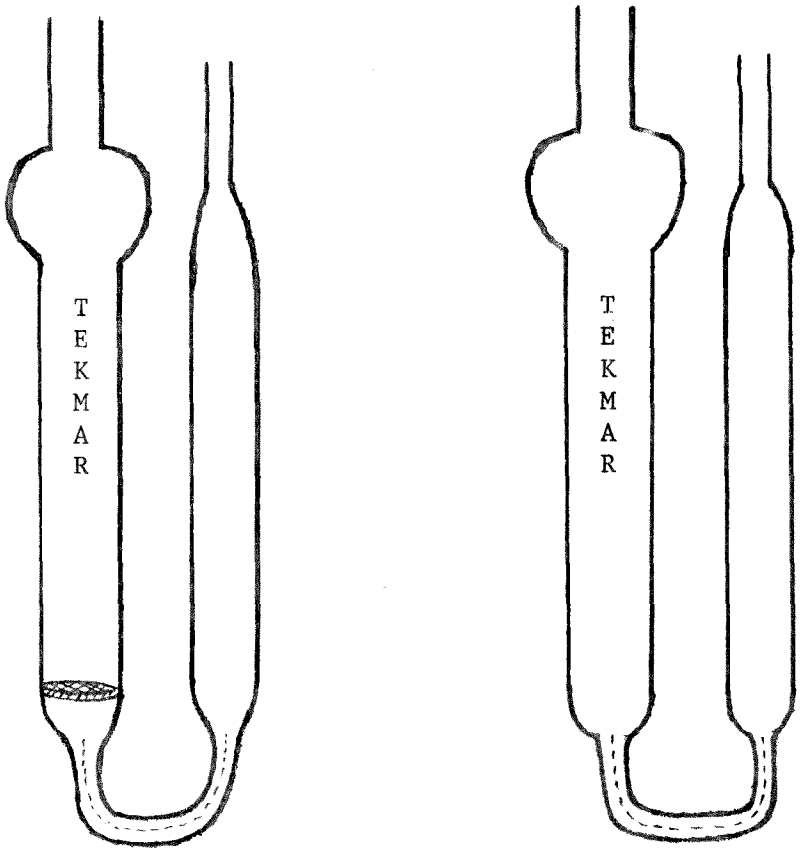
Dynamic headspace sampling employs the continuous removal of headspace vapors above a liquid or a solid sample by means of a gas flow with subsequent trapping of the sample components by solid-phase extraction or cold trapping. It is used to determine analytes which are too low in concentration or have unfavorable partition coefficients for their determination by static headspace methods[37–41].

The efficiency of the dynamic headspace method for solutions can be improved by passing the gas through the solution in the form of small bubbles (purge-and-trap) and by operating the extraction and trapping steps in a closed loop by continuous recirculating a fixed volume of gas through the solution and the trap (closed-loop stripping analysis). However, in all instances the amount of analyte stripped from solution will depend on the substance-specific partition coefficient and the experimental variables such as flow-rate, time and the total volume of stripping gas passed through the solution. Only when

the analyte has a low water solubility (<2%, w/w) and is relatively volatile (b.p. <200°C) can quantitative extractions be expected, albeit with a long sampling time[42].

Purge-and-trap techniques can improve the yield of organic volatiles from water or biological fluids by facilitating the transfer of volatiles from the liquid to the gas phase; it is also more suitable than dynamic headspace sampling when the sample volume is restricted[36–38,40,42–44]. The technique is used routinely in many laboratories for the analysis of water containing low-boiling pollutants such as chlorinated organics and aromatic solvents. Several automated equipments are commercially available. Purge-and-trap method differs from the dynamic headspace method in that the sampling gas is introduced below the liquid level through a fritted orifice; the finely dispersed bubbles provide maximum surface contact between the gas and liquid phase (Fig.1.1). As the inorganic volatiles transfer to the gas phase they are rapidly and continuously carried away. For volatile halocarbons in wastewater, the purging process is nearly complete and detection limits below the $\mu g\ l^{-1}$ level can be obtained.

Sorbent traps packed with Tenax are commonly used to trap the sample from the purge gas. For substances with boiling points below 30°C a segmented trap containing Tenax backed-up with silica gel, carbon or coated liquid phases is used to improve the trapping efficiency[45,46]. Cryogenic trapping is also used in the purge-and-trap technique for the recovery of organic volatiles, particularly when



(a) (b)

With porosity frit Without porosity frit

Figure 1.1: Sampling apparatus used for the determination of VOCs in water by purge-and-trap methods

open-tubular columns are used for the analysis[44,47]. Cold trapping has the advantage that thermally labile and polar compounds are less affected during the trapping and thermal desorption steps when solid-phase sorbent are used and fewer artifact peaks are likely to be produced.

A method for the isolation and concentration of organic compounds from aqueous samples by extraction with a stream of gas and adsorption on a solid sorbent in a closed system was popularized by Grob and others for the determination of very low levels of organic volatiles (ng l^{-1}) in various water samples[38,41,48–51]. A fixed volume of gas is recirculated through the sample and trap. The trace organics are recovered from the trap by micro-extraction with a few hundred microliters of solvent to avoid the need for a solvent concentration step prior to GC. The sensitivity of the procedure depends very much on the maintenance of low background levels in the apparatus. Poor quality trap material, contaminated purging gas, breakthrough of polar analytes that deposit on the apparatus and are slowly released, dust particles escaping from damaged filters that become deposited in the pump and lines and interact with samples giving ghost peaks have been recognized as the principal sources of background contamination[50,51]. The volatility and polarity of the sample can greatly influence the recovery and processing time. Heating at 45°C for 30 min is reasonable for large survey studies, whereas heating at 30-35°C for 2-24 hr will provide higher recoveries of less volatile analytes. An-

alytes of high water solubility and non-polar analytes with boiling points greater than that of eicosane are generally recovered in low yields. In general terms, the purge-and-trap technique is the method of choice for determining organic volatiles in water because of its ease of operation.

The range of applications of the purge-and-trap techniques has been expanding rapidly. It has been reported that there are no serious boiling-point limitations to this technique[52,53], and the method without fundamental limitations can be extended beyond C_{24} substances. Such a statement may be too optimistic, but the method has been used for the determination of semivolatile aromatic hydrocarbons in water [54]. The range of compounds isolated from water by the purge-and-trap technique has been extended beyond highly volatile substances detected by the original method to many semivolatile materials. Wide range of applications, good precision, and elimination of solvent preconcentration step ensure its continuing development. Application of selective detectors (e.g. FID,PID, ECD, ELCD) to the chromatographic analysis of the compounds liberated from the sorbent resulted in large improvements in the detection limits[55].

1.3 Problems and Limitations of The Methods

Several potential problems exist with the purge-and-trap method. The first is due to cross-contamination in the purging vessel, where high- and low- concentration samples are analysed in succession. Sam-

ple carry-over can be minimized by replicate rinses of the purging apparatus with organic-free water between samples. Purge-and-trap analysis of the final rinse water can be used as a check for sample carry-over[56]. Sample foaming can be a problem with samples obtained from certain sources. To prevent the foam from entering and contaminating the Tenax trap, an auxiliary antifoam trap is suggested. Other methods for breaking foams have been evaluated independently[57]. Some anti-foaming agents have been proposed[57,58], but the introduction of additional compounds into the sample, although non-volatile, alters the thermodynamic properties of the system. Low-level contamination normally might not be significant in the gases are used as the GC carrier gas, but when the same gases are used as the purge gas the contaminating materials are concentrated in the trap and may interfere with the analysis. This type of problem can be minimized by using only ultrapure gases for the purge-and-trap analysis. Solvent blanks may help to locate and quantify these types of interferences and are normally a part of the quality assurance/quality control program.

Most industrial wastewaters have a complex matrix containing organic pollutants of varying polarity. Although the determination of trace levels of organics in water with the purge-and-trap methods is well developed for the less polar volatile compounds, the determination of the polar volatile compounds in water with the method is more difficult because they are less easy to purge from the aqueous solution

due to their hydrophilicity[56]. Moreover, they are somewhat difficult to trap and desorb quantitatively. The high amount of water carried over into the trap from prolonged purging adds to the difficulty of injecting a sharply defined plug of analyte onto the high resolution gas chromatographic column. The objective of this research focused on the definition of conditions for accurate purge-and-trap analysis of wastewater samples for polar volatile organic compounds. Some of the compounds studied in this investigation are

Ethanol(EtOH)

Acetone(Ace)

Isopropanol(IPA)

Methyl Ethyl Ketone(MEK)

n-Butanol(ButOH)

Methyl Isobutyl Ketone(MIBK)

Pyridine(Pyr)

Dimethyl Formamide(DMF)

The concentrations of these compounds in wastewater have been required to be determined for a study of VOC emissions from an industrally impacted wastewater treatment plant, being carried out by the NJIT Air Pollution Research Laboratory.

Chapter 2

Experimental

2.1 Apparatus

The apparatus used in this study incorporates a Tekmar LSC-2000 Purge-and-Trap concentrator interfaced to a Varian 3400 Gas Chromatograph with a Flame Ionization Detector, Photoionization Detector and Electrolytic Conductivity Detector(Hall). Cryogenic trap is equipped in the Tekmar Capillary Interface for sample focusing before injection. Cryofocusing was done with liquid nitrogen. Data were collected and processed with a MiniChrom (R), Chromatograph Data System.

Columns utilized in this study were:

1. 25 m $\times$ 0.2 mm Crosslinked 5 % Ph Me Silicone with a 0.3 μm film thickness(Ultra 2);

2. 50 m $\times$ 0.2 mm Crosslinked Methyl Silicone Gem with a 0.5 μm film thickness(PONA).

2.2 Preparation of standard solutions

Standard solutions containing components of interest were prepared by a stepwise procedure.

1. Stock standard solution were prepared from pure standard materials using the following procedure:

   (a) About 9.8 ml of methanol was placed in a 10-ml ground-glass stopped volumetric flask. The flask was allowed to stand unstoppered until all alcohol-wetted surfaces have dried. Weigh to the nearest 0.1 mg;

   (b) A 10 μl syringe was used and 10 μl of analyte was immediately added to the flask without contacting the neck of the flask;

   (c) Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. The concentration was calculated in micrograms per microliter from the net gain in weight;

   (d) Stock standard solution was stored in 10-ml bottle equipped with Teflon-lined screw caps at about 4°C.

2. Standard solution was prepared as following:

   (a) About 9.0 ml of methanol was placed into a 10-ml ground-glass stopped volumetric flask. The flask was allowed to stand unstoppered until all alcohol-wetted surfaces have dried.

A certain volume of the stock standard solution of interest components was pipetted into the flask;

(b) Dilute to volume, stopper, then mix by inverting the flask several times. The concentration was calculated in ppm;

(c) The mixture standard solution was stored in 10-ml bottles equipped with Teflon- lined screw caps at about 4°C.

3. Calibration standard solution can be prepared by using a microsyringe and rapidly injecting the mixture standard solution into distilled water when it is needed.

2.3 Method Operations

Analytical procedure:

The analysis was done on a Tekmar LSC-2000 Purge-and-Trap concentrator interfaced to a Varian 3400 Gas Chromatograph. 5 ml of aqueous sample was loaded into a purge vessel. When Tekmar LSC-2000 was in "Purge Ready Status", "Start" key on the keyboard was pressed, and operations began automatically according to following steps:

(1) Preheat: A sample heater heated the sample in a static condition(without purge gas flow). This process allowed the sample temperature to equilibrate before purging, which enhanced quantitative reproducibility;

(2) Purge: Volatile organics were removed from the sample by passing purge gas through it;

(3) Dry purge: The purge gas remained on, but flowed only through the trap to remove the water vapors in the trap;

(4) Cooldown: The cryogenic trap was cooled with liquid nitrogen in order to freeze the analytes to improve peak shape during the injection;

(5) Desorb preheat: In this mode, the trap was heated before the 6-port valve was switched, so that the trap was hot before the analytes were backflushed;

(6) Desorb: The sample was backflushed into the cryogenic trap in this mode;

(7) Inject: The cryogenic trap was heated rapidly to release the analytes into the GC column in this step;

(8) Bake: The trap was cleaned for the next run by flowing purge gas at high temperature.

As soon as the purge-and-trap system was on the inject mode, the GC started to run.

With the Ultra 2 capillary column, the GC oven temperature program began at 30°C holding for 10 min., then programed to 180°C at

6°C/min.

With the PONA capillary column, the column was held at 20°C for 10 min., then programed to 180°C at 6°C/min.

The carrier gas was helium at 2 ml/min. All samples were cryofocused using liquid nitrogen before injection into the column. At the end of the column, the effluent splited to the FID and PID/ELCD, with 50% of the effluent going to the FID, 50% going to the PID/ELCD.

The detector operating conditions were:

FID	PID/ELCD
Air: 300 ml/min H_2: 30 ml/min He(make-up gas): 20 ml/min	H_2: 100 ml/min Electrolyte flow-rate: 20-50μl/min ELCD reactor temp: 850°C

2.4 Methods Improvements

The most important operating parameters of the purge-and-trap GC have been investigated in this study. Optimization of the system was accomplished by observing variations in sensitivity, resolution, and quantitative recovery as a function of operating parameters. For a particular trap material and compounds, the effect of salting-out, purge time, purge flow-rate, purge temperature, dry purge time, cryo-

genic trap temperature, desorption time, GC temperature program, and column stationary phases were studied.

When studying one parameter, other parameters were constant.

2.5 Recovery Determination

(1) 10 μl mixture standard solution containing the components of interest was spiked into 100ml of distilled water. Then the solution was transferred into 5ml of bottles with Teflon-lined screw caps. The bottles should be filled up so that there was no empty headspace, and stored in a refrigerator;

(2) 5 ml of above standard solution was pipetted into a purge vessel, and it was purged with helium gas at a purging flow-rate of 80ml/min for 10 min. Using above analytical procedure with optimum conditions, the chromatographic peak areas of the target components can be obtained. After finished first run, the same solution was repurged for another 10 min. and was run at the same conditions again. The procedure was repeated again and again until no peaks of interest components were observed;

(3) Other above standard solutions were run at different purge time: 10, 20, 40, 60 min. The corresponding peak areas of the target components were obtained. The recovery of each component was calculated by the equation:

$$Recovery_i = [\frac{(Area_i}{\sum Area)_i}] \times 100\% \qquad (2.1)$$

Where:

$Area_i$: the area of component i obtained in step (3)

$(\sum Area)_i$: the cumulative area of component i obtained in step (2)

2.6 Method Detection Limit

1. Calibration Method:

   Different volumes of the mixture standard solution were separately spiked into 100 ml of distilled water and then were transferred to 5ml of bottles with Teflon-lined screw caps without empty headspace. They were run with the optimum conditions. Four duplicate runs were done for each concentration level.

2. Method Detection Limit Determination:

   The diluted standard solutions obtained in section 2.2(3). were analyzed repeatedly 7 times by using the purge-and-trap GC method for each concentration level. The standard deviation were calculated by the equation:

$$S = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{(n-1)}} \qquad (2.2)$$

Where:

X_i: a value for each determination

$\bar{X}$: mean value of determination

n: determination times

The standard deviations were plotted as a function of concentration to obtain S_o by extrapolation. The method detection limit(MDL) at 95% confidence was defined as[59]:

$$MDL = 3S_o \tag{2.3}$$

Where:

S_o: a standard deviation as concentration of analyte was zero

Chapter 3

Results and Discussion

The purge-and-trap method was effective because the volatiles could be efficiently removed from a non-volatile matrix, concentrated on a trap, and then quantitatively desorbed from the trap onto a GC column in which the components could be separated and detected by a selective detector. The important operating parameters to enhance the sensibility of purge-and-trap system have been investigated.

According to discussion by Pankow[60], when gas bubbles incrementally through the sample volume V_s, the maximum purging of the volatile analytes is given by the equation:

$$\frac{C}{C_o} = \exp[-(\frac{H}{RT})\frac{V_g}{V_s}] \qquad (3.1) \qquad (3.1)$$

Where:

C_o: the initial concentration of the analyte of interest

C: the concentration remaining after passage of V_g

V_g: purge gas volume

$H(atm \cdot m^3/mol)$: the Henry's law constant of the analyte

R: the gas constant$[8.2\times\ 10^{-5} m^3 \cdot atm/(mol \cdot K)]$

$T(K)$: temperature

The maximum possible efficiency E(%) of the purging process is given by the following equation:

$$E = (1 - \frac{C}{C_o}) \times 100 \qquad (3.2) \qquad (3.2)$$

For a given value of V_g, increasing V_s would decrease the purging efficiencies, even though it would increase the signals obtained. However, response was probably not linear with sample size unless the purge volume was adjusted[61]. For compounds with high purge efficiency, the difference might be much less; for compounds with a low purge efficiency, the difference might be greater. In addition, if different sample sizes were used, calibration standards would have to be run for each sample size.

On the other hand, maximizing E for a compound would clearly maximize its signal for a given value of V_s. This would occur when V_g/V_s was large, that is, increasing the purge volume(equal to purge flow-rate $\times$ purge time) could significantly increase the recovery of some of the less volatile compounds. Thus, maintaining a high V_g/V_s ratio would promote method sensitivity and precision for a given V_s value. Therefore, increasing the purging volume could increase the recovery of a sample compound. However, if the purge volume was too great, the recovery might be low due to breakthrough of the

compounds. Most of analytes studied in this paper had strong hydrophilicity. It has been reported that their purging efficiency was quite low[62,63]. Increasing the purge volume could increase their purging efficiency. But their total recovery might decrease if purge volume excessed the breakthrough of the components. Therefore, in order to establish the optimal conditions for purge-and-trap method to analyze efficiently these trace polar volatiles, methods development has been studied first.

3.1 Methods Development

1. Effect of purge time

   The influence of the purge time on the recoveries was demonstrated in Table 3.1. For most of components, the recovery increased up to a purging time of 20 min. An increase in purge time from 10 min to 60 min could increase the recovery of Dimethyl Formamide(DMF). The influence of purge time on the recovery of EtOH was very small.

   As indicated by Table 3.1, at much longer purge time there was a reduction in apparent recovery. This was due to breakthrough on the trap. "Breakthrough" was an important concept in purge-and-trap methods. Understanding breakthrough could prevent the loss of essential sample compounds from the trap. Breakthrough occured when compounds were carried off the sorbent

trap by the purge gas if the sample was purged excessively. In other words, instead of the compounds being "trapped" on the sorbent as they passed through, they were carried through and completely off the trap into the air. As this point they were lost. The retention capability of the adsorbent has been exceeded. With the standard size EPA traps, breakthrough from the Tenax appeared to be occuring at about 650ml purge volume. The use of combination traps, Tenax/Silica Gel or Tenax/Silica Gel/Charcoal, could increase the breakthrough volume (900ml for Tenax/Silica Gel, 1250ml for Tenax/Silica Gel/Charcoal)[64]. However, silica gel and charcoal tended to absorb more water and did not desorb as efficiently as Tenax. If a compound that would normally be trapped on the Tenax was carried into the Silica gel or Charcoal, then broader peak shapes or even some losses in recovery might be experienced for that compound before the breakthrough volume was reached. In general, lower molecular weight compounds broke through more easily (as shown in Table 3.1). For DMF, recovery increases by longer purge time because its volatility was not high(boiling point is 149- 156°C).

2. Effect of purge flow-rate

   To find the optimum purge flow-rate, three replicates, each 5 ml, of sample solution containing a certain amount of target compounds, were purged for 20 min, with a flow-rate of 40, 60, and 80 ml/min. The resulting areas of the peaks of the components

Table 3.1 Effect of Purge Time

Compound	EtOH		Ace		IPA		MEK		ButOH		MIBK		Pyr		DMF	
Purge Time (min)	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
10	376	32.9	15101	29.2	2566	18.0	29747	11.0	8524	36.1	165531	9.7	950	13.8	102	46.6
20	388	15.8	19763	34.6	2957	33.7	32534	23.6	11974	18.4	196618	27.6	1024	23.9	117	26.5
40	333	39.1	8383	19.0	2063	10.3	12347	27.2	13343	29.6	166327	29.1	544	31.6	225	28.9
60	331	22.2	5711	15.4	1790	27.3	3686	16.8	10972	18.5	135994	24.9	411	8.6	424	14.5

were given in Table 3.2.

Because the purge volume was equal to purge flow-rate multiplied by purge time, increase of purge flow-rate should have the same effect on recovery as increase of purge time. Figure 3.2 showed that the recoveries for most compounds increased as purge flow-rate increased at constant purge time of 20min. Acetone(Ace) produced better recovery at purge flow-rate of 60 ml/min. For pyridine(Pyr), the effect of purge flow-rate on recovery was negligible. However, if the flow-rate was too high, the components had no enough time to be adsorbed on a adsorbent, especially for components whose adsorption capabilities were weak, such as DMF, which resulted the recovery was low. Thus the optimum flow-rate was about 80 ml/min.

3. Effect of purging temperature

In order to study the influence of purge temperature on recovery, a series of experiments with special test mixture were performed at temperatures of 20, 40, 60, and 80°C. Purge time(20 min) and purge flow-rate(80 ml/min) were kept unchanged.

In theory, purging the sample at elevated temperature could be used to increase the recoveries of many less volatile compounds without any increase in time required, owing to the increased vapour pressure of the compounds of interest. As indicated in Table 3.3, the recovery of most of components increased with a

Table 3.2 Effect of Purge Flow-rate

Compound	EtOH		Ace		IPA		MEK		ButOH		MIBK		Pyr		DMF	
Purge Flow-rate (ml/min)	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
40			18463	19.9	1512	22.7	10062	16.2	1561	38.7	57345	26.0	1195	17.4	637	17.7
60			33599	13.1	2367	10.5	23712	24.3	4305	9.3	132430	15.9	1115	38.4	227	10.9
80	388	15.8	19763	34.6	2957	33.7	32534	23.6	11974	18.4	196618	27.6	1024	23.9	117	26.5

increase of purge temperature from 20°C to 40°C. The recoveries of EtOH and ButOH increased as purge temperature increased from 20°C to 60°C. This indicated that higher purge temperature was better for highly soluble compounds. On the other hand, the recovery of DMF decreased as the purge temperature increased. Because the solubility of DMF in water would increase as temperature increases, it might be postulated that for DMF, the effect of increased solubillity was greater than the effect of increased vapor pressure.

If purging temperature was 60°C or higher, severe losses began to occur for all compounds. Recoveries of EtOH, Ace, IPA, MEK and DMF dropped to zero when sample was purged at 80°C. This effect seems to be due to the great amount of water transferred to the Tenax trap at high purge temperature. The use of dry purge before desorption could remove some of the water. However, an excessive dry purge would lead to breakthrough of the analytes.

4. Effect of dry purge time

In analysis of water samples with purge-and-trap method the water matrix was not absolutely non-volatile. It was inevitable that some water would be vaporized and carried through to the analytical system. According to calculation by Pankow, et al[40] using the ideal gas law, 0.0173mg of water was removed from the purge vessel per milliliter of purge gas. Using this figure

Table 3.3 Effect of Purging Temperature

Compound	EtOH		Ace		IPA		MEK		ButOH		MIBK		Pyr		DMF	
Purging Temperature (C)	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
20	158	39.0	7946	32.2	1086	16.8	8477	8.3	3637	27.1	161471	35.2	515	29.8	1185	36.1
40	388	15.8	19763	34.6	2957	33.7	32534	23.6	11974	18.4	196618	27.6	1024	23.9	117	26.5
60	488	14.3	1817	13.9	2258	27.5	423	18.8	16652	39.2	144596	28.1	358	18.8	148	20.0
80									3348	20.6	70496	14.7	264	31.3		

it could be readily seen that the total amount of water could become significant for typical purge volumes. A purge volume of 1600ml, for instance, would vaporize 27.68mg of water. If this entire volume of water were to be transferred to the GC, it would decrease with column resolution and effect detector performance.

Westendorf[65] found that traps containing Silica gel or charcoal could effectively trap water but could not be effectively dry purged to remove water. However, water could be dry purged from Tenax trap.

In Table 3.4, we saw that recoveries for EtOH, Ace, IPA, MEK, and Pyr decreased with longer dry purge time. For MIBK and DMF, the recoveries would decrease if dry purge time reached 8 min. The influence of dry purge time on the recovery of ButOH was negligible, which was consistent with the result obtained in the study of effect of purge time.

As we knew, the dry purge time was a part of what made up the total purge volume since during dry purge, dry purge gas was passed through the trap. Using excessive dry purge would lead to breakthrough just like an excessive purge. Therefore, the purge time as well as the dry purge time must be considered in the analysis to avoid breakthrough and loss of recovery.

5. Effect of desorb time

Desorption of the sample for subsequent analysis of organic com-

Table 3.4 Effect of Dry Purge Time

Compound	EtOH		Ace		IPA		MEK		ButOH		MIBK		Pyr		DMF	
Dry Purge Time (min)	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
2	949	13.3	106359	18.6	20683	24.7	53125	14.2	12169	19.7	247045	15.8	1923	10.9	228	18.4
4	593	16.1	18335	34.6	5086	14.5	44348	27.0	11265	16.3	249451	34.0	1905	28.2	232	23.7
8	338	29.6	2912	18.5	1300	23.2	30671	36.5	11551	39.6	245772	27.0	1342	17.7	144	20.8

pounds will depend upon the volatility of the analyte and the nature of the adsorbent. Thermal desorption offers increased sensitivity for the analysis of more volatile organic compounds. Thermal desorption is achieved through the interaction of the carrier gas and a controlled increase in the temperature of the adsorption material. Thermal desorption is a very important step in the whole purge-and-trap procedure and has a major influence on the final sensitivity of the analytical method. Hence it is important that the desorption time is sufficiently long that all the compounds concentrated in the sorbent trap are totally desorbed.

Experiments were done by purging 5 ml of test solutions containing target components for 20 min with a purge flow-rate of 80 ml/min at 40°C purging temperature. Subsequently, the loaded Tenax trap was thermally desorbed at 180°C with different desorb times. The desorbed components were collected in the cryotrap in a capillary interface cooled down −150°C by liquid nitrogen. This allowed a sharp injection on to a high-resolution capillary column.

In order to establish the optimal desorption conditions for the system, five different desorption times were investigated. The results were compared in Table 3.5. As shown by Table 3.5, the recoveries for all components increased with the increase in desorb time. The difference in recoveries for desorption of 12

min and 16 min was small for most of components. This indicated that a desorb time of 12 min was long enough so that all components concentrated on the sorbent trap were completely desorbed. Barnung and Grahl-Nielsen found that the desorption was complete for some aromatic compounds with desorption time of 10 min[66].

6. Effect of cryogenic temperature

   If volatile samples were injected from a purge-and-trap system by heating an adsorbent on which the sample was trapped, and backflushing it with the carrier gas to sweep the sample to the GC column, this process took a fair amount of time, resulting in a broad injection band incompatible with normal capillary column operation. Packed columns could generally accept such an injection with minimal loss in resolution. Obtaining good performance from a capillary system requires either narrowing the sample band before injection or increasing the capacity of the column so that it could efficiently refocus the sample. Therefore, an external cryotrap was often used to refocus the sample prior to injection in order to enrich samples and improve peak shape during the injection. The utility of cryogenic trapping has clearly been shown in a review by Brettell and Grob[67]. Takeoka and Jennings[68] have given a brief discussion of the principles governing cryogenic focusing and Hopkins and Pretorius[69] have given a more elaborated theory of band broadening during cryogenic

Table 3.5 Effect of Desorb Time

Compound	EtOH		Ace		IPA		MEK		ButOH		MIBK		Pyr		DMF	
Desorb Time (min)	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
2			1090	16.2	302	31.7	4326	38.1	1810	40.3	80774	19.9	504	37.5		
4	919	17.7	106317	10.1	20683	12.6	53125	16.1	11265	23.8	247045	32.9	1923	19.8	228	44.7
8	7909	28.2	437584	16.7	85973	19.0	100462	24.7	23108	19.2	357021	25.8	2586	28.6	385	25.8
12	10305	10.1	565344	10.7	109394	9.7	109628	12.7	23325	18.2	375192	17.2	2933	13.8	508	13.9
16	10441	6.2	551007	28.1	106782	35.3	127001	39.0	22973	28.8	369399	15.7	3255	18.6	617	23.1

trapping.

Cryotrap temperature varied significantly depending upon the most volatile compound analyzed, the column diameter, stationary phase, film thickness, flow rate, and whether a precolumn was used. The ability of cryotraps to retain compounds was dependent on the minimum temperature of the trap. In general, the higher the capacity of the column used, the higher the trap temperatures that could be tolerated. Lower capacity columns require lower temperatures.

As shown in Table 3.6, the peak areas of Ace, IPA, MIBK, Pyr, and DMF apparently decreased with the increase of temperatures from $-150°C$ to $-50°C$, while the peak area of EtOH remained almost unchanged. The peak areas of ButOH and MEK increased from $-150°C$ to $-100°C$ and then decreased from $-100°C$ to $-50°C$. Therefore, a cryotrap temperature of $-150°C$ was chosen for the rest of the investigation in order to analyze all components in the mixture samples, even though the recovery of ButOH and MEK were slightly smaller than that at $-100°C$.

7. Comparison of purge vessels with and without porous frit

An important consideration with purge-and-trap method application was the selection of glassware. To increase purge efficiency of organic compounds from the aqueous phase, it was necessary to maximize the gas-liquid contact surface. There were several

Table 3.6 Effect of Cryotrap Temperature

Compound	EtOH		Ace		IPA		MEK		ButOH		MIBK		Pyr		DMF	
Cryotrap Temperature (C)	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
-150	1085	16.7	62168	9.4	14665	9.3	58846	6.2	15333	8.9	451639	13.7	5163	15.0	530	26.6
-100	973	38.3	34400	40.9	7185	37.1	61951	13.3	16251	29.6	436467	18.0	3707	33.6	380	15.7
-50	1025	12.7	21485	29.4	5855	24.5	44495	8.0	14839	11.8	412335	19.1	3374	39.3	326	23.0

styles of commercially available glassware. One of them was a fritted sparger [Figure 1.1(a)]. In this sparger, the purge gas was dispersed by the porous frit into many small streams of bubbles traveling up through the sample and out the top through the sample line. The finely dispersed bubbles provided maximum surface contact between the gas and liquid phases. Another option was the fritless sparger [Figure 1.1(b)]. The purge gas flowed under the samples, then through it and out the top. No frit is present, so the bubbles are larger and flow in a single stream.

By testing these two styles of spargers, we found that the purge efficiency obtained with fritless sparge was lower than that obtained with a fritted sparge at the same experimental conditions(Table 3.7). For the compounds, ButOH and MIBK, the differences of purge efficiencies were slight. For lighter molecular weight compounds, EtOH, Ace, IPA, MEK, Pyr and DMF, the difference was much greater, especially for EtOH, Ace and IPA. Apparently the better efficiency of the fritted sparger was due to the finer dispersion of the purge gas, which increased the gas liquid contact area. Therefore, if maximum sensitivity was required, a fritted sparge remained the glassware of choice. However, if dirty samples with a high particulate content, such as sludges or effluent samples, were analyzed, the samples could clog a fritted disc. It was extremely difficult to thoroughly clean a fritted disc sparge after it has been loaded with solids. In this

case, fritless sparge should be used so that cleaning was easy.

8. Effect of salting-out

   Various inorganic salts might be used to lower the activity of the water in the aqueous phase, thus displacing solutes of high polarity more to the upper phase, that is, the solubility of polar-solutes decreased. In this case, the purge efficiency could increase. In the experiment, the effect of inorganic salts (0.1 mol)of KNO_3, KCl, $NaNO_3$ and NaCl have been studied. Table 3.8 showed that recoveries of EtOH and Ace increased apparently with addition of KNO_3, while recovery of other components showed no apparent change or showed a slight decrease. By adding other inorganic salts, the recovery decreased slightly except for Ace, IPA and DMF which showed better recoveries when NaCl was used.

   According to our results, addition of the salts was useful in increasing the recovery of some components. In most cases, no apparent increase of recovery of the components was observed. However, this did not mean that salting-out is no use. Other salts, especially higher charged inorganic ions, might yet be shown to have use. It might be worth investigated some of these salts.

Table 3.7 Comparison of Glassware

Glassware	frit disc		fritless	
Compound	Area	RSD	Area	RSD
EtOH	266	39.7		
Ace	41731	22.5	807	35.5
IPA	5938	38.2		
MEK	30166	10.7	10877	26.4
ButOH	4121	28.2	3254	37.8
MIBK	134445	16.0	103691	18.3
Pyr	1021	36.6	606	28.2
DMF	470	40.8	249	37.2

Table 3.8 Effect of Salting-out

Salt(0.1mol)	No salt		KNO3		KCl		NaNO3		NaCl	
Compound	Area	RSD	Area	RSD	Area	RSD	Area	RSD	Area	RSD
EtOH	296	18.6	2517	10.9						
Ace	6587	31.3	12968	17.9	3647	29.9	2103	13.8	10259	18.6
IPA	12850	29.4	11147	28.2	8749	37.6	2901	17.4	18509	20.2
MEK	49075	7.3	39902	10.7	41028	17.8	34363	29.2	39098	13.7
ButOH	8852	17.1	9424	29.4	9571	16.3	8559	30.7	7493	10.3
MIBK	122731	8.6	107668	15.7	11903	12.2	104337	19.0	105621	26.7
Pyr	973	26.9	934	30.4	805	15.2	824	18.6	838	11.1
DMF	253	37.1	202	33.8	256	21.7	243	13.1	1350	17.7

3.2 Discussion of Recovery of The Method

To quantitatively determine the VOC concentrations in water, the recovery of each component with this method would be estimated first. According to above discussion, the breakthrough volume of these polar volatile organic compounds on Tenax trap was not very large. If purge volume was large enough so that all analytes would be purged out from the water sample, the breakthrough volume for each analyte would be exceeded and a great amount of water would be transferred to the trap. There would be a loss of analytes resulting in negative error. Therefore, we developed a new approach – multiple purge extraction method(MPE) to determine the recovery of compounds of interest from the water sample.

Some workers[70-73] have investigated a similar technique called multiple headspace extraction(MHE) procedures and discussed how much both the distribution constant and the phase ratio influenced the precision and the accuracy. The principle of the MPE was based on stepwise gas purging at equal time intervals and started with the usual purge-and-trap analysis of the sample. If the sample had reasonable volatility, the amount of the compound that was taken from the gas phase for the analysis altered the phase equilibrium, which needed some time for re-establishment. The concentration of the volatile compound in both the gas phase and the sample now became smaller, but the ratio remained constant. The second analysis would therefore

result in a smaller peak and, by continuing this procedure, it was possible to strip off all the volatile compounds from the sample. This stepwise extraction procedure was similar to a continuous stripping process but there was no loss of compounds. If carried out till all the pollutants in the matrix were exhausted, the peak areas from different steps for a certain compound would be added up to give a total area value, which represented the total amount of that compound in the sample vial. This therefore was independent of its distribution between the two phase in the sampling vial. Apparently the influence of the sample matrix on the phase equilibrium was completely eliminated.

Recovery studies with the compounds of interest were performed in triplicate by adding a certain amount of standard solution in drinking water, tap-water and wastewater obtained from LRSA plant. According to above discussion(section 3.1), the following experimental conditions were chosen:

1. Tekmar LSC 2000 operation parameters:

   Purging preheat: 40°C(2 min)

   Purge time: 15 min

   Purge gas flow-rate: 80 ml/min

   Dry purge: 2 min

   Cryotrap cooldown: −150°C

   Desorb time: 12 min(180°C)

   Inject time: 1 min(180°C)

Bake time: 10 min(225°C)

2. Varian 3400 GC temperature program:

   Initial temperature: 20°C held 10 min

   A rate of temperature program: 6°C/min

   Final temperature: 180°C held 8 min

Operation procedures:

1. 5 ml of standard solution was run with multiple purge extraction method under above operation parameters. The total area of peak for each target component which corresponds to the total amount of the component could be obtained (Table 3.9);

2. 5ml of water sample was pipetted into a sparger, then it was run with above operation parameters. The areas(A_1) of the peaks of all target compounds could be obtained;

3. 0.25 μl of mixture standard solution containing all target compounds was spiked into 5 ml of water sample and was run with the same procedure. The areas(A_2) of the peaks for all compounds could be obtained;

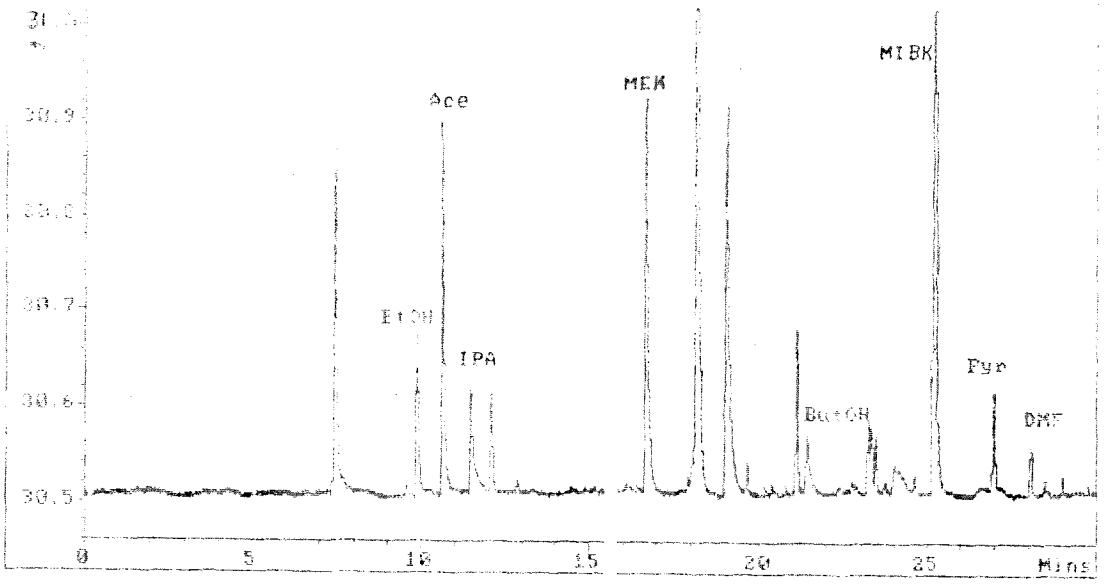
4. The difference of areas of the peaks between water samples without and with addition of standard mixture solution was calculated. Then recovery could be estimated by using equation 2.1.

The chromatograms of the water samples with and without addition of standard were shown in Figure 3.1, 3.2 and 3.3. The overall recoveries of the compounds were listed in Table 3.10. The recoveries of all compounds with various water samples for this method were in the range of 62–114%. For most compounds, the recoveries were less than 90% with drinking and tap water samples. It was likely that the losses of the compounds were due in part to their hydrophilicity which resulted in low purging efficiency and in part to their low breakthrough volumes which caused loss of compounds of interest from the trap.

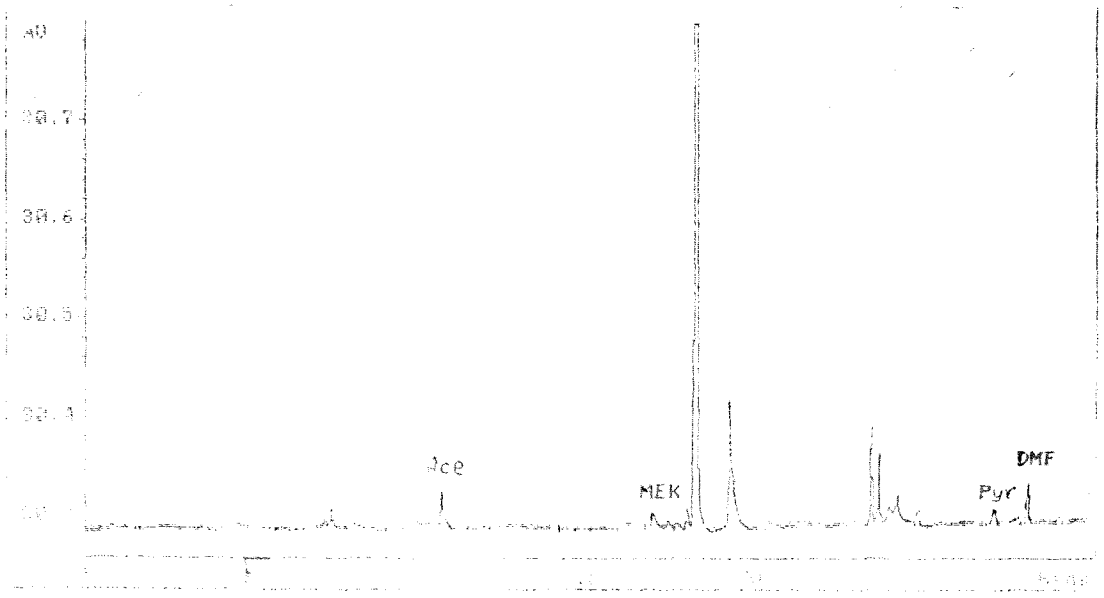
With wastewater sample, the recoveries of alcohols and Acetone were larger than 100% while the recoveries of the rest of the components were smaller. Wastewater was a complex system which contained various compounds including some inorganic salts, which might result in increase in recovery of alcohol compounds and Acetone. This phenomenon was consistent with the results obtained from the salting-out studies (ref. Table 3.8).

3.3 Linearity, Accuracy and Precision

For the determination of linearity, standard solutions for the compounds was prepared at five concentration levels for by carefully adding a certain volume of mixture standard solution to 100 ml of reagent water. Each calibration standard solution was analyzed seven times using the operation parameters and procedure used in section 3.2.

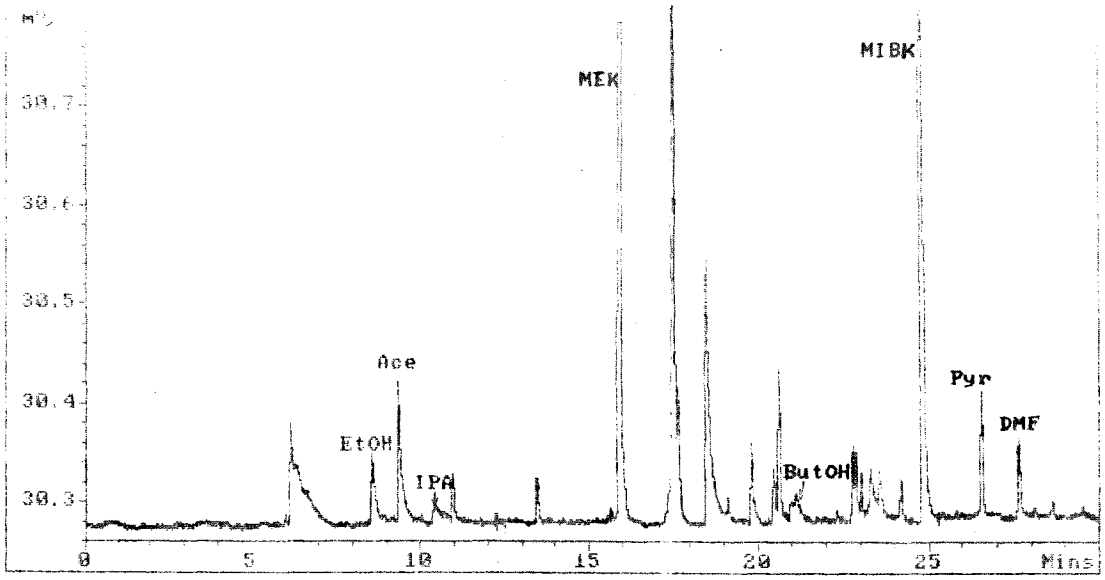


(a)

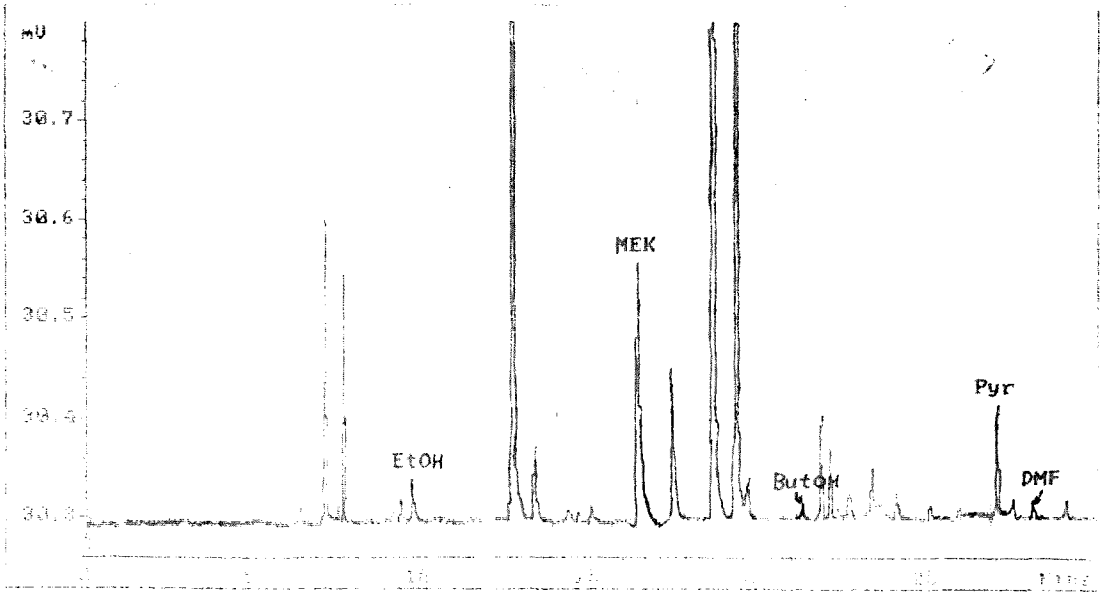


(b)

Figure 3.1: Chromatogram of drinking water with(a) and without(b) addition of standard

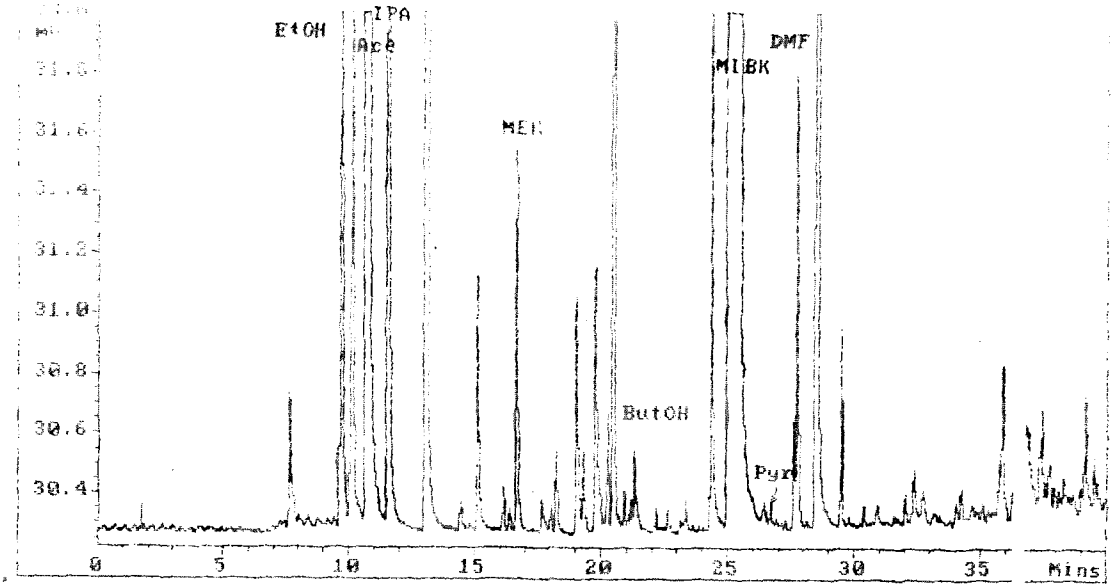


(a)

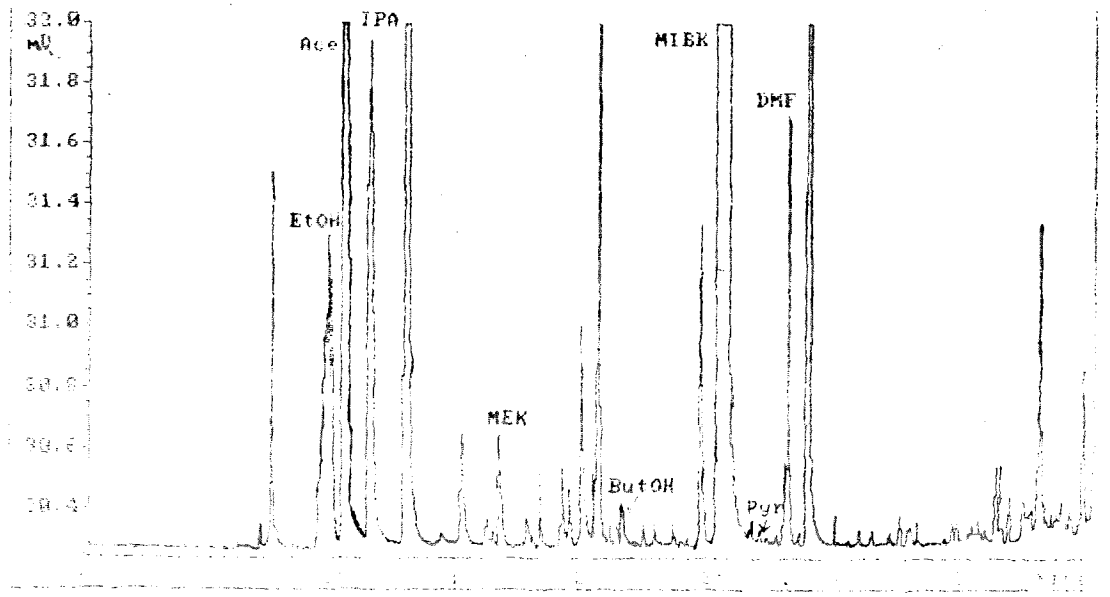


(b)

Figure 3.2: Chromatogram of tap-water with(a) and without(b) addition of standard



(a)



(b)

Figure 3.3: Chromatogram of wastewater with(a) and without(b) addition of standard

Table 3.9 Results of Stepwise Purging Experiment

Compound	Concentration (ppb)	Purge Time (min)	Peak Area	R.S.D.	Cumulative Purge Time (min)	Cumulative Peak Area
EtOH	25	15	357	22.0	15	357
		15	131	20.6	30	488
Ace	10	15	507	18.6	15	507
		15	227	33.6	30	734
		15	59	40.4	45	793
IPA	25	15	299	16.1	15	299
		15	167	29.1	30	466
MEK	5	15	3831	20.1	15	3831
		15	1232	9.5	30	5063
		15	590	25.8	45	5653
ButOH	5	15	448	29.6	15	448
		15	230	40.0	30	678
MIBK	5	15	6572	19.1	15	6572
		15	826	11.4	30	7398
Pyr	10	15	200	28.3	15	200
		15	87	19.7	30	287
DMF	10	15	196	19.7	15	196
		15	71	42.7	30	267

Table 3.10 Recovery Studies from Various Types of Water Samples

Compound	Drinking water					Tap water					Wastewater				
	Without std added		With std added		Recovery	Without std added		With std added		Recovery	Without std added		With std added		Recovery
	Area	RSD	Area	RSD	(%)	Area	RSD	Area	RSD	(%)	Area	RSD	Area	RSD	(%)
EtOH			379	29.7	77.66	57	27.7	363	18.2	62.70	12539	31.4	13096	36.1	114.1
Ace			725	34.1	91.42	161	37.9	817	14.6	82.72	165723	39.7	166586	44.4	108.8
IPA			404	19.6	86.70			385	42.6	82.62	23402	24.9	23930	44.1	113.3
MEK			4263	19.2	75.41	4749	21.8	9627	26.5	86.29	2250	18.5	6322	12.7	72.03
ButOH			532	13.5	78.47			604	37.1	89.09	870	36.9	1584	19.3	105.3
MIBK			6246	6.3	84.43			6800	28.4	91.92	204282	14.6	210483	8.2	83.82
Pyr			229	9.7	79.79	282	13.8	520	20.3	82.93	194	41.2	420	38.5	78.74
DMF	159	21.3	363	25.8	76.40			251	16.6	94.01	8776	19.2	8986	27.7	78.65

The area of peak of each component could be measured with different detector responses(Table 3.11). The relationship between concentration and peak areas for all components of interest was shown in Figure 3.4 and 3.5. All compounds exhibited a linear response over 1–30 ppb for MEK, ButOH and MIBK, 2–60 ppb for Ace, Pyr and DMF, 5–150 ppb for EtOH and IPA.

Table 3.11 indicated that the relative standard deviation was between 10–30% for most of the components. The method showed a better precision for lower concentration levels. The principal reasons which influenced the precision were purging efficiency and adsorption capability of a trap. The effect of these two factors on the precision of the method was more apparent for higher concentration levels than that for lower concentration levels.

Table 3.10 showed that the method for analyzing the polar volatile organic compounds generated acceptable accuracy (recovery between 76–114% for most of the compounds in various types of water samples).

3.4 Method Detection Limit

The method detection limit(MDL) was based on a method's ability to determine an analyte in a sample matrix, regardless of its source of origin. This was based on the variance for the analysis of samples. A sufficient number of samples at each of the three concentration levels (at least seven times) were analyzed, and the standard deviations

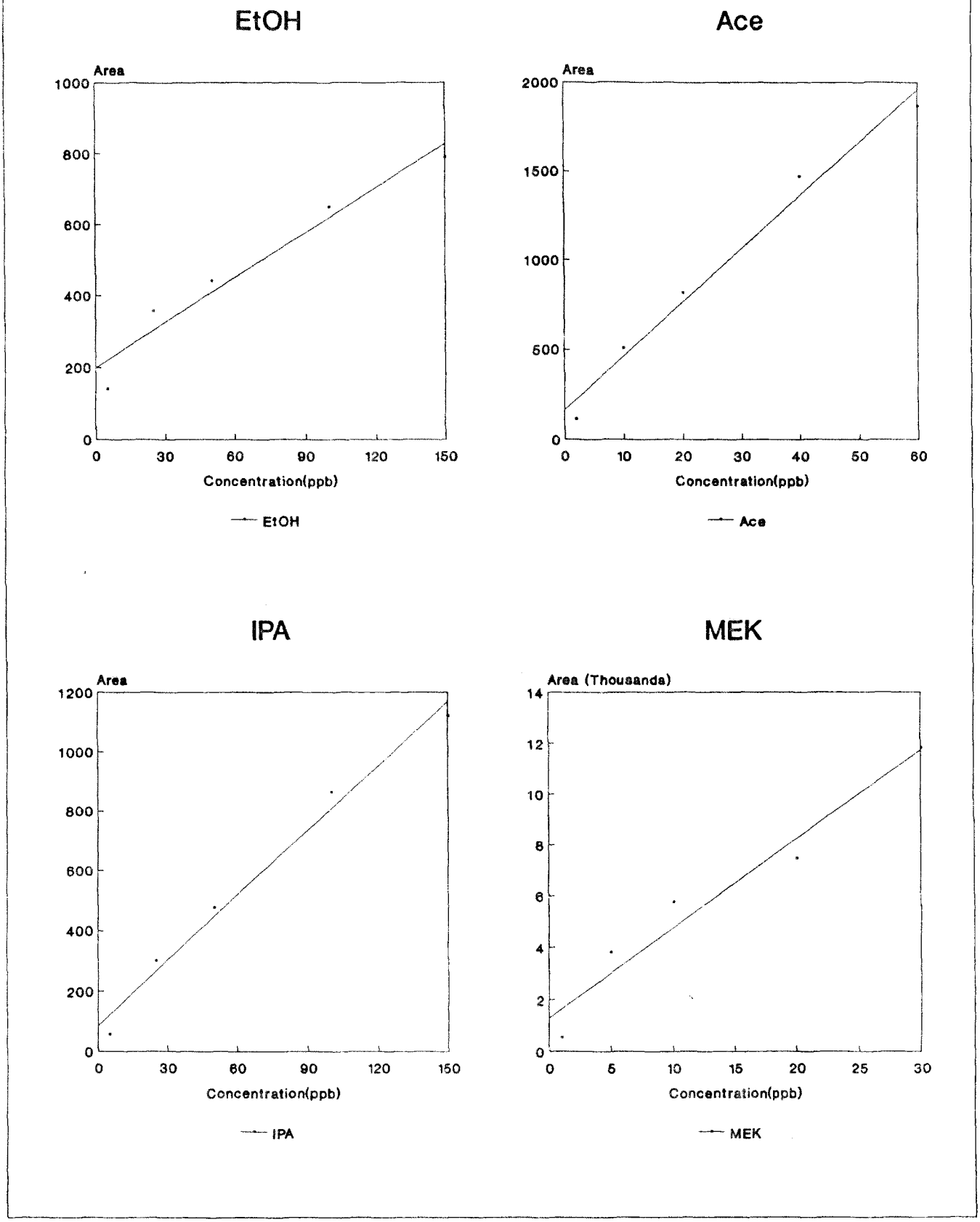


Figure 3.4: Relationship between concentration and peak area for EtOH, Ace, IPA and MEK

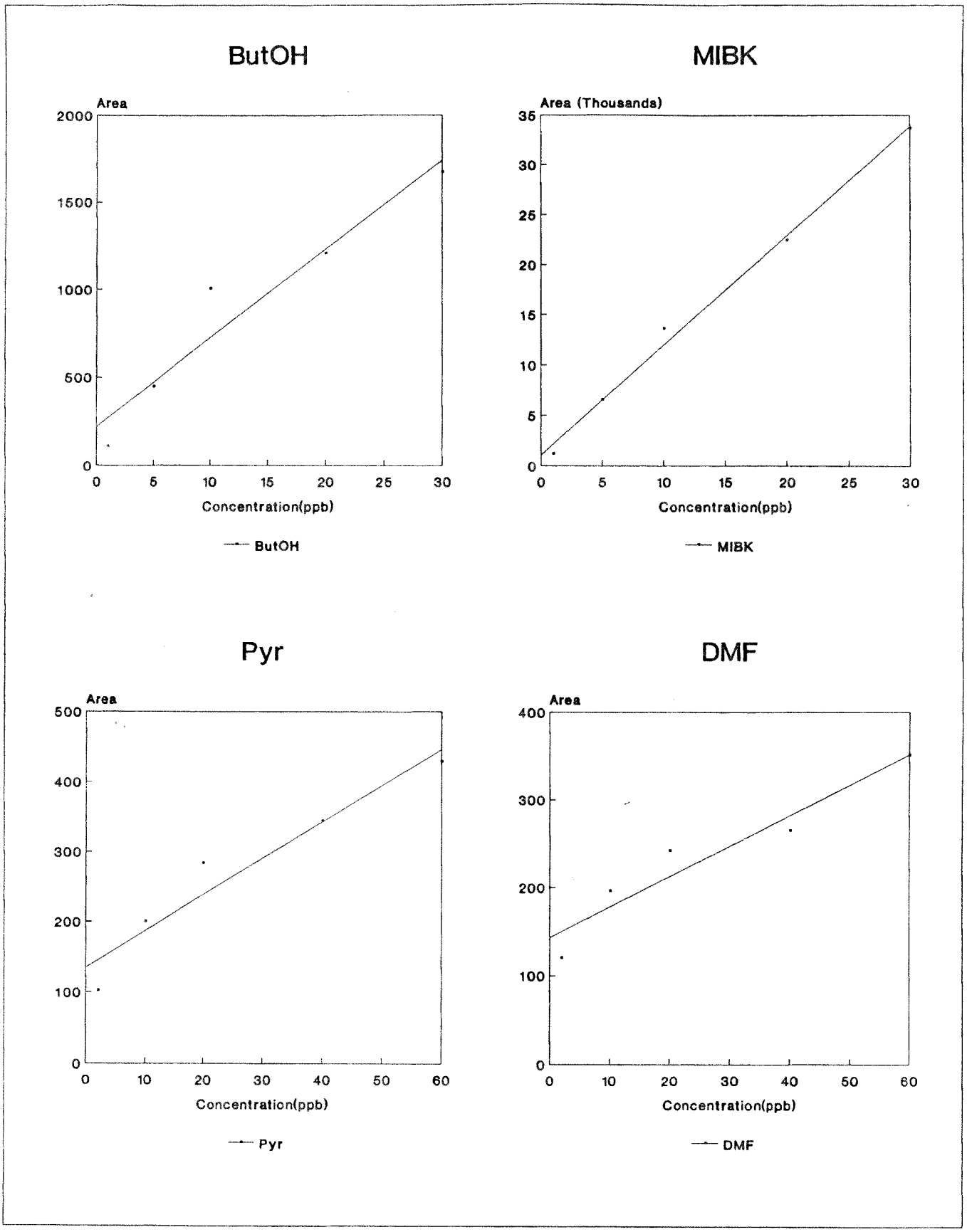


Figure 3.5: Relationship between concentration and peak area for ButOH, MIBK, Pyr and DMF

Table 3.11 Calibration Data

Cancentration(ppb)	30			20			10			5			1		
Compound	Area	S.D.	RSD	Area	S.D.	RSD	Area	S.D.	RSD	Area	S.D.	RSD	Area	S.D.	RSD
EtOH*	790	211.7	26.8	650	131.3	20.2	441	141.2	32.0	357	78.6	22.0	141	12.4	8.8
Ace**	1866	380.7	20.4	1469	230.7	15.7	814	182.6	22.4	507	94.4	18.6	116	17.6	15.2
IPA*	1119	181.3	16.2	863	116.5	13.5	475	80.4	16.9	299	48.1	16.1	57	6.3	11.1
MEK	11805	1613.9	13.7	7481	1501.2	20.1	5771	1233.8	21.4	3831	768.2	20.1	526	60.4	11.5
ButOH	1674	251.3	15.0	1208	219.6	18.2	1005	219.6	21.9	448	132.7	29.6	108	12.8	11.9
MIBK	33703	3460.4	10.3	22445	2840.5	12.7	13599	1902.8	14.0	6572	1252.6	19.1	1206	64.5	5.3
Pyr**	429	136.7	31.9	344	143.0	41.6	284	94.8	33.4	200	56.6	28.3	102	6.4	6.3
DMF**	351	139.0	39.6	265	131.0	49.4	242	97.7	40.4	196	38.6	19.7	120	14.8	12.3

*: concentration levels are 150, 100, 50, 25 and 5 ppb

**: concentration levels are 60, 40, 20, 10 and 2 ppb

of the results were estimated (Table 3.11). The standard deviations might be plotted as a function of concentration as shown in Figure 3.6 and 3.7. By extrapolation, S_o (standard deviation at C $\longrightarrow$ 0) was obtained. Using the equation (2.3), the MDL at 95% confidence could be calculated for each component. The MDL values were shown in Table 3.12.

It was shown that the method was sensitive to MIBK, MEK, and ButOH which had low solubility in water matrix. For other compounds, which were soluble in water, the method detection limit was higher.

3.5 Application of The Method

As a practical application, water obtained from different sources were analyzed for VOCs studied in this paper. The chromatograms shown in Figure 3.1, 3.2 and 3.3 were obtained from drinking water, tapwater, and wastewater obtained from LRSA plant, respectively. This method permitted the determination of a wide variety of volatile organic compounds from water in a single step. The use of three selective detectors (FID, PID, ELCD) enabled separate classes of components containing halogens, aromatic groups, unsaturated groups and saturated hydrocarbons to be selectively measured.

By using a capillary column(Ultra 2), the ButOH could not be separated from Benzene and there was only one peak for MIBK, Pyr and DMF [Figure 3.8 (a)]. With capillary column(PONA), the separation

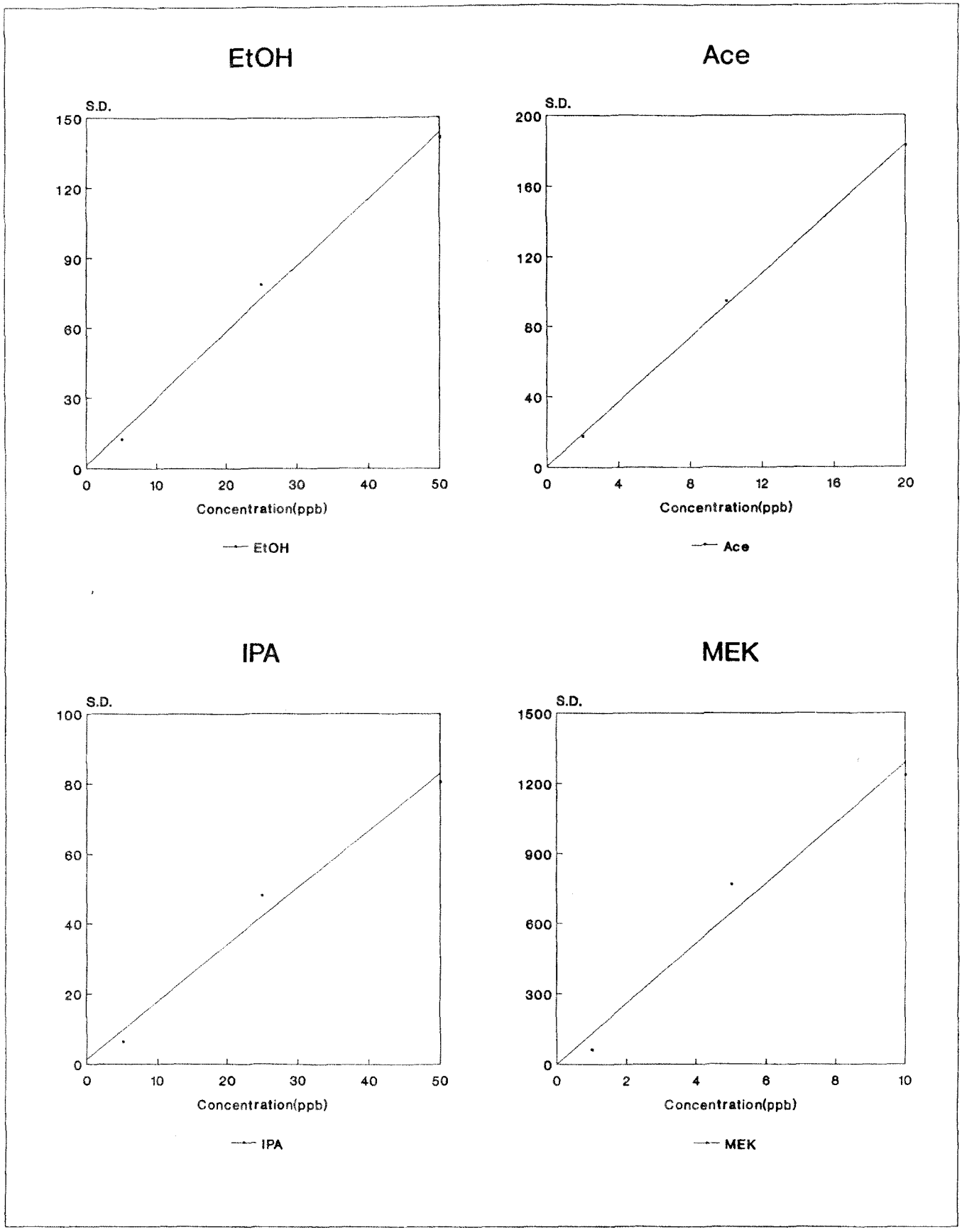


Figure 3.6: Standard Deviation vs. concentration(1)

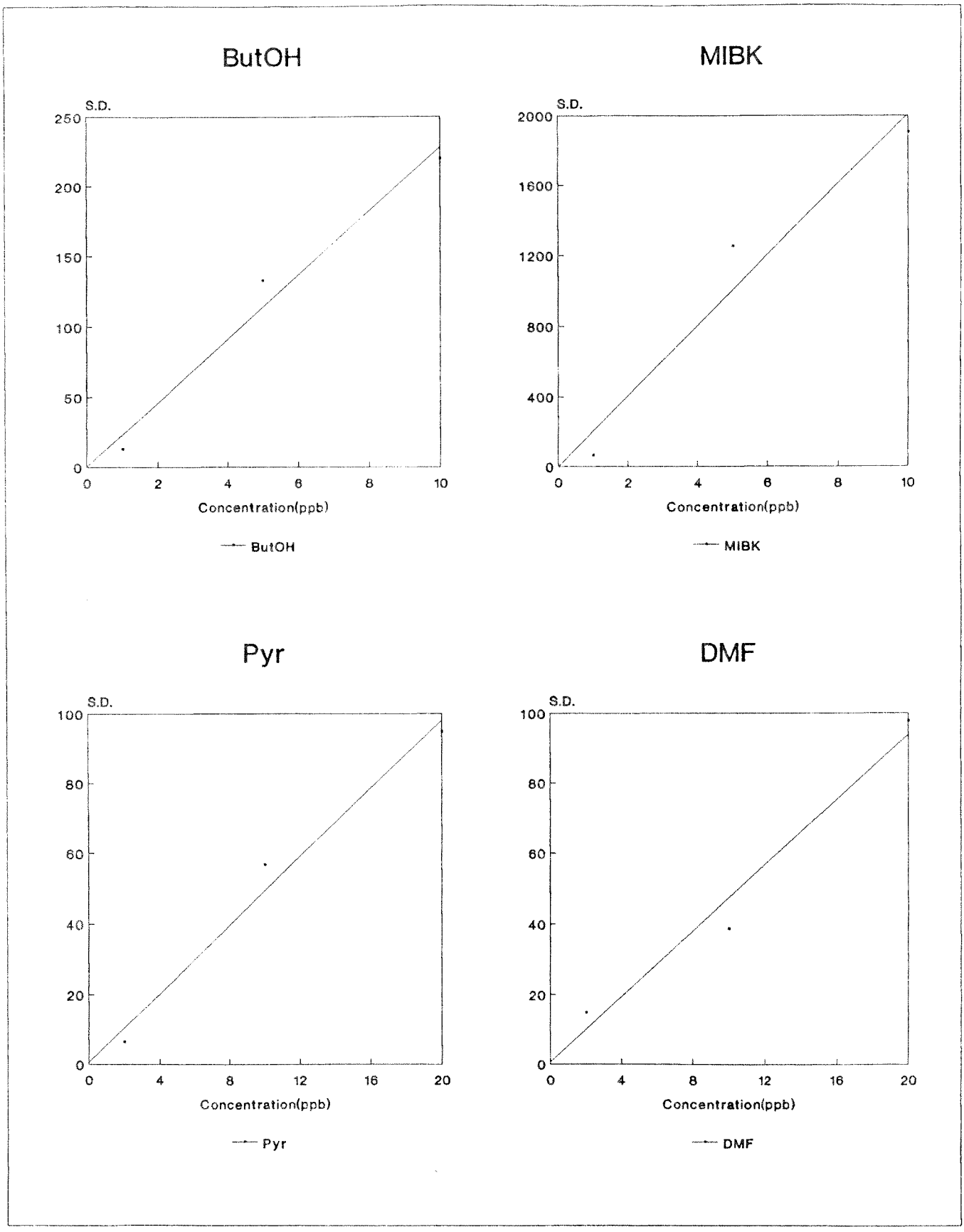


Figure 3.7: Standard Deviation vs. concentration(2)

Table 3.12 Method Detection Limit

Compound	So	MDL(ppb)
EtOH	1.46	4.38
Ace	0.57	1.71
IPA	1.41	4.23
MEK	0.26	0.78
ButOH	0.38	1.14
MIBK	0.16	0.48
Pyr	0.69	2.07
DMF	0.67	2.01

for these compounds was better [Figure 3.8 (b)]. On the other hand, PID had no response to ButOH but responded well to Benzene. So the amounts of ButOH and Benzene could be calculated by combining the response values from FID and PID.

The area values of peaks in Table 3.13 were corresponding to Figure 3.1, 3.2 and 3.3. Because there was linearity between concentration and areas of peaks of the target compounds. Standard addition could be used to calculate the concentration of the compounds in samples.

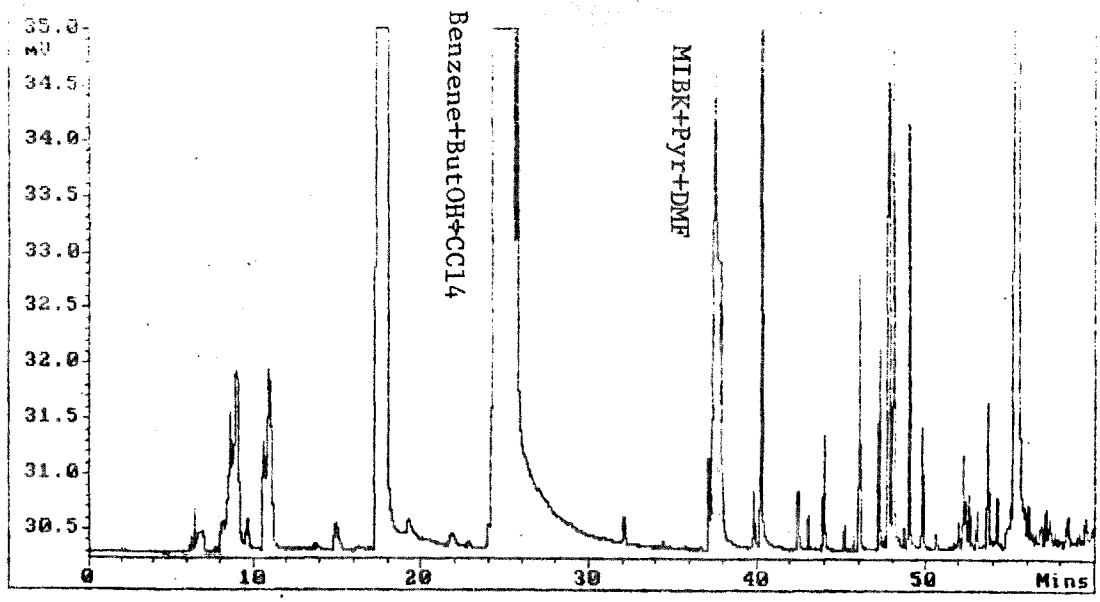
With the data in Table 3.10, the concentration of the target compounds were calculated by using following equation:

$$C_x = \frac{C_s V_s A_x}{A_{x+s}(V_x + V_s) - V_x A_x} \tag{3.1}$$

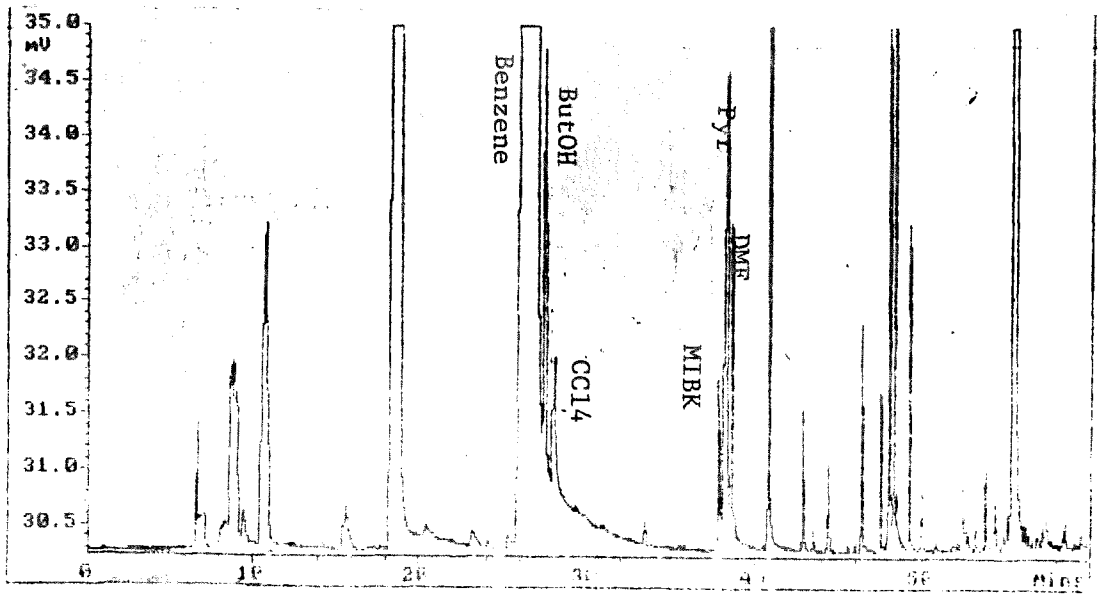
Where:

C_x(ppb): concentration of a target component in water sample
C_s(ppb): concentration of a target component in standard solution
V_x(ml): volume of water sample
V_s(ml): volume of standard solution added
A_x(μVs): area of the peak of a target component in water sample
A_{x+s}(μVs): area of the peak of a target component in water sample with addition of standard solution

The concentrations of each component in water from different sources were listed in Table 3.13.



(a)



(b)

Figure 3.8: Chromatograms with different capillary columns

Table 3.13 Determination of Various Water Samples

Sample	Drinking water				Tap water				Wastewater			
Compound	Area	RSD	Concentration(ppb) SAM	LRM	Area	RSD	Concentration(ppb) SAM	LRM	Area	RSD	Concentration(ppb) SAM	LRM
EtOH					57	27.7	4.40	--	12539	31.4	258.69	--
Ace					161	37.9	2.31	--	165723	39.7	180.28	--
IPA									23402	24.9	339.26	--
MEK					4749	21.8	4.43	9.94	2250	18.5	2.56	2.75
ButOH									870	36.9	5.48	12.83
MIBK									204282	14.6	61.07	--
Pyr					282	13.8	10.68	28.37	194	41.2	7.85	11.40
DMF	159	21.3	7.16	4.57					8776	19.2	133.11	--

SAM: standard addition method

LRM: linear regression method

Chapter 4

Conclusion

A purge-and-trap method was studied to analyze trace level of polar volatile organic compounds in water samples in this paper. It was found that the accuracy of the method was influenced by various factors. The principal factors were purging efficiency and absorption capacity of the trap. Since polar VOCs were hydrophylic and were soluble in water, their purging efficiency was low under normal conditions. In order to increase purging efficiency, higher purge temperatures and large purge volumes should be used (ref. Table 3.1, 3.2, 3.3). However, Since the breakthrough volumes of the polar VOCs on the Tenax trap were relatively small and the compounds could be lost if the purge volume exceeded the breakthrough volume. Recovery also decreased if purge gas flow-rate was too high because compounds had insufficient time to adsorb on the trap. Therefore, purge volume was limited by the adsorption capacity of the Tenax trap. In order to obtain the highest purge efficiency and not exceed the adsorption capacity of the Tenax trap, the optimum purge parameters were ob-

tained in a series of experiments:

Purge time: 15 – 20 min
Purge temperature: 40°C
Purge gas flow-rate: 80 ml/min

However, the purge volume was not large enough and the polar VOCs could not be purged completely from the water matrix. Thus, recovery of these compounds was limited. It was necessary to increase purge volume to increase recovery. For this purpose, other adsorbents should be tested. According to studies by Westendorf[65], silica gel or charcoal could effectively trap water and could not be effectively dry purged to remove water. Using larger purge volume or higher purge temperature resulted in larger quantity of water being transferred to the trap. Water could not only influence adsorption capacity of the trap, but also cause problems in injection and result in poor resolution on the GC column. Therefore, a suitable adsorbent which had a large breakthrough volume and adsorption capacity for polar VOCs and from which water could be removed should be studied in future.

Figure 3.4 and 3.5 indicated that the linearity between peak areas and concentration was not good if concentration was too high or too low. The results were unsatisfactory if a linear calibration factor was used to calculate the concentration of a component in water sample. If calculation was done in the range of linearity, the results were acceptable (ref. Table 3.13).

With the analytical method developed in this study, the method detection limit was between 0.48 – 4.38 ppb for the compounds of interest. The recovery ranged from 75 – 114% except 62.70% of EtOH in tap-water. The relative standard deviation was smaller than 50%. For trace concentration levels, the relative standard deviation was smaller than 15%.

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