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“Analysis of Volatile Organic Priority Pollutants in Water by
Headspace Technique”

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Analysis of Volatile Organic Priority Pollutants in water by Headspace technique

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Abstract

In this study, a headspace technique was developed for the determination of some volatile chlorinated hydrocarbons i.e. , methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene in water samples. Various factors having effect on the percent recovery were studied and evaluated. The temperature of 60°C , equilibration time of 60 minutes, the liquid to gas phase volume ratio of 30:30 in 60 ml serum vial, 1.50 ml of injection volume, and salting out with 13.00 g of anhydrous sodium sulfate were chosen as the optimal headspace analysis condition for the determination of the volatile chlorinated hydrocarbons in water samples. The minimum detectable level of this technique was lower than 0.50 ppb ($\mu\text{g/L}$) for all studied compounds and the percent recoveries were in the range of 62.43 - 89.95% with \pm 2.40 - 4.81 % RSD. The accuracy of this technique was also studied by means of internal standardization method, the percent errors were in the range of 0.31 - 6.4 % at the ppb level of concentration. Moreover, the developed technique was also applied to analyze water samples collected in the Central Bangkok Metropolitan area. Result showed that methylene chloride and chloroform were

found in the range of 15.50 - 214.88 and 1.05 - 38.98 ppb, respectively in drinking waters produced from several companies, and 33.43 - 49.50 and 0.78 - 48.32 ppb, respectively in tap water samples collected from several places.

Introduction

Volatile chlorinated hydrocarbons such as methylene chloride, chloroform, carbon tetrachloride, 1,1,1-Trichloroethane and trichloroethylene are extensively used as a solvent or diluent in many industries for oils, fats, waxes, lacquers, varnishes, rubber, paints and plastics, and as a raw materials in the manufactures of other chemical products especially fluorocarbons. They are also used as a propellant, a fumigant to control weeds, fungi in soil and insect pests, a fire extinguishing agent and a dry-cleaning agent (1,2,5). Product residues and the waste water from those manufactures are the source of the entry of these organic into the environment. In addition, some volatile chlorinated hydrocarbons are produced during water treatment by reaction of chlorine, used for disinfection or oxidation, with the naturally occurring organic compounds in the water (1,3). Methylene chloride, chloroform, carbon tetrachloride, 1,1,1-Trichloroethane and trichloroethylene are a group of volatile compounds that has been classified as priority pollutant by EPA (1,15). The toxicity and metabolism of these organic have been studied by many investigators and shown to be mutagenic and carcinogenic substances. (1,2,4,5) Hence, the concentration of these organic in water are determinate to protect harmful effect i.e. , chloroform recommended by World Health Organization (WHO) should not exceed 30.0 µg/L in drinking water (9) and national primary drinking water regulation by

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

Analytical methods for determination of trace amount of these chlorinated hydrocarbons in water generally require a preconcentration step prior to gas chromatographic analysis. Three procedure are mainly recommended and in practical use for the analysis of these pollutants in water samples. Solvent extraction is simple and needs no specialized equipment but Onodera and Tabucanon (3) commended possible disadvantage for this method were interference i.e. non-volatile compounds and impurities were coextracted into the extracting solvents and time consumption because the coextraction non-volatile compounds required several minutes to be eluted from the column with late analysis. The method that EPA recommend for the determination of trace volatile priority pollutants in water was Purge and Trap technique. (7,11,12) Dietz and Singley (8) have found that This method needs the most complicated instruments to separate the organic from water and the chromatograms are much poorer quality than those observed with the head space technique with regard to peak tailing, detector noise and the interference of impurities in adsorbent trap or stripping gas. Headspace analysis (10,13,14) is based on the equilibrium system between the water sample phase and the gas phase. In this paper, the headspace technique is chosen for determination of a trace amounts of chlorinated hydrocarbons in water samples because it is a simple, rapid reliable and economical method and can detect volatile pollutants in low concentration level of part per billion (ppb).

Experimental

1. Reagents

The standard of volatile chlorinated hydrocarbons ; methylene chloride , chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene , and the internal standard ; 2-bromo-1-chloropropane were purchased from Chem Service, Inc.(West Chester, PA,USA.) Absolute methanol (AR Grade) and anhydrous sodium Sulfate (AR Grade) were purchased from J.T.Baker Chemical Company. (Deventer, Holland) Sodium chloride (AR Grade) and Calcium carbonate (AR Grade) were obtained from E. Merck (Darmstadt, Germany).

2. Instrument and Apparatus

a) Gas Chromatograph Model HP 5890 (Hewlett Packard) equipped with Electron Capture Detector (ECD) and Hewlett Packard HP 3393 A integrator. Injector and detector of 150°C and 250°C were used respectively, and a 25 m x 0.32 mm id HP-5 fused silica capillary column, 0.25 µm film thickness (Hewlett Packard) was temperature - programmed from 36°C hold 1 min. to 100°C hold 10 min. at 5°C/min. The injector was in the splitless mode for 0.6 min. after injection, then, the split was turned on at a split ratio of 25:1 for the duration of the run. Carrier gas (He) flow rate was 1.5 ml/min. Auxiliary gas (N₂) flow rate was 40ml/min.

b). Apparatus used in this headspace technique

- 1) 60 ml Serum Vial ; height 70 mm, base diameter 40 mm.
- 2) aluminum foil, black rubber septum and aluminum cap ; diameter

18.0 mm.

- 3) Manual Hand Operated Crimper (Supelco.Inc, Bellefonte, PA,USA)
- 4) Griffin No.7 constant temperature water bath (Griffin & George Ltd., GT. Britain)
- 5) Pressure-Lok series A2 Gas tight Syringe 2.00 ml (Scientific Glass Engineering , SGE)

3. Headspace Procedure

Water sample are collected in 60 ml of serum vials and the vials are sealed immediately with aluminum foil, black rubber septum and aluminum cap sequentially using Manual Hand Operated Crimper. These vials are placed in a constant temperature water bath until they reach an equilibration time. The headspace vapor in the vials are removed with gas tight syringe and then inject on gas chromatograph equipped with an electron capture detector.

4. The study of various parameters on the sensitivity of Headspace technique

The various parameters which have the effect on the sensitivity of headspace technique for determination of volatile chlorinated hydrocarbons in water sample were studied in order to find its optimum condition. The parameters studied were :

- The equilibration times of the sample i.e., 0, 10, 20, 30, 40,...,etc. minutes.
- The temperature for equilibrating sample i.e. , 50°C, 60°C, 70°C and 80°C.

- The liquid to gas phase volume ratio i.e., 10:50, 20:40, 30:30, 40:20 and 50:10.
- The headspace gas injection volume i.e., 0.50, 1.00, 1.50 and 2.00 ml.
- The salting out effect with sodium chloride, anhydrous sodium sulfate and calcium carbonate.

5. Quantitative Headspace Analysis

The internal standardization method was chosen as the quantitative method for determination of each chlorinated hydrocarbon in unknown water sample. Standard solutions of increasing concentrations of the compounds and the constant concentration of the internal standard being investigated were prepared and analyzed by using Headspace Technique at the optimum condition prior to gas chromatograph.

An internal standard curve was performed for each compound by plotting the peak area ratios obtained from GC chromatogram against the concentration ratios between standard and internal standard. This curve was used to determine the concentration of the volatile chlorinated hydrocarbons by headspace in drinking water and tap water samples.

RESULTS AND DISCUSSIONS

1. The Study of Equilibration Time.

The result of the study of equilibration time for each volatile chlorinated hydrocarbon, i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene at the lower and higher concentration of ppb level using headspace technique analysis with GC condition as described in Table 1 are given in Figures 1 - 5. The equilibration time of each studied compound showed in the graphs plotted the peak area (A) of each volatile chlorinated hydrocarbon against time is 40 minutes and 50 minutes for methylene chloride at 192.95 and 964.75 ppb, respectively, 50 minutes for chloroform at both 188.10 and 940.49 ppb, 50 minutes for carbon tetrachloride at both 199.71 and 998.57 ppb, 50 minutes and 60 minutes for 1,1,1-trichloroethane at 199.44 and 997.21 ppb, respectively and 40 minutes for trichloroethylene at both 194.60 and 973.01 ppb. Therefore, the time interval of 60 minutes is chosen as the optimum equilibration time for the studied compounds and it is used for the entire studies to ensure that the system is in the equilibrium.

2. The Study of Temperature.

The effect of temperature on the distribution coefficient (K) and the sensitivity (S) of each volatile chlorinated hydrocarbon i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene is studied. The results of the study on the distribution coefficient (K) are presented in Tables 2 and 3 and the graphs showing the relationship of the

Table 1 The gas chromatographic conditions

GC Parameters	GC Conditions
Analytical Column	25 m x 0.32 mm ID. , HP - 5 (5 % Phenyl Methyl silicone) Capillary column.
Temperature Program	36°C (1 min.) to 100 °C (10 min.) at 5°C/ min.
Splitless time	0.60 min.
Split Ratio	25 : 1
Flow Rate of Carrier Gas (He)	1.50 mL/min.
Detector Temperature	250 °C
Inlet Temperature	150 °C
Detector	- Flame Ionization Detector (FID)
	Flow rate of H ₂ 40.00 ml/min.
	Air 380.00 ml/min.
	N ₂ 50.00 ml/min.
	- Electron Capture Detector (ECD)
	Flow rate of N ₂ 40.00 ml/min.

Figure 1. The result of the effect of equilibration time on peak area of methylene chloride at concentration of 192.95 and 964.75 ppb. using FID as GC detector.

Time (min.)	Peak Area of Methylene chloride	
	192.95 ppb	964.75 ppb
0	1369	10632
10	2167	14591
20	2286	16733
30	2511	18143
40	2689	19171
50	2664	19403
60	2730	20501
80	2748	20304
100	2683	20408
120	2745	19550

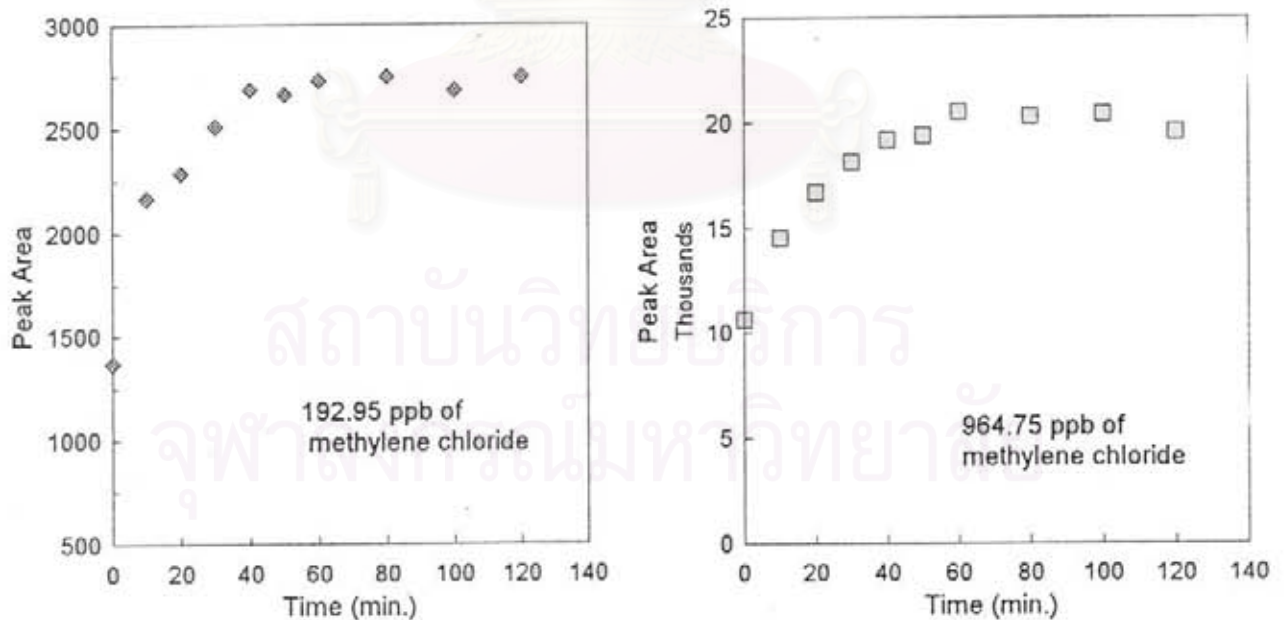


Figure 2. The result of the effect of equilibration time on peak area of chloroform at concentration of 188.10 and 940.49 ppb. using FID as GC detector.

Time (min.)	Peak Area of Chloroform	
	188.10 ppb	940.49 ppb
0	1851	6341
10	2644	9982
20	2960	12855
30	3050	14315
40	3159	15322
50	3241	16324
60	3152	15952
80	3203	16260
100	3307	15266
120	3344	16337

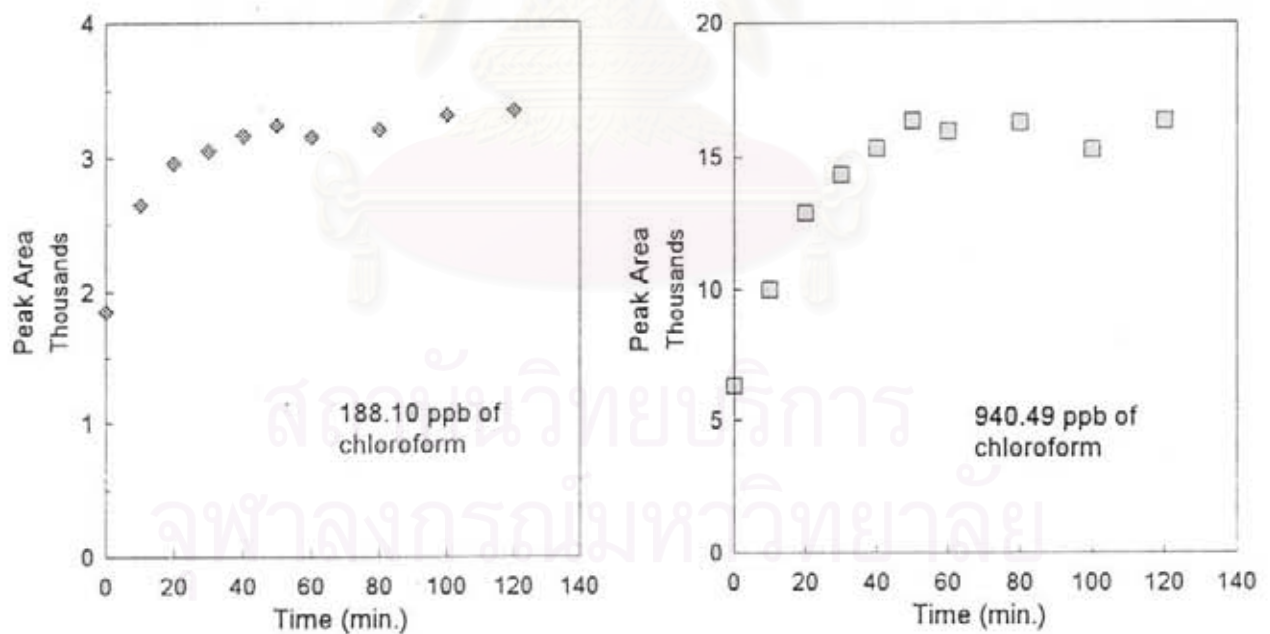


Figure 3. The result of the effect of equilibration time on peak area of carbon tetrachloride at concentration of 199.71 and 998.57 ppb. using FID as GC detector.

Time (min.)	Peak Area of Carbon tetrachloride	
	199.71 ppb	998.57 ppb
0	2529	8613
10	2877	13711
20	3477	17512
30	3843	18330
40	4455	19609
50	4562	20402
60	4692	19509
80	4667	20216
100	4322	20937
120	4734	21465

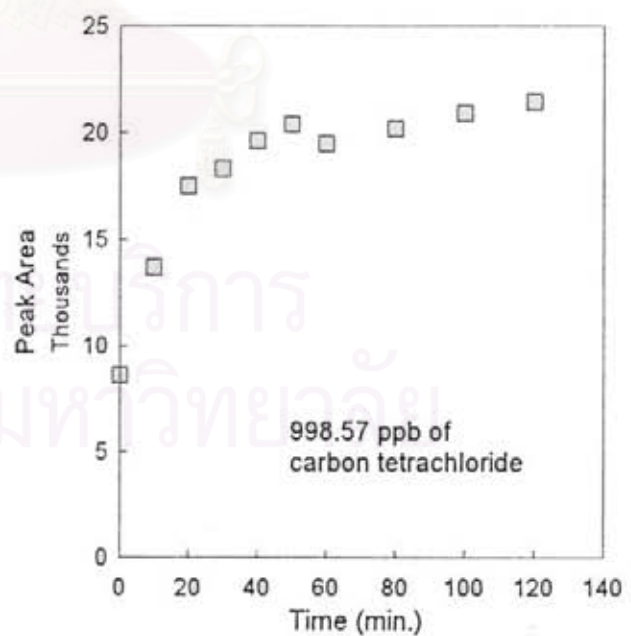
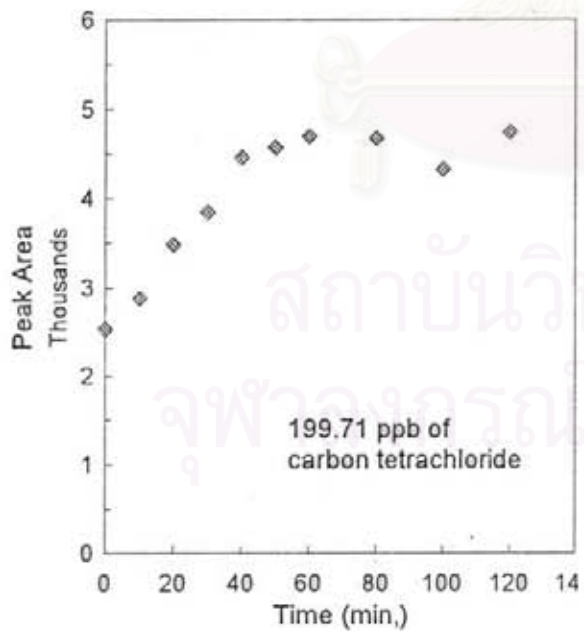


Figure 4. The result of the effect of equilibration time on peak area of 1,1,1-trichloroethane at concentration of 199.44 and 997.21 ppb, using FID as GC detector.

Time (min.)	Peak Area of 1,1,1-Trichloroethane	
	199.44 ppb	997.21 ppb
0	11245	45544
10	11505	49711
20	12924	50289
30	13290	50939
40	13902	53384
50	14122	54795
60	14278	55246
80	14370	54583
100	14346	56084
120	14145	55926

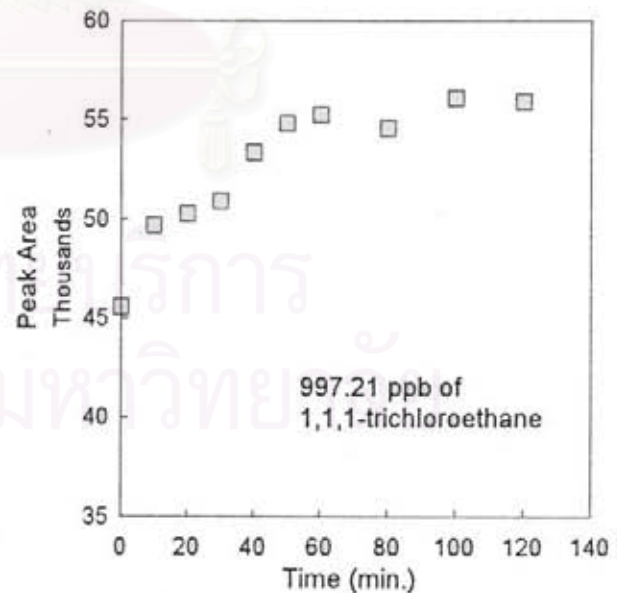
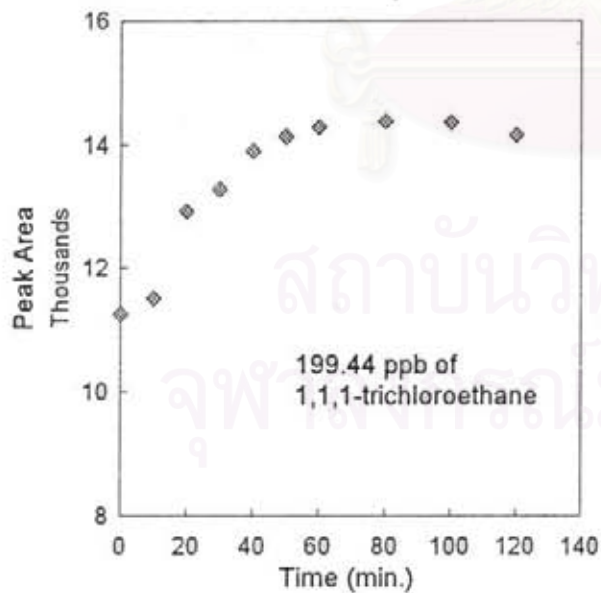
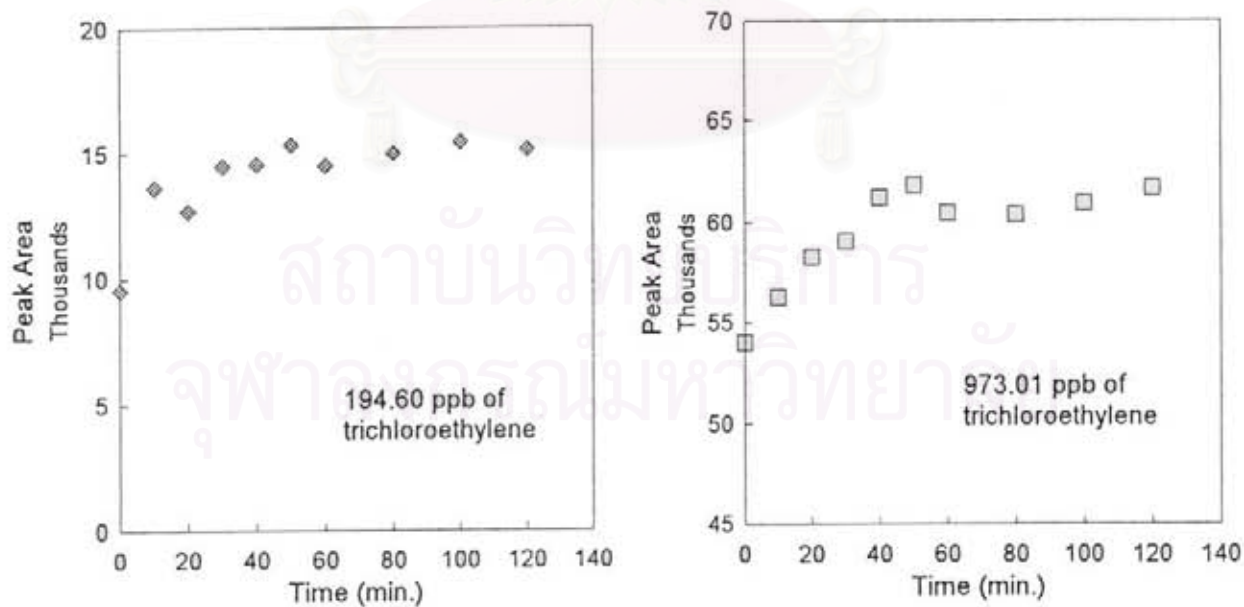


Figure 5. The result of the effect of equilibration time on peak area of trichloroethylene at concentration of 194.60 and 973.01 ppb. using FID as GC detector.

Time (min.)	Peak Area of Trichloroethylene	
	194.60 ppb	973.01 ppb
0	9539	54023
10	13657	56259
20	12724	58286
30	14478	59078
40	14564	61259
50	15335	61847
60	14517	60509
80	15011	60407
100	15438	60957
120	15129	61702



relationship of the distribution coefficient of each volatile chlorinated hydrocarbon with temperature are in Figure 6. It indicates that the distribution coefficient of each volatile chlorinated hydrocarbon decreases when the temperature of system increases. Hence, the temperature has the effect on the distribution coefficient of each compound and it can be explained by the fact that raising temperature will increase the vapor pressure of each compound and therefore, their solubility in the solution will be decreased as the concentration of each compound in the gas phase will be increased as the results shown in Tables 2 and 3.

The results of the effect of the temperature on sensitivity of each volatile chlorinated hydrocarbon are shown in Tables 4 and 5 and the graphs plotted the sensitivity of each compound against temperature are shown in Figure 7. It demonstrates that the temperature has the effect of sensitivity of each volatile chlorinated hydrocarbon and therefore increasing temperature of the system will result in the enhancement of the sensitivity of headspace analysis technique. According to the results in Tables 4 and 5, it can be seen that the highest sensitivity of the headspace analysis technique is obtained at the temperature of 80 °C which is different from the temperature used in the study. The reason is that increasing the temperature of the system build up the pressure in it and is causing the leak of the components from headspace sample vials. Moreover, the water vapor in the headspace gas will be increased at high temperature result in the decrease in the detector response. Therefore, the temperature of 60 C is selected as an optimum temperature for this headspace analysis due to it gives a high precision as shown the percent relative standard deviation (%RSD) in Tables

Figure 6. The effect of temperature on the distribution coefficient of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.

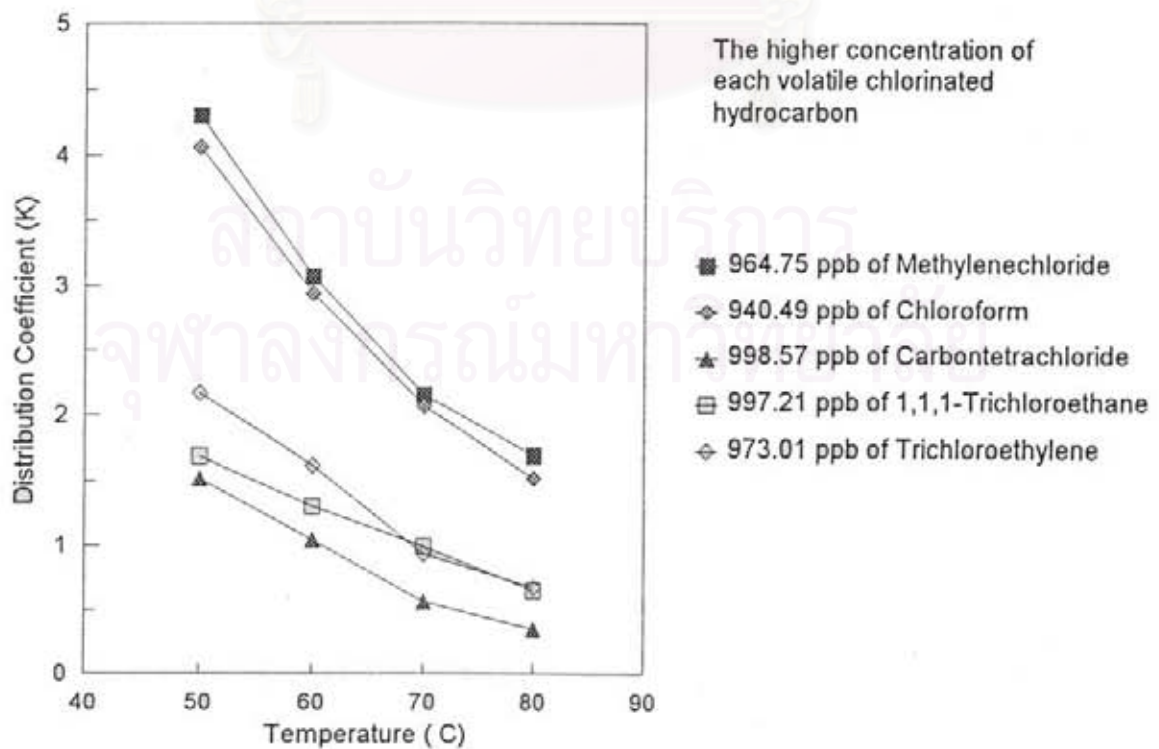
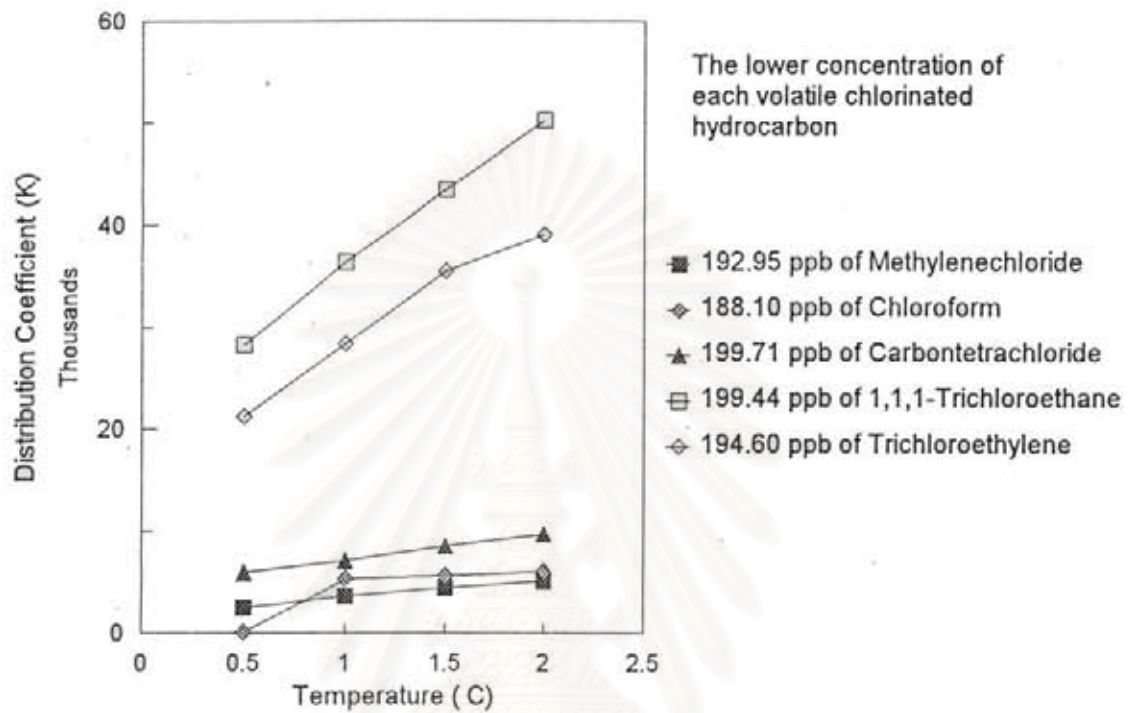


Table 2 The effect of temperature on the distribution coefficient and the equilibrium concentration of each volatile chlorinated hydrocarbon in gas phase with concentration of aqueous standard solution in lower level of ppb.

Compounds	Temperature (°C)	K	Cg (ppb)
Methylene chloride (192.95 ppb)	50.0	3.42	43.64
	60.0	3.01	48.07
	70.0	2.25	59.33
	80.0	1.59	74.38
Chloroform (188.10 ppb)	50.0	2.88	48.45
	60.0	2.48	54.09
	70.0	2.31	56.92
	80.0	1.87	65.60
Carbon tetrachloride (199.71 ppb)	50.0	1.24	89.10
	60.0	0.92	103.89
	70.0	0.66	120.09
	80.0	0.45	137.33
1,1,1 - Trichloroethane (199.44 ppb)	50.0	1.96	67.50
	60.0	1.34	85.08
	70.0	0.96	101.91
	80.0	0.69	118.21
Trichloroethylene (199.44 ppb)	50.0	3.07	47.81
	60.0	1.73	71.36
	70.0	1.07	93.83
	80.0	0.81	107.70

Triplicate analyses

Table 3 The effect of temperature on the distribution coefficient and the equilibrium concentration of each volatile chlorinated hydrocarbon in gas phase with concentration of aqueous standard solution in higher level of ppb.

Compounds	Temperature (°C)	K	Cg (ppb)
Methylene chloride (964.75 ppb)	50.0	4.30	181.89
	60.0	3.07	237.02
	70.0	2.15	306.54
	80.0	1.69	359.24
Chloroform (940.49 ppb)	50.0	4.06	185.73
	60.0	2.94	238.28
	70.0	2.07	306.08
	80.0	1.52	373.90
Carbon tetrachloride (998.57 ppb)	50.0	1.52	396.16
	60.0	1.04	490.77
	70.0	0.56	640.14
	80.0	0.35	738.01
1,1,1 - Trichloroethane (997.21 ppb)	50.0	1.69	370.35
	60.0	1.30	433.71
	70.0	0.99	500.07
	80.0	1.65	606.03
Trichloroethylene (973.01 ppb)	50.0	2.17	307.43
	60.0	1.62	307.43
	70.0	0.93	504.77
	80.0	0.67	582.85

Triplicate analyses

Table 4 The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

Compounds	Temperature (C ^o)	Sensitivity (S)	%RSD
Methylene chloride (192.95 ppb)	50.0	14.81	±6.12
	60.0	16.31	±2.89
	70.0	20.13	±8.15
	80.0	25.23	±3.82
Chloroform (188.10 ppb)	50.0	16.52	±3.10
	60.0	18.44	±3.88
	70.0	19.40	±4.32
	80.0	22.37	±1.11
Carbon tetrachloride (199.71 ppb)	50.0	16.12	±2.68
	60.0	18.79	±4.30
	70.0	21.72	±7.40
	80.0	24.84	±8.42
1,1,1 - Trichloroethane (199.44 ppb)	50.0	67.54	±4.37
	60.0	85.13	±2.60
	70.0	101.96	±4.98
	80.0	118.27	±5.96
Trichloroethylene (199.44 ppb)	50.0	49.17	±3.20
	60.0	73.39	±3.10
	70.0	96.49	±7.53
	80.0	110.76	±6.29

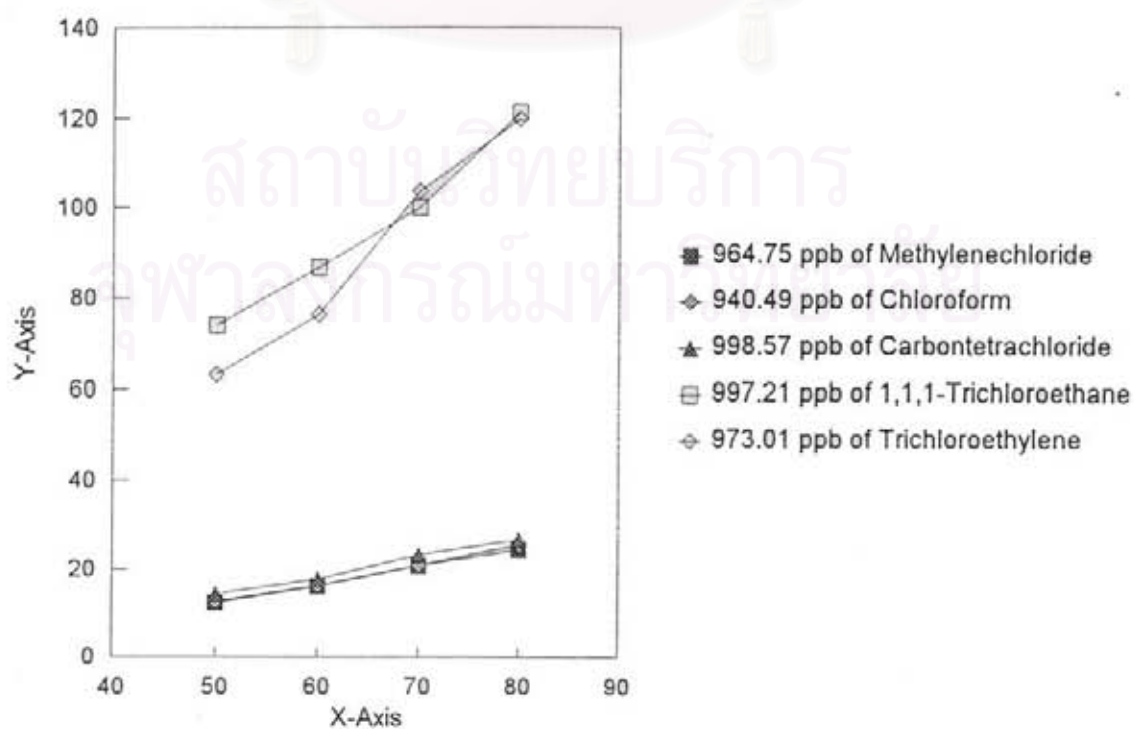
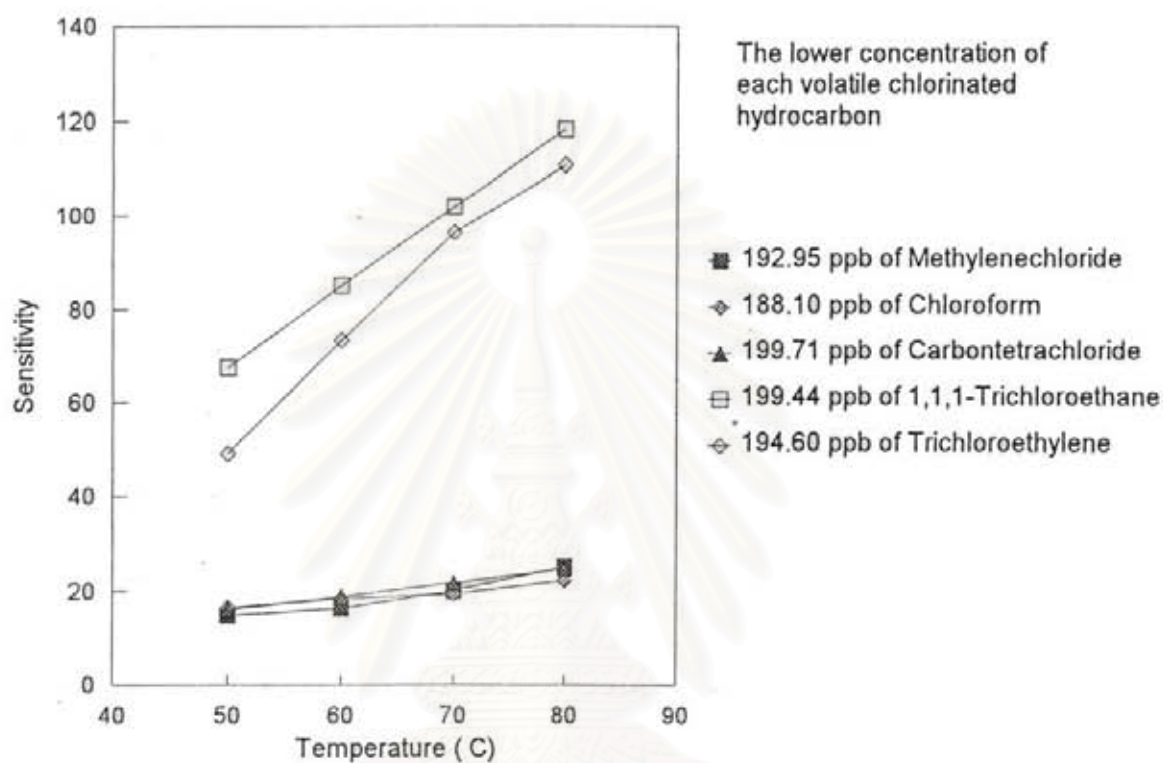
Triplicate analyses

Table 5 The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

Compounds	Temperature ($^{\circ}\text{C}$)	Sensitivity (S)	%RSD
Methylene chloride (964.75 ppb)	50.0	12.34	± 4.67
	60.0	16.08	± 2.69
	70.0	20.80	± 5.70
	80.0	24.38	± 6.53
Chloroform (940.49 ppb)	50.0	12.67	± 3.50
	60.0	16.25	± 2.79
	70.0	20.87	± 4.71
	80.0	25.50	± 7.00
Carbon tetrachloride (998.57 ppb)	50.0	14.33	± 4.11
	60.0	17.75	± 1.34
	70.0	23.15	± 12.27
	80.0	26.69	± 15.86
1,1,1 - Trichloroethane (997.21 ppb)	50.0	74.11	± 1.47
	60.0	86.79	± 2.80
	70.0	100.06	± 3.52
	80.0	121.26	± 6.30
Trichloroethylene (973.01 ppb)	50.0	63.23	± 3.30
	60.0	76.46	± 1.59
	70.0	103.82	± 2.53
	80.0	119.88	± 8.36

Triplicate analyses

Figure 7. The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.



4 and 5 and is a sufficient sensitivity for the determination of each volatile chlorinated hydrocarbon.

3. The Study of Liquid to Gas Phase Volume Ratio.

The factor affecting the sensitivity of headspace analysis technique is also the liquid to gas volume ratio. The selection of the correct liquid to gas phase volume ratio will result in enhancing sensitivity and accuracy of the analysis. Therefore, its effect of the distribution coefficient and the sensitivity of each volatile chlorinated hydrocarbon is studied in order to determine the optimum liquid to gas phase volume ratio for the headspace analysis.

The results of liquid to gas phase volume ratio on the distribution coefficient and the sensitivity of each volatile chlorinated hydrocarbon i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene are presented in Tables 6 - 7 and 8 - 9 , respectively. The graphs plotted the distribution coefficient (K) and the sensitivity (S) of each volatile chlorinated hydrocarbon against the liquid to gas phase volume ratio are shown in Figures 8 and 9 , respectively. It shows that the distribution coefficient of each volatile chlorinated hydrocarbon decreases when the value of liquid to gas phase volume ratio increases. The decrease in the value of distribution coefficient will continue until the ratio of V_l / V_g reaches 1.0 (30:30) and it will remain constant up to higher phase ratios. Therefore the sensitivity of each volatile chlorinated hydrocarbon is not much different in the liquid to gas phase volume ratios ranging from 30:30 to 50:10 as seen in Figures 9 and increasing the phase volume ratio of V_l / V_g tends to decrease the precision of the analysis as shown in Tables 8 and 9 due to

Table 6 The effect of liquid to gas phase volume ratio on the distribution coefficient and the equilibrium concentration of each volatile chlorinated hydrocarbon in gas phase with concentration of aqueous standard solution in lower level of ppb.

Compound	Vl : Vg	K	Cg (ppb)
Methylene chloride (196.87 ppb)	10 : 50	6.63	27.96
	20 : 40	5.83	29.60
	30 : 30	5.26	32.90
	40 : 20	5.13	34.99
	50 : 10	5.13	36.94
Chloroform (203.21 ppb)	10 : 50	4.84	24.13
	20 : 40	3.76	35.31
	30 : 30	3.30	47.26
	40 : 20	3.13	56.01
	50 : 10	2.98	63.94
Carbon tetrachloride (197.78 ppb)	10 : 50	2.56	51.61
	20 : 40	1.42	57.89
	30 : 30	1.34	84.53
	40 : 20	1.11	123.06
	50 : 10	0.87	184.63
1,1,1 - Trichloroethane (197.51 ppb)	10 : 50	6.98	16.49
	20 : 40	2.54	43.47
	30 : 30	1.90	68.15
	40 : 20	1.47	100.03
	50 : 10	1.32	130.08
Trichloroethylene (198.56 ppb)	10 : 50	3.90	22.32
	20 : 40	3.38	36.89
	30 : 30	2.11	63.79
	40 : 20	1.86	84.10
	50 : 10	1.69	105.26

Triplicate analyses

Table 7 The effect of liquid to gas phase volume ratio on the distribution coefficient and the equilibrium concentration of each volatile chlorinated hydrocarbon in gas phase with concentration of aqueous standard solution in higher level of ppb.

Compounds	VI : Vg	K	Cg (ppb)
Methylene chloride (984.40 ppb)	10 : 50	7.54	78.48
	20 : 40	6.15	120.84
	30 : 30	6.05	139.59
	40 : 20	5.74	157.66
	50 : 10	5.85	162.69
Chloroform (984.40 ppb)	10 : 50	4.33	118.18
	20 : 40	3.67	194.05
	30 : 30	3.28	230.02
	40 : 20	2.97	283.46
	50 : 10	2.96	309.07
Carbon tetrachloride (988.60 ppb)	10 : 50	2.35	134.52
	20 : 40	1.28	258.82
	30 : 30	1.31	427.87
	40 : 20	1.08	623.87
	50 : 10	0.99	830.35
1,1,1 - Trichloroethane (987.60 ppb)	10 : 50	4.69	101.93
	20 : 40	3.08	194.59
	30 : 30	1.88	342.58
	40 : 20	1.46	502.85
	50 : 10	1.30	658.15
Trichloroethylene (992.50 ppb)	10 : 50	3.81	112.62
	20 : 40	2.67	212.53
	30 : 30	2.19	311.49
	40 : 20	1.17	371.14
	50 : 10	1.90	473.19

Triplicate analyses

Table 8 The effect of liquid to gas phase volume ratio on the sensitivity of concentration of each volatile chlorinated hydrocarbon in gas phase with concentration of aqueous standard solution in lower level of ppb.

Compounds	VI : Vg	Sensitivity (S)	%RSD
Methylene chloride (196.87 ppb)	10 : 50	18.60	±4.08
	20 : 40	19.69	±4.24
	30 : 30	21.88	±1.85
	40 : 20	23.27	±3.19
	50 : 10	24.56	±6.42
Chloroform (203.21 ppb)	10 : 50	14.51	±4.48
	20 : 40	22.28	±3.56
	30 : 30	29.83	±3.90
	40 : 20	35.35	±4.80
	50 : 10	40.36	±8.89
Carbon tetrachloride (197.78 ppb)	10 : 50	9.56	±1.20
	20 : 40	21.14	±1.78
	30 : 30	30.88	±2.70
	40 : 20	44.95	±3.83
	50 : 10	67.44	±4.11
1,1,1 - Trichloroethane (197.51 ppb)	10 : 50	33.32	±2.72
	20 : 40	87.83	±1.66
	30 : 30	137.71	±3.45
	40 : 20	202.11	±3.97
	50 : 10	262.85	±5.46
Trichloroethylene (198.56 ppb)	10 : 50	44.99	±2.58
	20 : 40	74.37	±2.61
	30 : 30	128.58	±4.16
	40 : 20	169.52	±4.20
	50 : 10	212.18	±7.30

Triplicate analyses

Table 9 The effect of liquid to gas phase volume ratio on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

Compounds	VI : Vg	Sensitivity (S)	%RSD
Methylene chloride (984.40 ppb)	10 : 50	10.44	±1.64
	20 : 40	16.07	±4.23
	30 : 30	18.57	±2.36
	40 : 20	20.97	±3.00
	50 : 10	21.64	±4.65
Chloroform (984.40 ppb)	10 : 50	15.40	±12.10
	20 : 40	25.28	±3.23
	30 : 30	29.97	±2.36
	40 : 20	36.93	±2.90
	50 : 10	40.27	±3.70
Carbon tetrachloride (988.60 ppb)	10 : 50	9.83	±3.69
	20 : 40	18.91	±4.42
	30 : 30	31.27	±2.63
	40 : 20	45.59	±4.80
	50 : 10	60.68	±6.64
1,1,1 - Trichloroethane (987.60 ppb)	10 : 50	41.19	±6.64
	20 : 40	78.63	±1.42
	30 : 30	138.43	±2.16
	40 : 20	203.20	±1.16
	50 : 10	265.96	±9.22
Trichloroethylene (992.50 ppb)	10 : 50	45.42	±1.00
	20 : 40	85.71	±1.59
	30 : 30	125.62	±0.65
	40 : 20	149.67	±3.09
	50 : 20	190.83	±6.26

Triplicate analyses

Figure 8. The effect of liquid to gas phase volume ratio on the distribution coefficient of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.

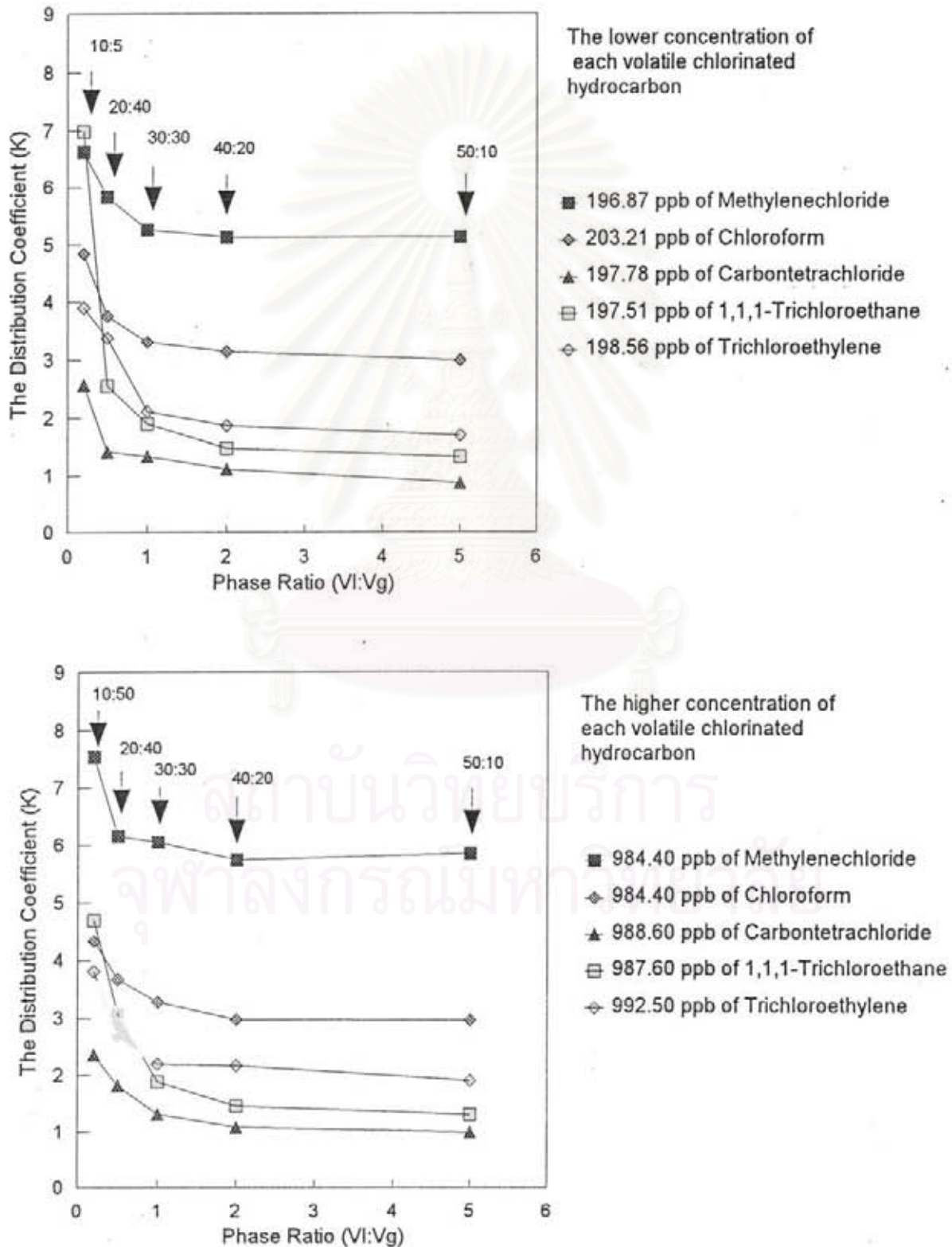
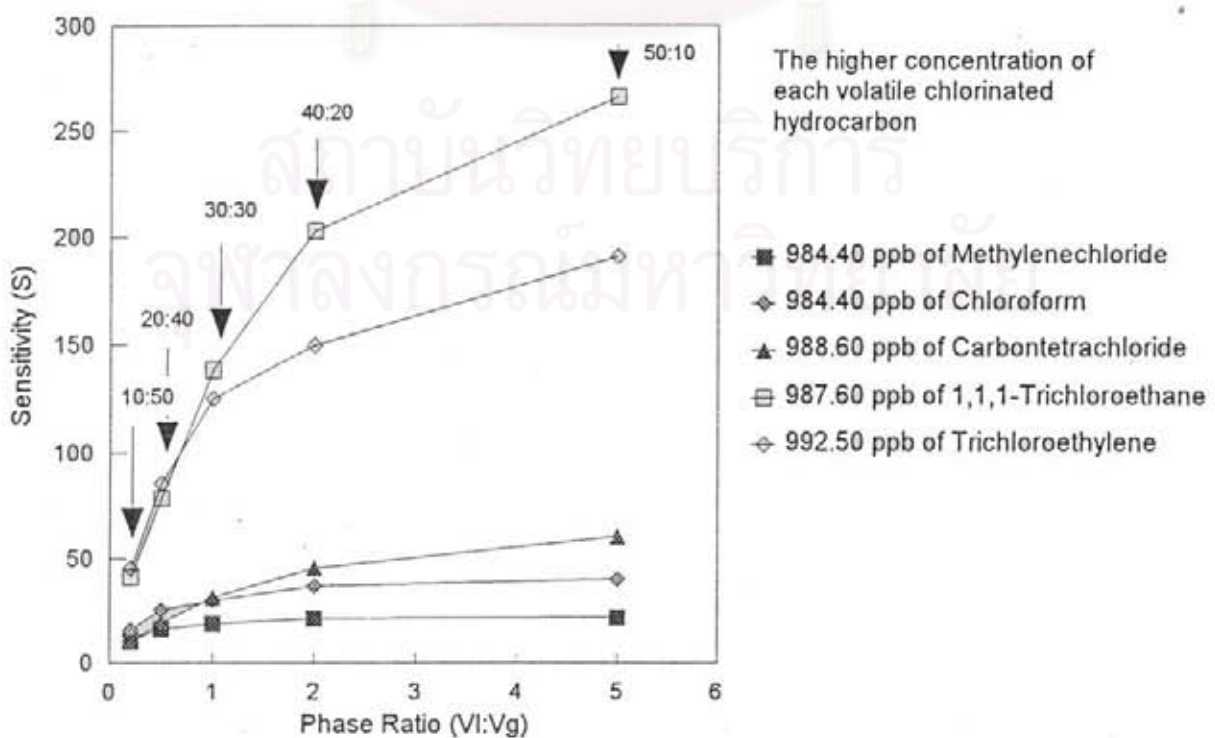
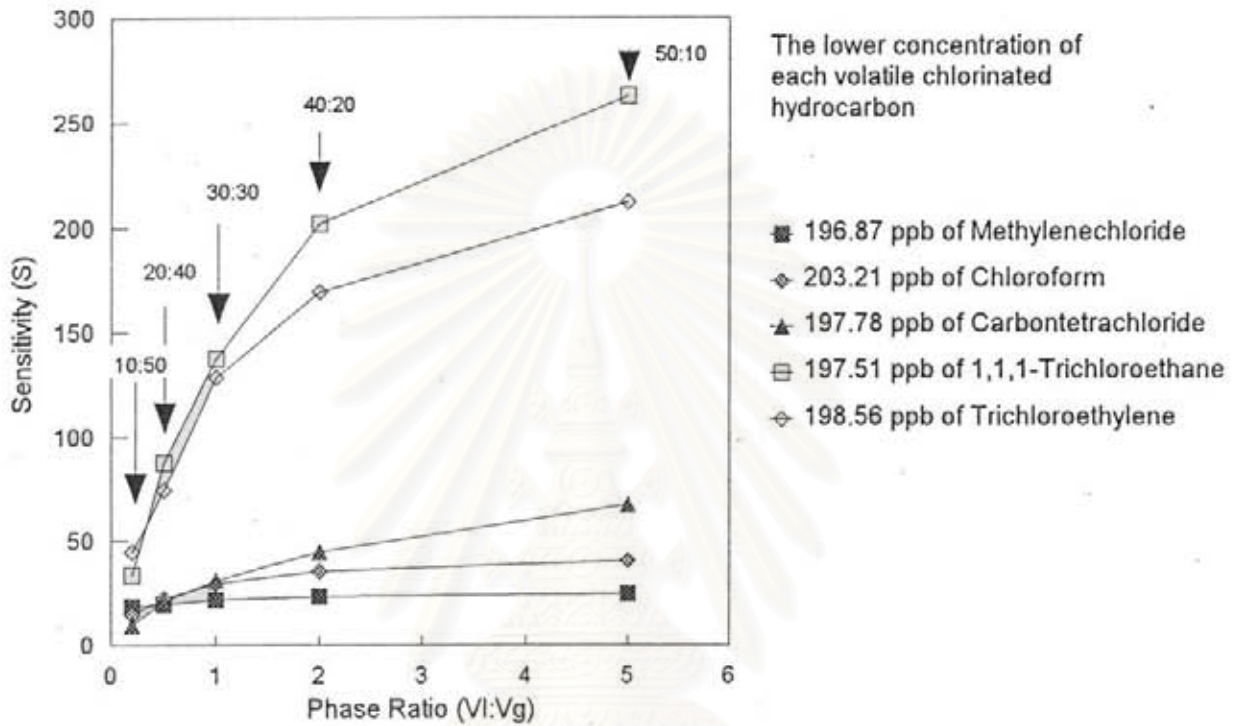


Figure 9. The effect of liquid to gas phase volume ratio on the sensitivity of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.



the high concentration of each interested compound in gas phase (C_g) as shown in Tables 6 and 7. Hence, the liquid to gas phase volume ratio of 30:30 is chosen as a suitable ratio for a headspace analysis.

4. The Study of Injection Volume.

The peak area which is corresponding to the sensitivity of the headspace analysis can be increased by means of the increase of the injection volume of the headspace gas. Therefore, the effects of the sample size or injection volume of the headspace gas on the peak area and the sensitivity of each volatile chlorinated hydrocarbon i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene are studied. The results of the study are presented in Tables 10 and 11, respectively. It is found that the peak area of each volatile chlorinated hydrocarbon increases linearly with the injection volume and the maximum sensitivity of each volatile chlorinated hydrocarbon is found at the highest injection volume (2.00 mL) for two concentration levels as seen in Figure 10 and 11. However, the precision of some volatile chlorinated hydrocarbons are lower or their percent relative standard deviations (%RSD) are higher than the level of the acceptable analysis (5.00%) as can be seen from Tables 10 and 11. Hence, the injection volume of 1.50 mL is selected as the optimum injection volume for this headspace analysis.

5. The Study of Salting Out Effect.

The effect of adding salt i.e., 10.50 g of sodium chloride, 13.00 g of anhydrous sodium sulfate and 0.10 g of calcium carbonate on the distribution coefficient, the sensitivity and the percent recovery of each volatile chlorinated

Table 10 The effect of injection volume on peak area and sensitivity (S) of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

Compounds	Injection Volume (mL)	Peak Area	S	%RSD
Methylene chloride (192.95 ppb)	0.50	2543	21.82	±6.71
	1.00	3647	27.54	±4.92
	1.50	4490	31.91	±4.38
	2.00	5125	35.20	±3.83
Chloroform (188.10 ppb)	0.50	4904	31.24	±2.58
	1.00	5340	33.56	±1.37
	1.50	5626	35.08	±2.42
	2.00	6024	37.20	±3.84
Carbon tetrachloride (199.71 ppb)	0.50	5952	30.20	±6.15
	1.00	7040	35.65	±3.66
	1.50	8437	42.64	±0.94
	2.00	9674	48.84	±8.93
1,1,1 - Trichloroethane (199.44 ppb)	0.50	28206	132.83	±7.27
	1.00	36406	173.95	±1.43
	1.50	43445	209.24	±3.08
	2.00	50278	243.50	±8.01
Trichloroethylene (194.60 ppb)	0.50	21230	108.26	±5.16
	1.00	28364	144.91	±2.94
	1.50	35519	181.68	±3.28
	2.00	39138	200.28	±6.83

Triplicate analyses

Table 11 The effect of injection volume on peak area and sensitivity(S) of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

Compounds	Injection Volume (mL)	Peak Area	S	%RSD
Methylene chloride (964.75 ppb)	0.50	13541	15.76	±9.55
	1.00	23369	25.95	±2.85
	1.50	33046	35.98	±1.61
	2.00	39488	42.66	±8.90
Chloroform (940.49 ppb)	0.50	20220	22.53	±4.60
	1.00	30744	33.72	±2.11
	1.50	43083	46.84	±3.32
	2.00	52840	57.22	±4.47
Carbon tetrachloride (998.57 ppb)	0.50	25621	25.74	±3.17
	1.00	36484	36.62	±3.53
	1.50	46018	44.16	±0.94
	2.00	59013	49.16	±3.02
1,1,1 - Trichloroethane (997.21 ppb)	0.50	128030	126.67	±2.76
	1.00	161608	173.37	±2.29
	1.50	195917	194.74	±4.46
	2.00	238822	237.77	±4.48
Trichloroethylene (973.01 ppb)	0.50	95470	97.95	±1.48
	1.00	122371	146.15	±2.16
	1.50	156884	171.34	±4.06
	2.00	194602	199.83	±5.28

Triplicate analyses

Figure 10. The effect of injection volume on peak area of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.

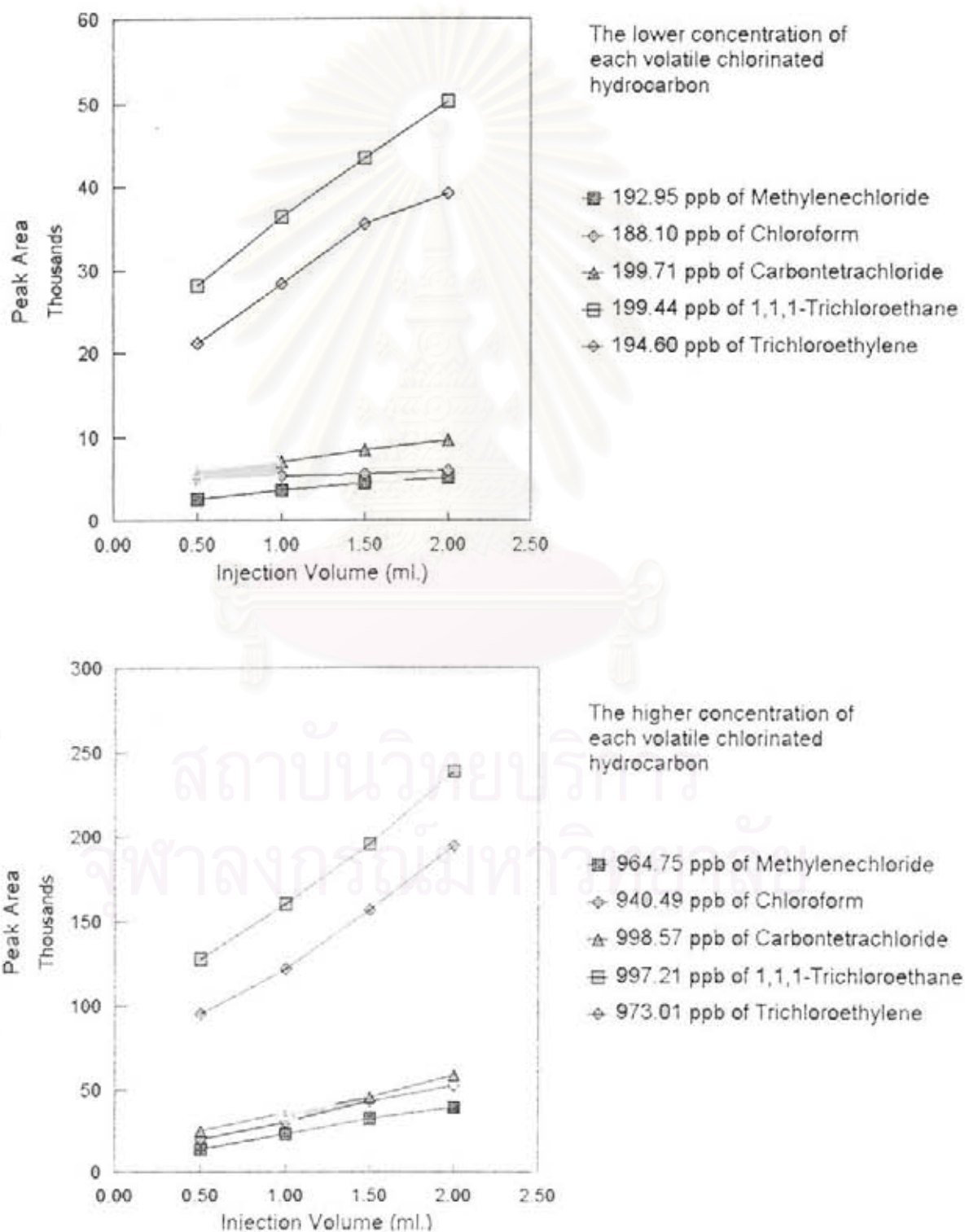
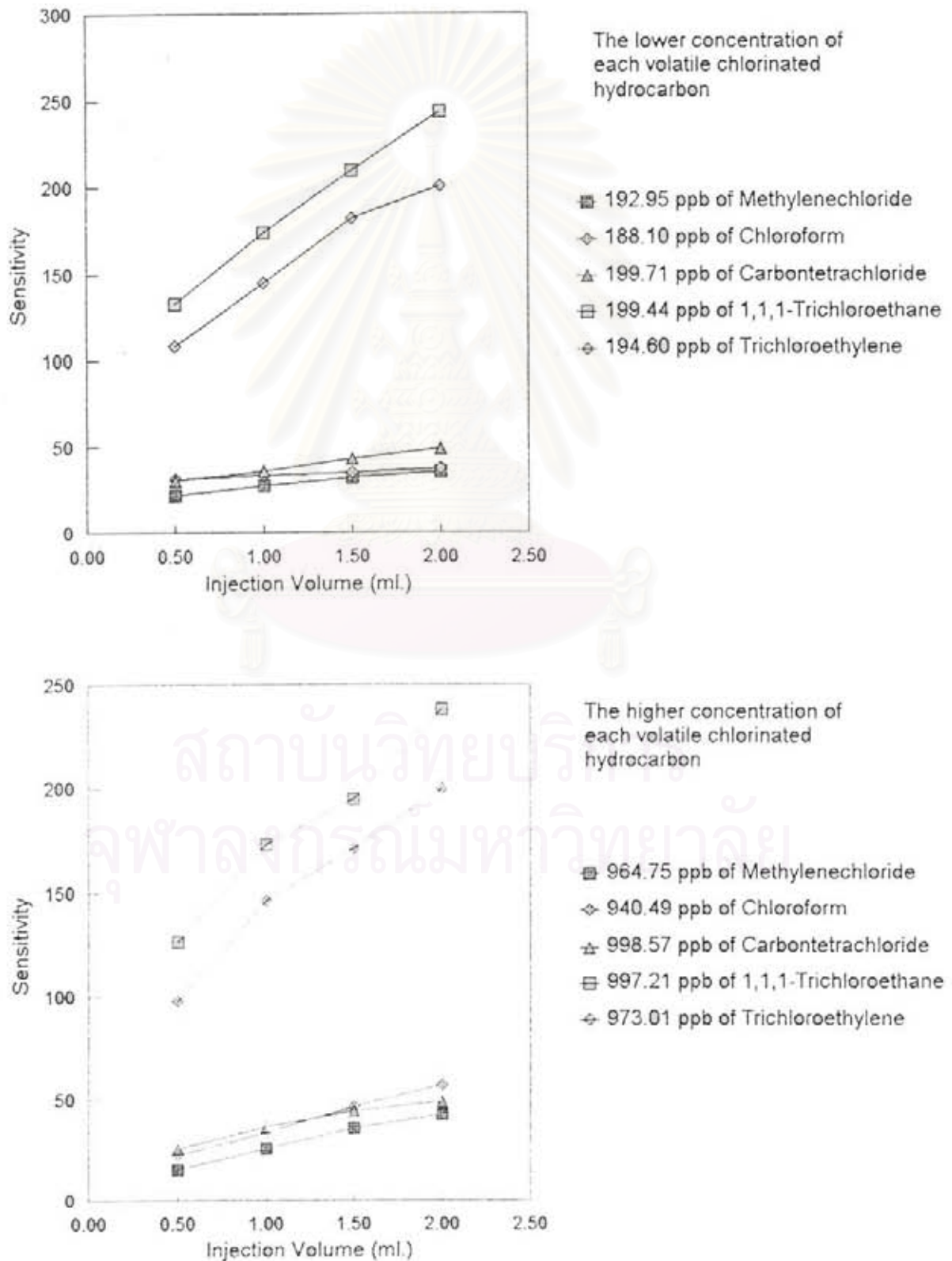


Figure 11. The effect of injection volume on sensitivity of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.



hydrocarbon i.e., methylene chloride, chloroform, carbon tetrachloride 1,1,1-trichloroethane and trichloroethylene in solution is studied at two concentration levels with two detectors i.e. , flame ionization detector (FID) and electron capture detector (ECD). The results of the study are shown in Tables 12-15. The graphs correlated to the percent recovery are shown in Figure 12 as FID detector and Figure 13 as ECD detector. It is found that the distribution coefficient of each volatile chlorinated hydrocarbon in solution will be decreased, the sensitivity and the percent recovery will be increased when there is an salt added into the solution at two concentration levels with both detectors. However, adding anhydrous sodium sulfate yields the percent recovery of all interested compounds at two concentration levels higher than sodium chloride and calcium carbonate do as seen in Tables 12 -15. The reason of this is that adding anhydrous sodium sulfate into the solution yields the higher ionic strength than other salts i.e., sodium chloride, calcium carbonate. The ionic strength of sodium sulfate solution is 0.275, sodium chloride solution is 0.180 and calcium carbonate solution is 0.004.

The result in Table 16 shows that the percent recovery of methylene chloride ranges from 55.14 to 62.43 with $\pm 2.20 - 4.81$ %RSD, chloroform ranges from 79.68 to 83.15 with $\pm 1.34 - 3.70$ %RSD, carbon tetrachloride ranges from 89.27 to 89.95 with $\pm 2.32 - 4.40$ %RSD, 1,1,1-trichloroethane ranges from 81.96 to 84.35 with $\pm 1.75 - 3.49$ %RSD and trichloroethylene ranges from 75.47 to 80.83 with $\pm 1.45 - 4.44$ %RSD. It can be summarized as follows :

(1) The percent recovery of each volatile chlorinated hydrocarbon in solution at the two different concentrations is insignificantly different.

Table 12 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

Compound	Salt	K	S	%E	%RSD
Methylene chloride (192.95 ppb)	No salt	4.40	12.04	15.31	±1.74
	NaCl	2.69	17.60	33.97	±2.65
	Na ₂ SO ₄	0.98	32.80	55.14	±2.71
	CaCO ₃	4.16	12.60	17.57	±6.06
Chloroform (188.10 ppb)	No salt	3.16	8.63	26.21	±1.81
	NaCl	0.75	20.50	58.66	±3.66
	Na ₂ SO ₄	0.20	29.71	80.83	±1.34
	CaCO ₃	2.69	9.72	29.19	±10.72
Carbon tetrachloride (199.71 ppb)	No salt	0.91	12.55	52.66	±6.35
	NaCl	0.26	18.95	79.17	±2.57
	Na ₂ SO ₄	0.12	21.41	89.37	±4.10
	CaCO ₃	0.85	12.96	54.32	±6.31
1,1,1 - Trichloroethane (199.44 ppb)	No salt	1.19	54.22	46.55	±7.80
	NaCl	0.36	87.18	74.44	±3.76
	Na ₂ SO ₄	0.22	97.53	83.20	±1.75
	CaCO ₃	1.11	56.12	48.16	±3.81
Trichloroethylene (194.60 ppb)	No salt	1.65	53.21	38.15	±2.80
	NaCl	0.61	87.58	62.31	±5.16
	Na ₂ SO ₄	0.32	106.30	75.47	±3.35
	CaCO ₃	1.61	54.07	38.75	±5.96

Triplicate analyses

Table 13 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in mixture solution with concentration aqueous standard solution in higher level of ppb using FID as a detector.

Compounds	Salt	K	S	%E	%RSD
Methylene chloride (964.75 ppb)	No salt	4.08	12.79	21.31	±1.14
	NaCl	2.15	20.60	33.08	±3.01
	Na ₂ SO ₄	0.77	36.69	57.33	±2.94
	CaCO ₃	4.06	12.84	21.38	±1.29
Chloroform (940.49 ppb)	No salt	3.35	8.24	23.55	±4.61
	NaCl	0.73	20.74	58.45	±3.95
	Na ₂ SO ₄	0.26	28.34	79.68	±3.64
	CaCO ₃	2.43	10.45	29.73	±3.02
Carbon tetrachloride (998.57 ppb)	No salt	1.23	10.72	47.64	±3.19
	NaCl	0.33	17.93	79.56	±1.33
	Na ₂ SO ₄	0.18	20.25	89.85	±2.32
	CaCO ₃	0.96	12.22	54.26	±3.28
1,1,1 - Trichloroethane (997.21 ppb)	No salt	1.44	48.71	41.04	±2.65
	NaCl	0.34	88.60	74.53	±3.17
	Na ₂ SO ₄	0.22	97.44	81.96	±2.01
	CaCO ₃	1.12	56.07	47.22	±3.71
Trichloroethylene (194.60 ppb)	No salt	1.90	48.60	34.52	±2.39
	NaCl	0.47	95.85	67.94	±3.33
	Na ₂ SO ₄	0.26	111.28	78.85	±3.27
	CaCO ₃	1.58	54.72	38.84	±2.94

Triplicate analyses

Table 14 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

Compounds	Salt	K	S	%E	%RSD
Methylene chloride (4.90 ppb)	No salt	13.98	1414	23.83	±9.55
	NaCl	3.54	4663	36.34	±5.01
	Na ₂ SO ₄	0.85	11435	62.43	±4.81
	CaCO ₃	8.65	2197	26.84	±1.30
Chloroform (4.90 ppb)	No salt	3.45	118059	32.06	±2.40
	NaCl	0.83	288104	60.39	±2.67
	Na ₂ SO ₄	0.24	424680	83.15	±2.40
	CaCO ₃	2.95	133216	34.59	±3.18
Carbon tetrachloride (5.00 ppb)	No salt	1.19	1098303	59.64	±3.17
	NaCl	0.35	1780120	80.77	±3.53
	Na ₂ SO ₄	0.16	2076419	89.95	±0.94
	CaCO ₃	1.04	1176119	62.05	±3.02
1,1,1 - Trichloroethane (4.98 ppb)	No salt	1.11	201554	51.20	±3.01
	NaCl	0.41	301440	79.92	±6.23
	Na ₂ SO ₄	0.21	351061	83.71	±3.49
	CaCO ₃	1.09	204287	51.80	±2.45
Trichloroethylene (4.87 ppb)	No salt	1.83	277081	40.80	±2.77
	NaCl	0.60	491751	65.84	±4.51
	Na ₂ SO ₄	0.27	620239	80.83	±4.06
	CaCO ₃	1.79	281147	41.28	±5.28

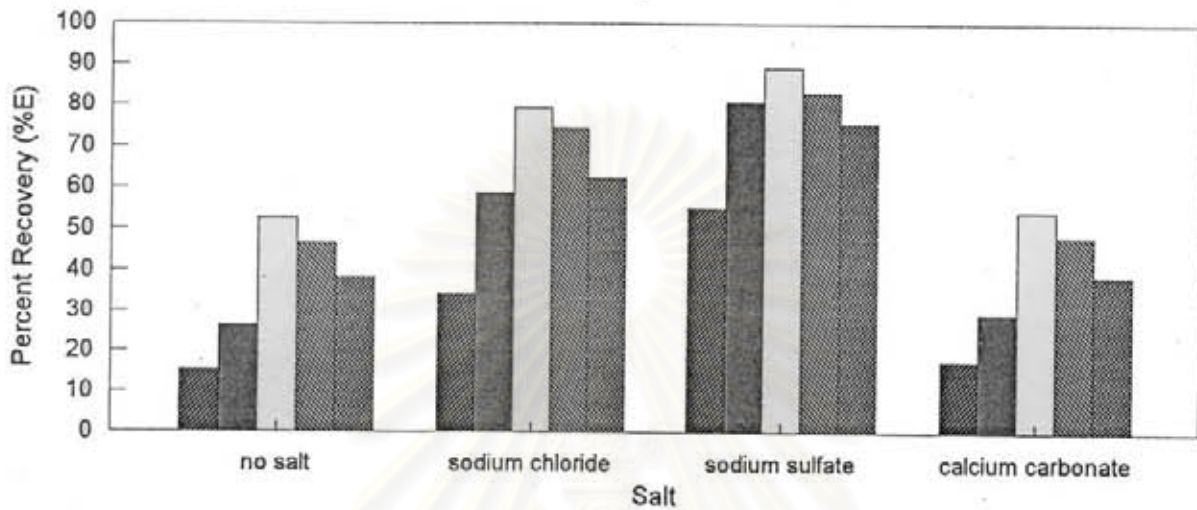
Triplicate analyses

Table 15 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

Compounds	Salt	K	S	%E	%RSD
Methylene chloride (49.01 ppb)	No salt	5.76	3137	16.68	±10.31
	NaCl	2.09	6849	33.82	±1.53
	Na ₂ SO ₄	0.78	11905	57.15	±2.20
	CaCO ₃	4.39	3934	20.36	±3.77
Chloroform (49.98 ppb)	No salt	2.40	154760	30.42	±5.66
	NaCl	0.66	316746	60.80	±2.63
	Na ₂ SO ₄	0.24	425321	81.16	±3.70
	CaCO ₃	2.95	133216	31.90	±3.59
Carbon tetrachloride (49.98 ppb)	No salt	1.24	1404160	59.87	±4.03
	NaCl	0.35	2066093	86.53	±1.32
	Na ₂ SO ₄	0.16	2134260	89.27	±2.78
	CaCO ₃	1.04	1548749	65.69	±3.30
1,1,1 - Trichloroethane (49.75 ppb)	No salt	1.24	190133	45.27	±3.02
	NaCl	0.45	294299	69.64	±1.56
	Na ₂ SO ₄	0.19	357186	89.27	±2.78
	CaCO ₃	1.24	190329	45.32	±2.99
Trichloroethylene (49.65 ppb)	No salt	1.62	299862	39.79	±5.60
	NaCl	0.46	538627	68.94	±2.48
	Na ₂ SO ₄	0.30	601611	76.89	±1.45
	CaCO ₃	1.59	303448	39.24	±2.13

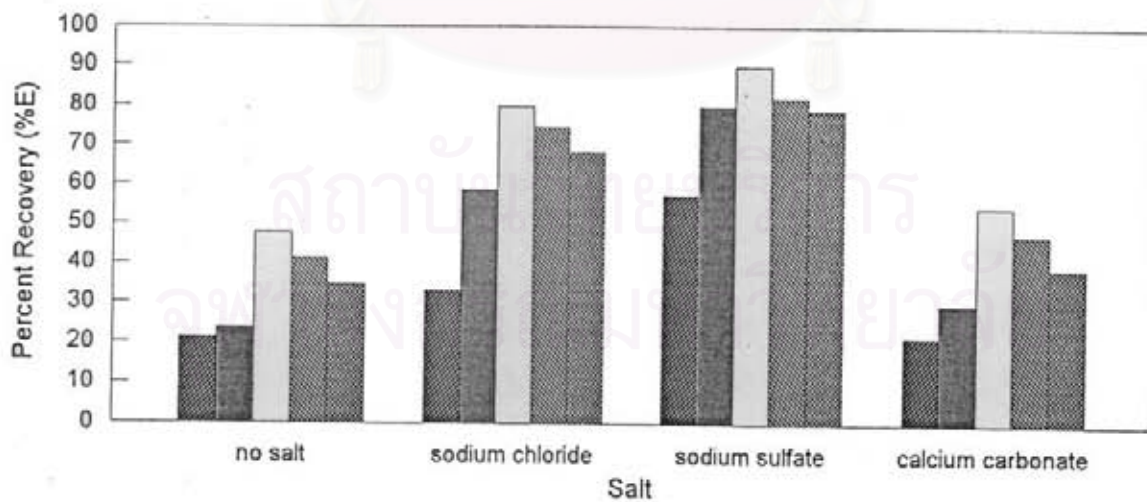
Triplicate analyses

Figure 12. The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon with concentration in lower and higher level using FID as GC detector.



The lower concentration of each volatile chlorinated hydrocarbon

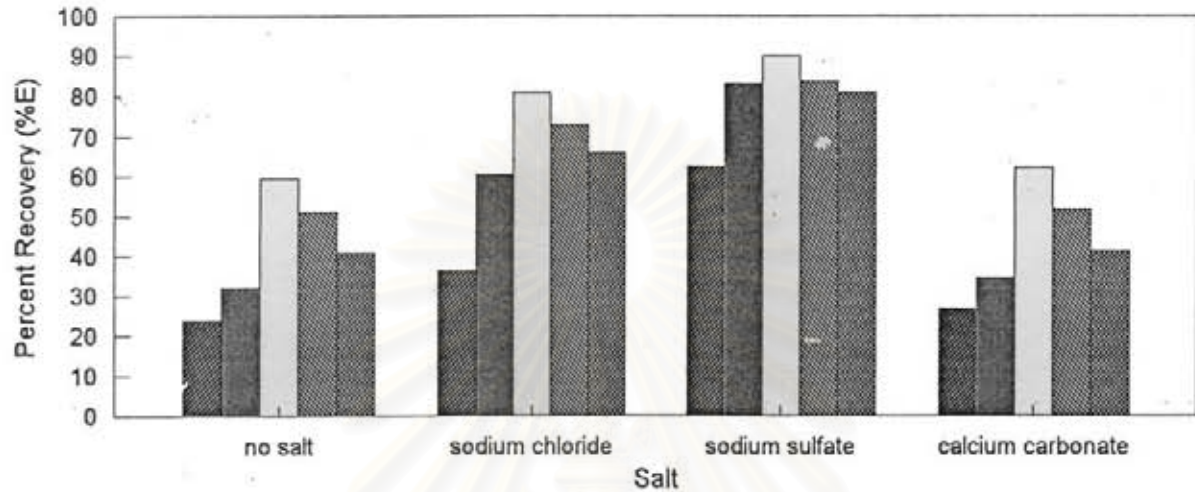
- 192.95 ppb of Methylenechloride
- 188.10 ppb of Chloroform
- 199.71 ppb of Carbontetrachloride
- 199.44 ppb of 1,1,1-Trichloroethane
- 194.60 ppb of Trichloroethylene



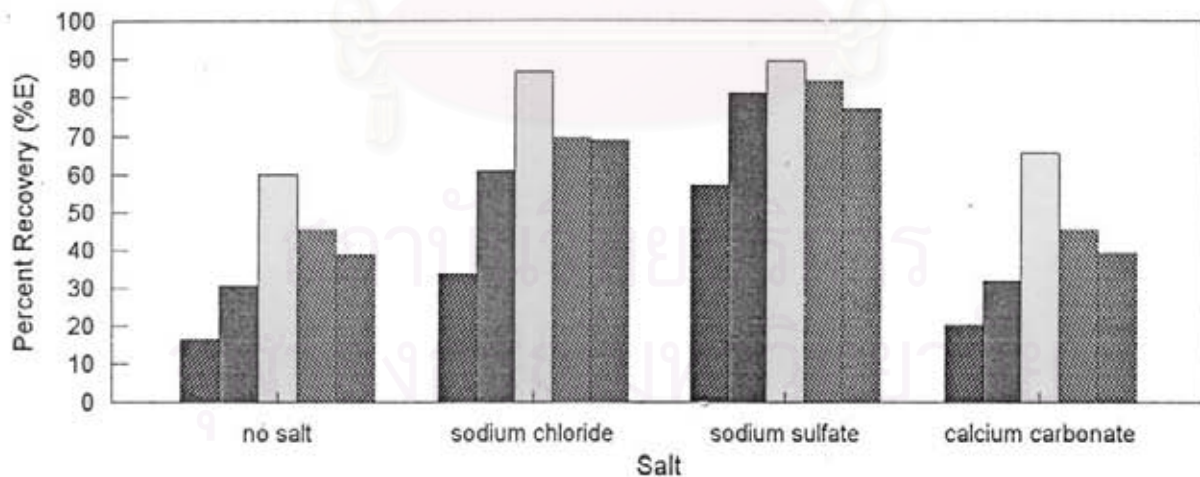
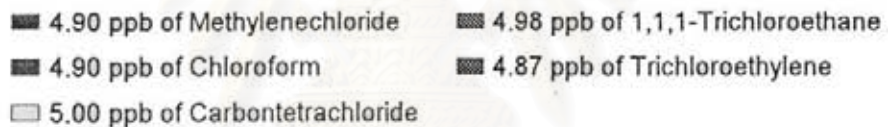
The higher concentration of each volatile chlorinated hydrocarbon

- 964.75 ppb of Methylenechloride
- 940.49 ppb of Chloroform
- 998.57 ppb of Carbontetrachloride
- 997.21 ppb of 1,1,1-Trichloroethane
- 973.01 ppb of Trichloroethylene

Figure 13. The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon with concentration in lower and higher level using ECD as GC detector.



The lower concentration of each volatile chlorinated hydrocarbon



The higher concentration of each volatile chlorinated hydrocarbon

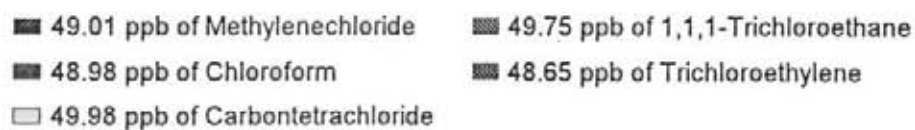


Table 16 The percent recovery of each volatile chlorinated hydrocarbon at two concentration levels in solution with anhydrous sodium sulfate.

Compounds	The percent recovery (%E) (%RSD)			
	FID		ECD	
	Concentration level Lower	Concentration level Higher	Concentration level Lower	Concentration level Higher
Methylene chloride	55.14 (±2.71)	57.33 (±2.94)	62.43 (±4.81)	57.15 (±2.20)
Chloroform	80.83 (±1.34)	79.68 (±3.64)	83.15 (±2.40)	81.16 (±3.70)
Carbon tetrachloride	89.37 (±4.10)	89.85 (±2.32)	89.95 (±4.40)	89.27 (±2.78)
1,1,1 - Trichloroethane	83.20 (±1.75)	81.96 (±2.01)	83.71 (±3.49)	84.35 (±2.02)
Trichloroethylene	75.47 (±3.35)	78.85 (±3.27)	80.83 (±4.44)	76.89 (±1.45)

Triplicate analyses

Table 17 The sensitivity of each volatile chlorinated hydrocarbon at two concentration levels in solution with anhydrous sodium sulfate.

Compounds	Sensitivity (S) (%RSD)			
	FID		ECD	
	Concentration level Lower	Concentration level Higher	Concentration level Lower	Concentration level Higher
Methylene chloride	33 (±2.71)	37 (±2.94)	11435 (±4.81)	11905 (±2.20)
Chloroform	30 (±1.34)	28 (±3.64)	424680 (±2.40)	425321 (±3.70)
Carbon tetrachloride	21 (±4.10)	20 (±2.32)	2076419 (±4.40)	2134260 (±2.78)
1,1,1 - Trichloroethane	98 (±1.75)	97 (±2.01)	351061 (±3.49)	357186 (±2.02)
Trichloroethylene	106 (±3.35)	111 (±3.27)	620239 (±4.44)	601611 (±1.45)

Triplicate analyses

(2) The percent recovery of each volatile chlorinated hydrocarbon in solution with FID as detector study is close to the percent recovery of each compound in solution with ECD as detector.

This indicates that the percent recovery of each volatile organic compound is independent of the concentration of the compound, and the detector of gas chromatograph. Moreover, it is not affected by the presence of the other organic compounds in water samples.

The sensitivity of each volatile chlorinated hydrocarbon at two concentration levels in mixture component solution with anhydrous sodium sulfate is shown in Table 17. It shows that the sensitivity of each compound at two concentration levels is slightly different. Hence, the concentration of each interested compound does not have any effect of the sensitivity of each compounds. However, the sensitivity of each interested compound studied by using ECD as a detector of gas chromatograph is higher than the one using FID as a detector. Therefore, ECD is chosen as the detector of gas chromatograph for this headspace technique.

6. Minimum Detectable Level (MDL).

The minimum detectable level is defined as the smallest amount of solute required to produce a signal that is twice the noise level . The optimum headspace analysis condition used in the investigation of the minimum detectable level of each volatile chlorinated hydrocarbon in aqueous solution under GC condition as described in Table 1 is shown in Table 18. This condition would be used in the investigation of the accuracy and

Table 18 The optimum headspace analysis condition used in the investigation of the minimum detectable level, the accuracy and analyses of the real water samples.

Equilibration time	60 minutes
Temperature	60 °C
Liquid to gas phase volume ratio	30 : 30 in 60 mL serum vial
Injection volume	1.50 mL
Salt used	13.00 g of anhydrous Na ₂ SO ₄

Triplicate analyses



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Table 19 The minimum detectable level of each volatile chlorinated hydrocarbon in aqueous solution.

Compounds	Minimum detectable level (MDL) (ppb)
Methylene chloride	0.50
Chloroform	0.05
Carbon tetrachloride	0.03
1,1,1 - Trichloroethane	0.05
Trichloroethylene	0.04

Triplicate analyses

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analyses of the synthetic samples. The results obtained from the minimum detectable level study of each interested compound are shown in Table 19.

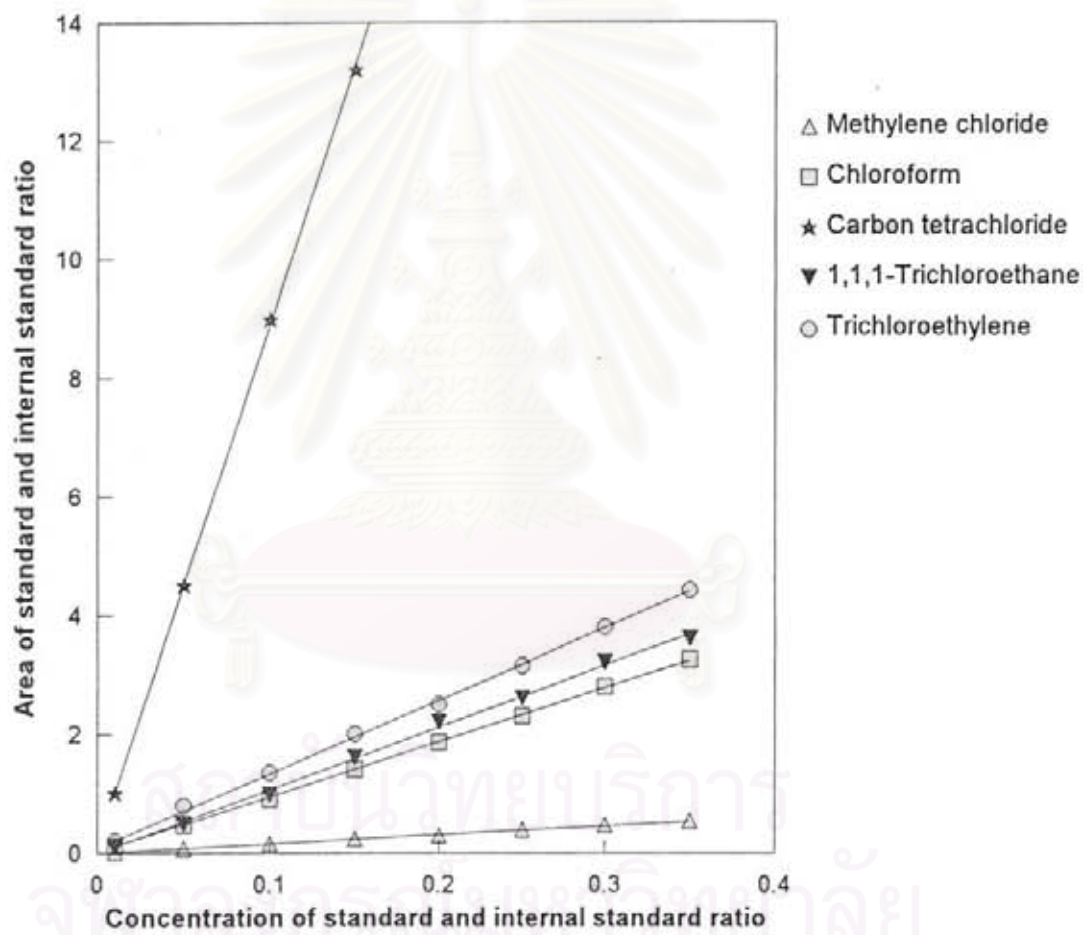
7. The Accuracy of Headspace Analysis Technique.

The accuracy of headspace analysis technique is investigated by comparing the results of the concentration of each volatile chlorinated hydrocarbon obtained from the analysis with the true concentration of each compound in synthetic unknown mixture solution. The unknown is prepared in methanol and it is diluted with distilled water prior to the analysis. The concentration of each compound in the synthetic unknown solution is determined by means of the internal standardization method as shown the internal standard curve in Figure 14 and the standard chromatogram of the studied volatile chlorinated hydrocarbon is shown in Figure 15.

The results obtained from the study are presented in Table 20. The percent error and the percent relative standard deviation in the determination of the concentration of each volatile organic compound in the synthetic unknown mixture component solution is in the range of 0.31 - 6.44 % and 0.59 - 3.34 %, respectively.

All of the results obtained from the above studies indicate that the headspace analysis technique seems to be the best alternative method for the determination of volatile chlorinated hydrocarbons in water samples. The reasons for this maybe expressed as follow :

Figure 14 The internal standard calibration curve of volatile chlorinated hydrocarbons using headspace technique analysis with ECD as GC detector.



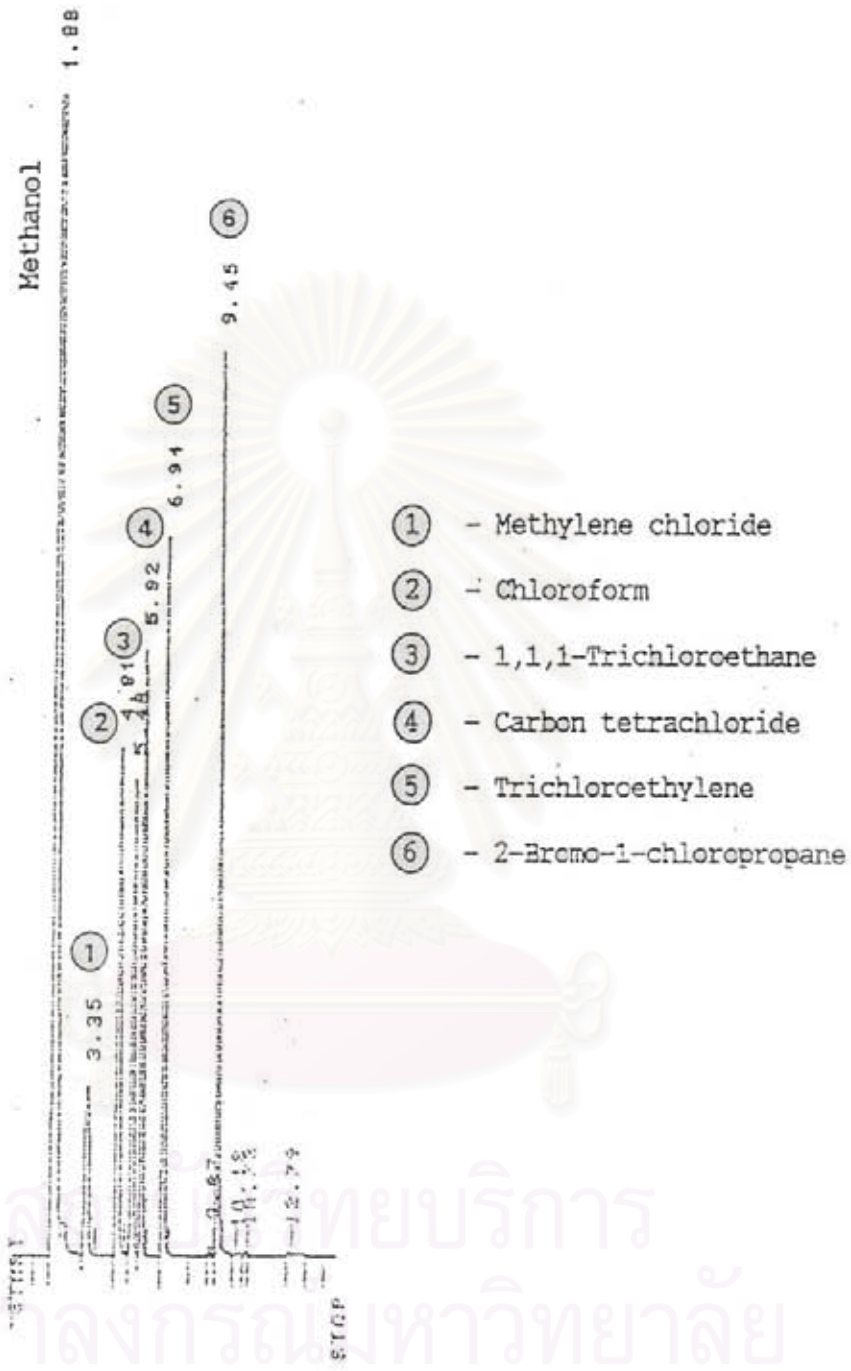


Figure 15. The gas chromatogram of standards in aqueous solution.

Condition - Headspace : described in Table 18
 - GC : described in Table 1

Concentration of the component :

- methylene chloride	83.34 ppb
- chloroform	1.88 ppb
- 1,1,1-trichloroethane	1.87 ppb
- carbon tetrachloride	0.28 ppb
- trichloroethylene	1.31 ppb
- 2-bromo-1-chloropropane	131.16 ppb
(internal standard)	

Table 20 The result of the analysis of the synthetic unknown mixture solution.

Compounds	Concentration (ppb)		%Error	%RSD
	True	Experiment		
Methylene chloride	100.02	106.46	6.44	±3.34
Chloroform	2.82	2.89	2.48	±3.98
Carbon tetrachloride	3.27	3.26	0.31	±0.59
1,1,1 - Trichloroethane	1.87	1.82	2.67	±2.17
Trichloroethylene	3.74	3.65	2.41	±2.03

Triplicate analyses

Table 21 The comparison of the price of materials used in the headspace technique developed in this study with the commercially available headspace sampler.

Item	Quantity	Price (US.\$)
A : Serum vials	36	3
B : Serum vials	36	33
A : Black rubber/aluminum foil septa	1000	4
B : Teflon/rubber septa	1000	380
A : Aluminum caps	1000	8
B : Aluminum caps	1000	90
A : Temperature water bath	1	600
B : Headspace sampler option	1	13,000

Note.....

A = materials used in this headspace technique.

B = materials used in the commercial headspace sampler.

(a) This technique gives the good precision and good accuracy.

(b) It required no preconcentration step for the determination of trace volatile chlorinated hydrocarbons in water.

(c) No interference peaks of uninterested non - volatile organic compounds appear on the chromatogram, so the chromatographic analysis time is short.

(d) The minimum detectable level is found to be lower than the ppb level using electron capture detector.

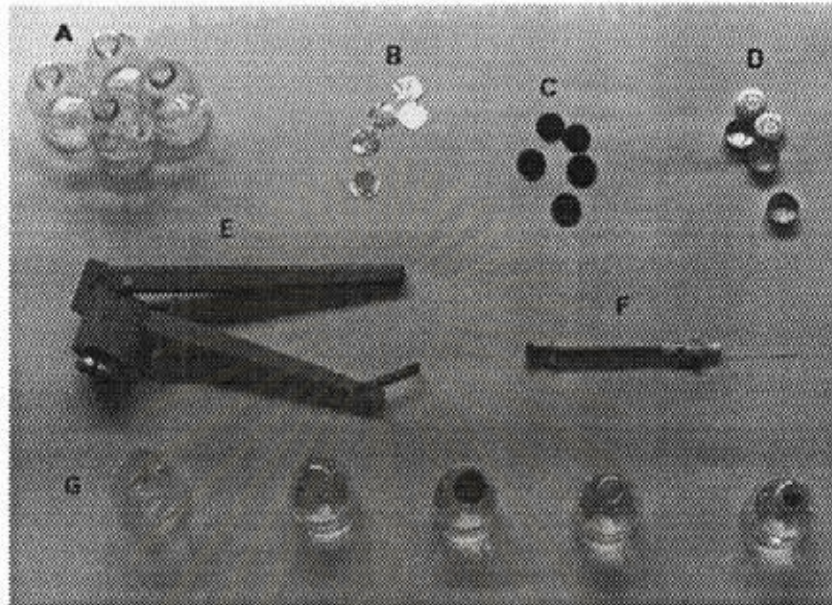
(e) It is an economical method. The reasons of this are that the septa, aluminum foils, aluminum caps and serum vials used in this technique water bath used in this study is cheaper than the one of a commercial headspace sampler used in the conventional headspace analysis technique as shown in Table 21. The materials used in this headspace technique are shown in Figure 16.

(f) It can analyze 24 samples/day (8h).

8. Analysis of Water Sample by Headspace Method.

Drinking water samples produced from many companies and tap water samples collected from the Central Bangkok Metropolitan area are analyzed the volatile chlorinated hydrocarbons by using the headspace analysis method developed in this study under the optimal condition. Only methylene chloride and chloroform are found in water samples and the results of analysis are

Figure 16 The materials use in this headspace technique



- A: 60 mL serum vial; height = 70 mm., base diameter = 40 mm.
- B: Aluminum foil; diameter = 18 mm., thickness = 0.02 mm.
- C: Black rubber septum; diameter = 18 mm., thickness = 3.3 mm.
- D: Aluminum cap; diameter = 18.0 mm.
- E: Manual Hand Operated Crimper.
- F: Pressure-lok series A2 gas tight syringe 2.00 mL.
- G: The procedure of sealed serum vial for headspace study.

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shown in Tables 22 and 23 for drinking water and tap water samples, respectively. Chloroform was found in all collected water samples in the range of 1.05 to 31.99 ppb for drinking waters and 0.78 to 48.32 ppb for tap waters, and methylene chloride was found in the 15 drinking waters among the 21 samples, ranging 15.50 to 214.88 ppb and the 4 tap waters among the 13 samples, ranging 33.43 to 49.50 ppb. To confirm this result, all samples are spiked with the standard mixture solution of the interested compounds in methanol and their peaks eluted at the same time as the peaks of the standard. Moreover, gas chromatograph equipped with mass spectrometer (GC-MS) is used to give the positive identification for the suspected compounds in the water samples. Figure 17 (A) and (B) show the chromatogram of the tap water from Bangkok-Nontaburi Road, Bang Sue, Bangkok and the spiked tap water samples with the interested standard. When the samples were run by GC/MS and the library search of the mass spectrum of each peak in Total Ion Chromatogram (TIC) was performed. The results are methylene chloride and chloroform as suspected with probability-based matching 94 and 97 %, respectively.

Conclusion

In this paper, a headspace method was developed for determination of some volatile chlorinated hydrocarbons in water samples. The method is based on the equilibrium system between the water sample phase and the gas phase. Various factors such as temperature, equilibration time, liquid to gas phase volume ratio, injection volume and salting out effect are studied and selected to used as the optimum condition. From the study, this method shows good precision and accuracy, and can detect the chlorinated hydrocarbons lower than to ppb level using electron capture detector. It

Table 22 The concentration of the volatile chlorinated hydrocarbons in drinking water samples from several company.

company	brand	concentration of (ppb)	
		methylene chloride	chloroform
1. V.S. Group Ltd.	V.S.Cooler	ND*	38.98
2. VP.Water Drink Ltd.	V.P. Cooler	31.87	10.98
3. Wichai Marketing Ltd.	Pury	28.59	31.62
4. Thaitiptong Ltd.	Poly	ND	4.40
5. Prasopchok Ltd.	Prasopchok	ND	29.99
6. Pitaknamdeam Ltd,Part	Fivestar	15.50	25.95
7. Petchtae Ltd, Part	Petchtae	ND	2.47
8. June Water Drink Ltd.	June	28.76	3.32
9. Porntep Ltd.	Porntep	34.74	1.48
10. Charoenporn Ltd.	Taruea	36.79	3.10
11. Pouhirun Ltd.	P.S.C.	34.33	12.65
12. Nophadol Marketing Ltd.	NangPimp	214.88	26.28
13. Pantthip Ltd.	Pantthip	35.56	30.92
14. Idea Intertrading Ltd.	Idea	36.79	31.62
15. Pongthip Ltd.	Pongthip	34.74	29.90
16. North Star Ltd.	Polarist	45.82	1.66
17. Visit - Vannee Ltd.	Fresh	ND	8.20
18. M-Water Ltd.	Springkale	ND	7.08
19. Porist Ltd.	Porist	34.74	31.99
20. One Way Ltd.	One Way	35.97	30.83
21. Boonrod Bewery Ltd.	Singha	36.59	1.05

*ND = Non - detectable level

Table 23 The concentration of the volatile chlorinated hydrocarbons in tap water samples in several places.

sample	concentration of the component (ppb)	
	methylene chloride	chloroform
1. Bangkok-nontaburi Rd.,BangSue	33.43	48.32
2. Bangpongpan, Yanawa	49.50	43.82
3. Charansanitwong, Bangkok Noi	44.05	28.37
4. Phaya Thai Rd.,Phatumwan	ND	0.78
5. Israphrap Rd.,Bangkok Yai	ND	25.10
6. Bangwa, Paseechoen	ND	29.83
7. Ratchadumri Rd.,Phatumwan	ND	1.75
8. Praweth, Prakhanong	ND	4.23
9. Bangchak, Prakhanong	ND	33.13
10. Municipal Water Authorities, Samsen	ND	15.22
11. Bangphlee, Samutprakan	33.51	33.22
12. Muang, Nonthaburi	ND	20.51
13. Raw water from Klong Prapa, Samsen	ND	2.68



Figure 17. The gas chromatogram of (A) the tap water sample
 (B) the tap water sample + standard mixture in solution
 Condition - Headspace : described in Table 18
 - GC : described in Table 1

- | | |
|---------------------------|-----------------------------|
| 1 = methylene chloride | 2 = chloroform |
| 3 = 1,1,1-trichloroethane | 4 = carbon tetrachloride |
| 5 = trichloroethylene | 6 = 2-bromo-1-chloropropane |

requires no preconcentration step for the analysis and no interference peaks of uninterested non-volatile organic compounds appear on the chromatogram, so the chromatographic analysis time is short. This developed headspace method can be analyzed 24 samples/day (8 hr.) and can be used for the routine analysis.

A preliminary survey for the volatile chlorinated hydrocarbons in water samples was conducted by the use of headspace technique method. The survey demonstrated that only chloroform and methylene chloride are found in water samples. The range of chloroform detected is 1.05 - 38.98 ppb for drinking waters and 0.78 - 48.32 ppb for tap waters and the range of methylene chloride detected is 15.50 - 214.88 ppb for drinking waters and 33.43 - 49.50 ppb for tap waters.

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