CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 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 obtained from the procedure in the experimental Section 3.5.1 are given in Tables 4.1-4.10. The graphs plotted the peak area (A) of each volatile chlorinated hydrocarbon against time are shown in the Figures 4.1 - 4.10. Itis found that the equilibration time obtained from the study 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.

Table 4.1 The result of the effect of equilibration time on the peak area of 192.95 ppb methylene chloride.

Time (min.)	Peak Area	% RSD
0	1369	±28.28
10	2167	±11.46
20	2286	± 4.70
30	2511	± 6.61
40	2689	±11.43
50	2664	± 5.12
60	2730	± 3.76
80	2748	± 4.18
100	2683	± 6.08
120	2745	± 4.59

Triplicate analyses

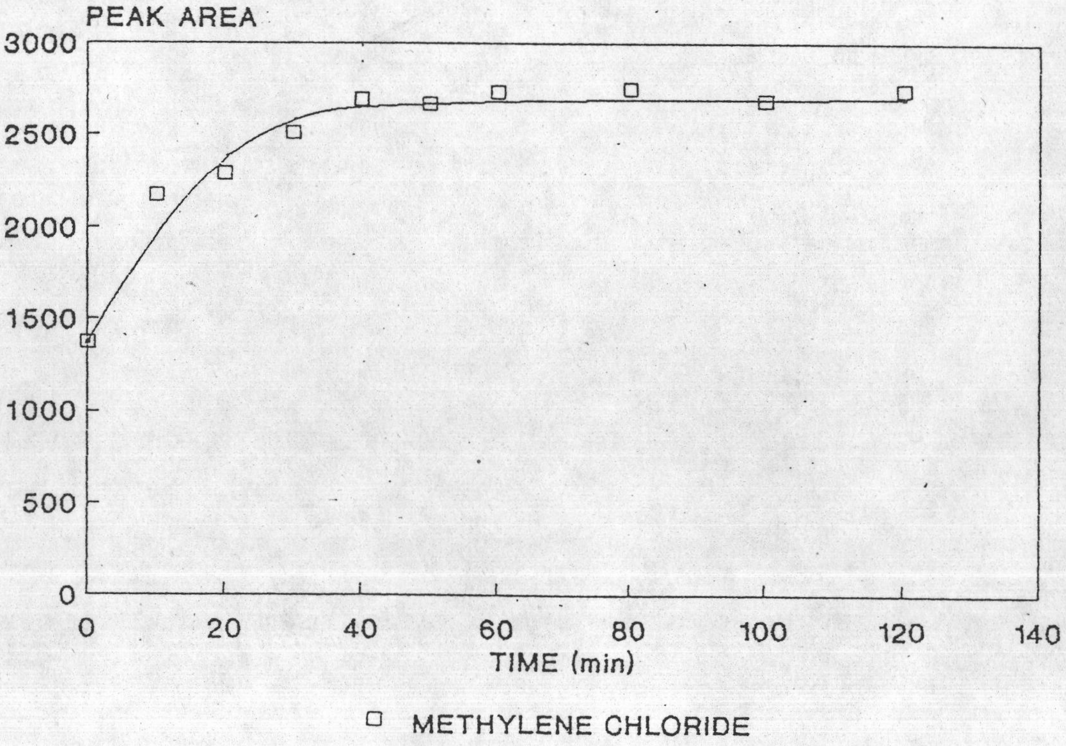


Figure 4.1 The effect of equilibration time on the peak area of 192.95 ppb methylene chloride.

Table 4.2 The result of the effect of equilibration time on the peak area of 964.75 ppb methylene chloride.

Time (min.)	Peak Area	% RSD
0	10632	±15.41
10	14591	±12.03
20	16733	± 2.43
30	18143	± 2.76
40	19171	± 7.04
50	19403	± 2.23
60	20501	± 4.09
80	20304	± 8.21
100	20408	± 5.03
120	19550	± 4.31

Triplicate analyses

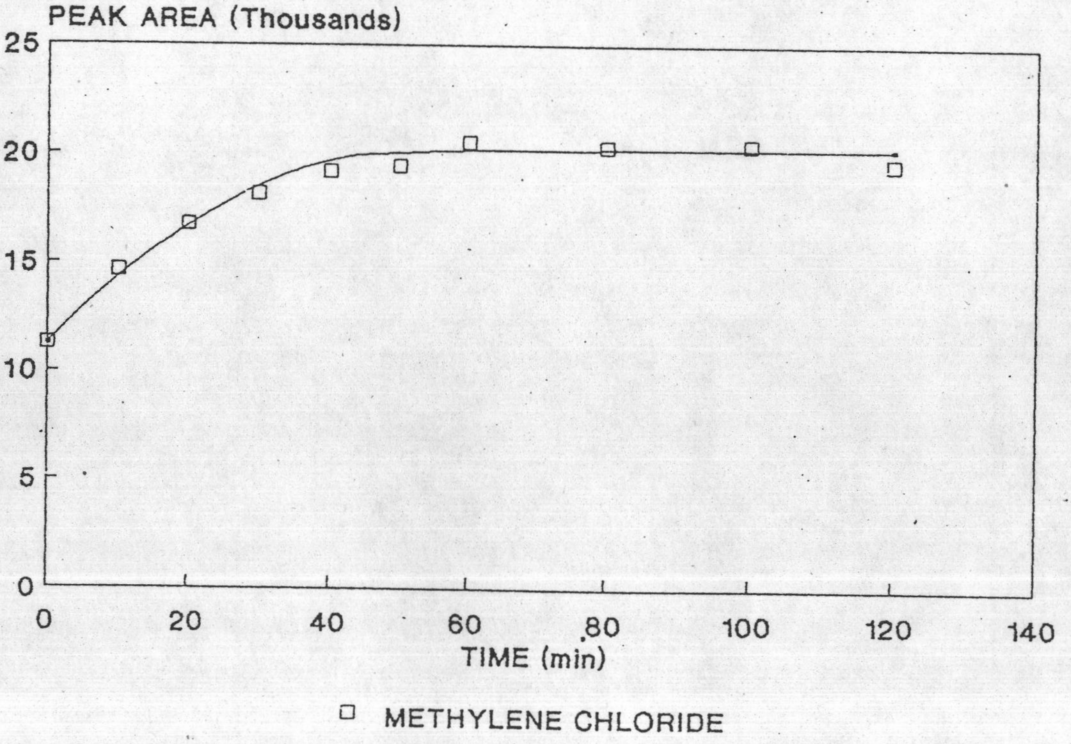


Figure 4.2 The effect of equilibration time on the peak area of 964.75 ppb methylene chloride.

Table 4.3 The result of the effect of equilibration time on the peak area of 188.10 ppb chloroform.

Time (min.)	Peak Area	% RSD
0	1851	± 7.19
10	2644	± 9.51
20	2960	±10.22
30	3050	± 3.07
40	3159	± 7.48
50	3241	± 4.38
60	3152	± 4.71
80	3203	± 3.46
100	3307	± 1.20
120	3344	±10.37

Triplicate analyses

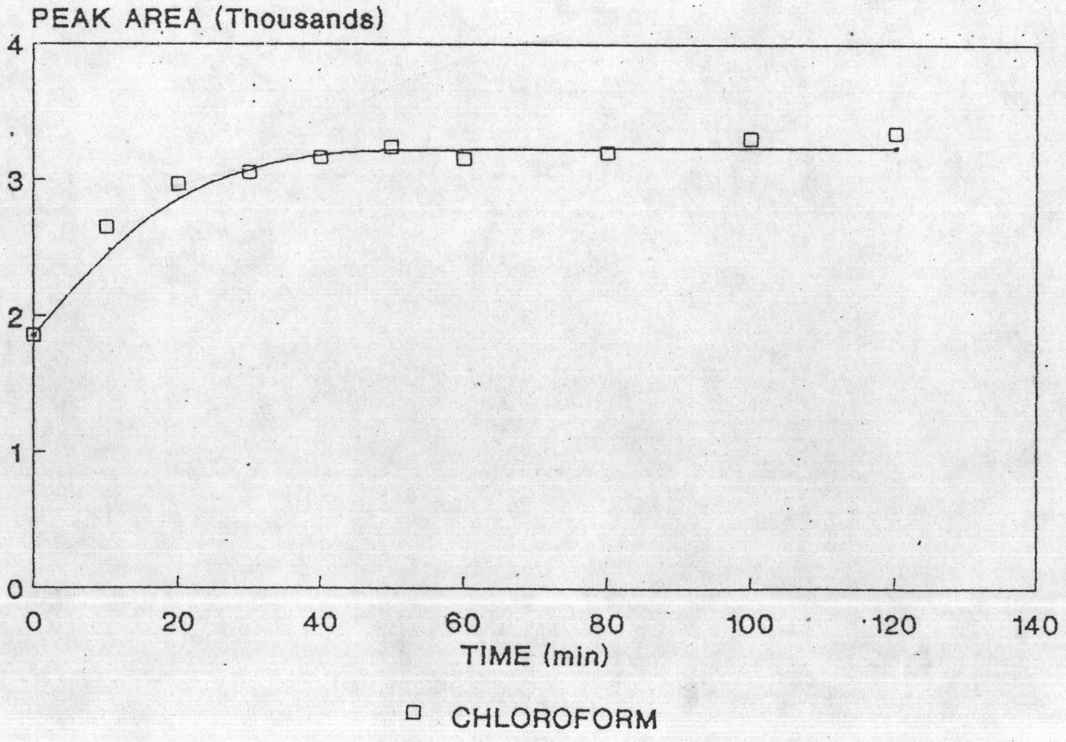


Figure 4.3 The effect of equilibration time on the peak area of 188.10 ppb chloroform.

Table 4.4 The result of the effect of equilibration time on the peak area of 940.49 ppb chloroform.

Time (min.)	Peak Area	% RSD
0	6341	± 8.13
10	9982	± 6.21
20	12855	±10.50
30	14315	±10.63
40	15322	± 5.76
50	16324	± 5.51
60	15952	± 4.28
80	16260	± 3.83
100	15266	± 4.03
120	16337	±12.38

Triplicate analyses

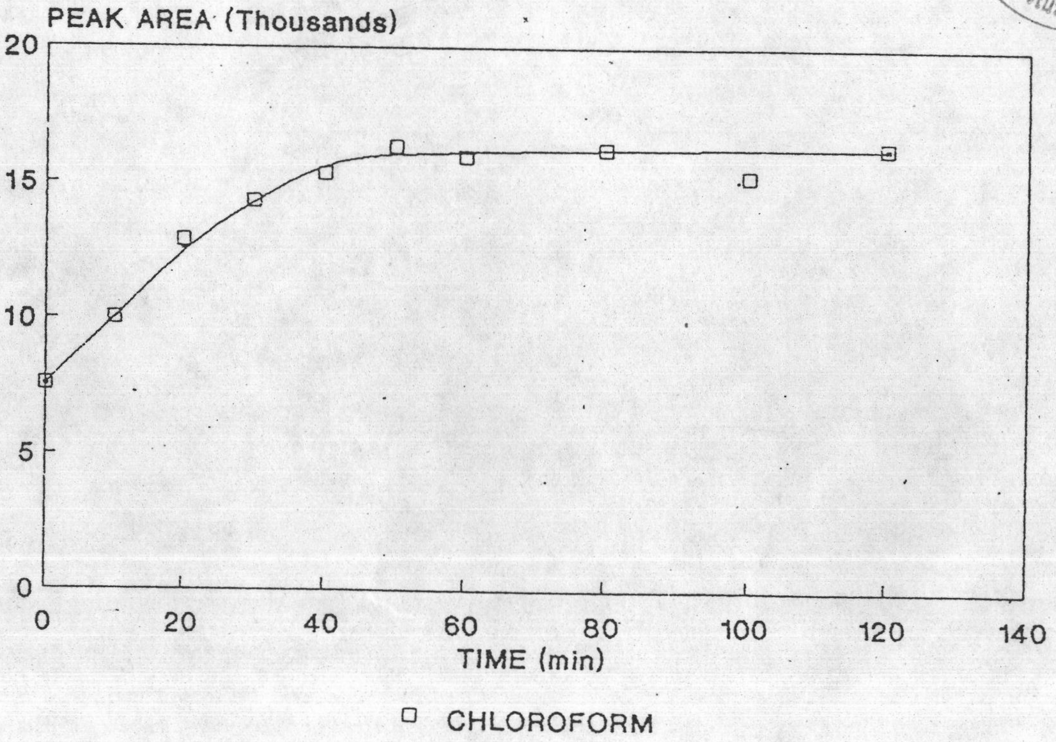


Figure 4.4 The effect of equilibration time on the peak area of 940.49 ppb chloroform.

Table 4.5 The result of the effect of equilibration time on the peak area of 199.71 ppb carbon tetrachloride.

Time (min.)	Peak Area	% RSD
0	2529	±14.10
10	2877	± 3.31
20	3477	± 7.44
30	3843	±11.04
40	4455	± 3.88
50	4562	± 7.17
60	4692	± 6.23
80	4667	± 1.64
100	4322	± 4.56
120	4734	± 5.39

Triplicate analyses

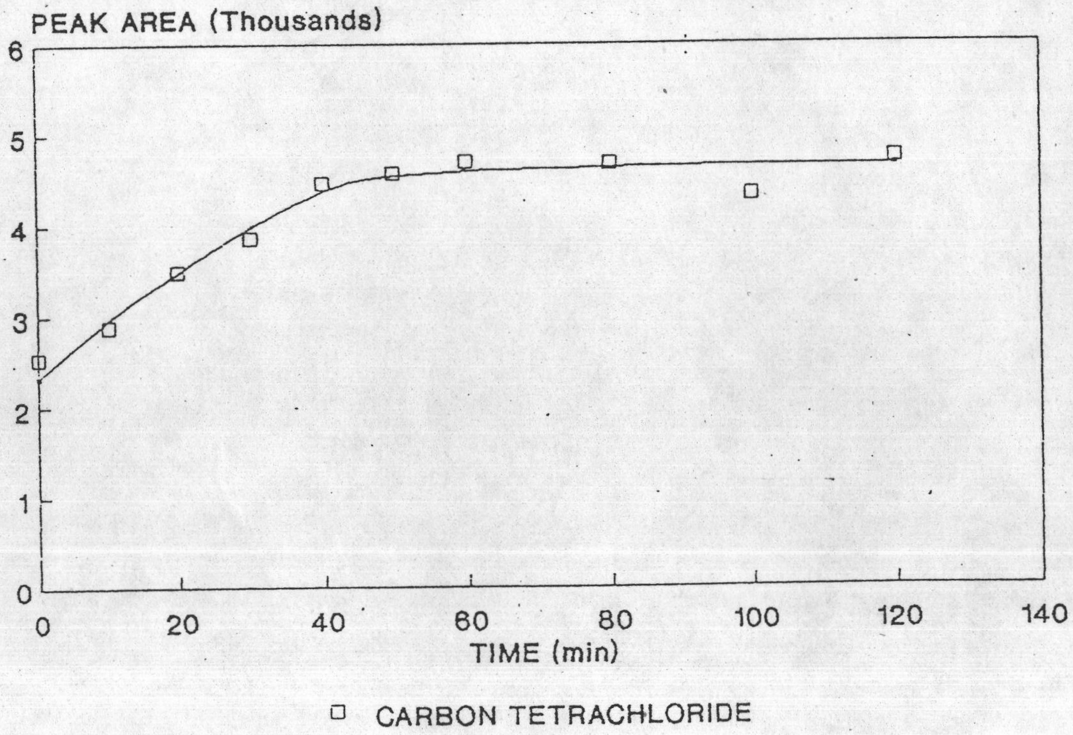


Figure 4.5 The effect of equilibration time on the peak area of 199.71 ppb carbon tetrachloride.

Table 4.6 The result of the effect of equilibration time on the peak area of 998.57 ppb carbon tetrachloride.

Time (min.)	Peak Area	% RSD
0	8613	±11.31
10	13711	±15.62
20	17512	± 5.34
30	18330	±11.70
40	19609	± 3.51
50	20402	± 7.86
60	19509	± 1.64
80	20216	± 4.53
100	20937	± 4.19
120	21465	± 9.66

Triplicate analyses

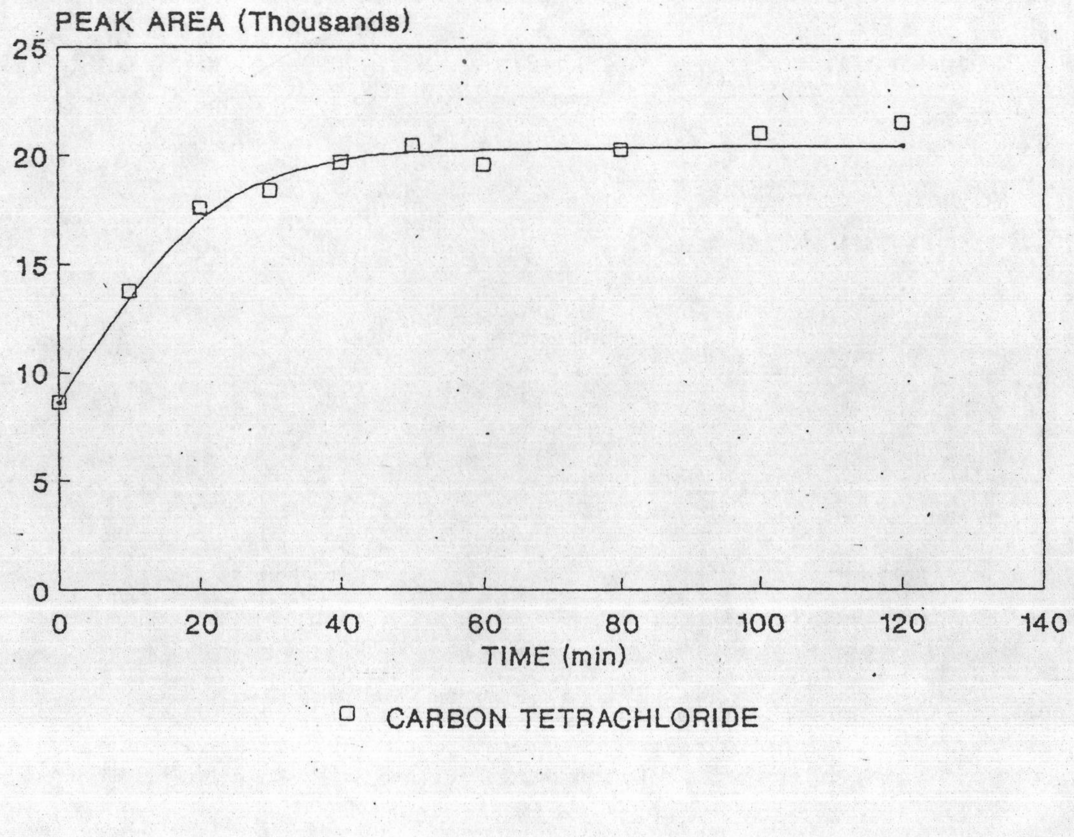


Figure 4.6 The effect of equilibration time on the peak area of 998.57 ppb carbon tetrachloride.

Table 4.7 The result of the effect of equilibration time on the peak area of 199.44 ppb 1,1,1-trichloroethane.

Time (min.)	Peak Area	% RSD
0	11245	± 8.16
10	11505	± 2.30
20	12924	± 5.54
30	13290	± 5.06
40	13902	± 2.44
50	14122	± 4.65
60	14278	± 3.51
80	14370	± 3.87
100	14346	± 2.64
120	14145	± 1.49

Triplicate analyses

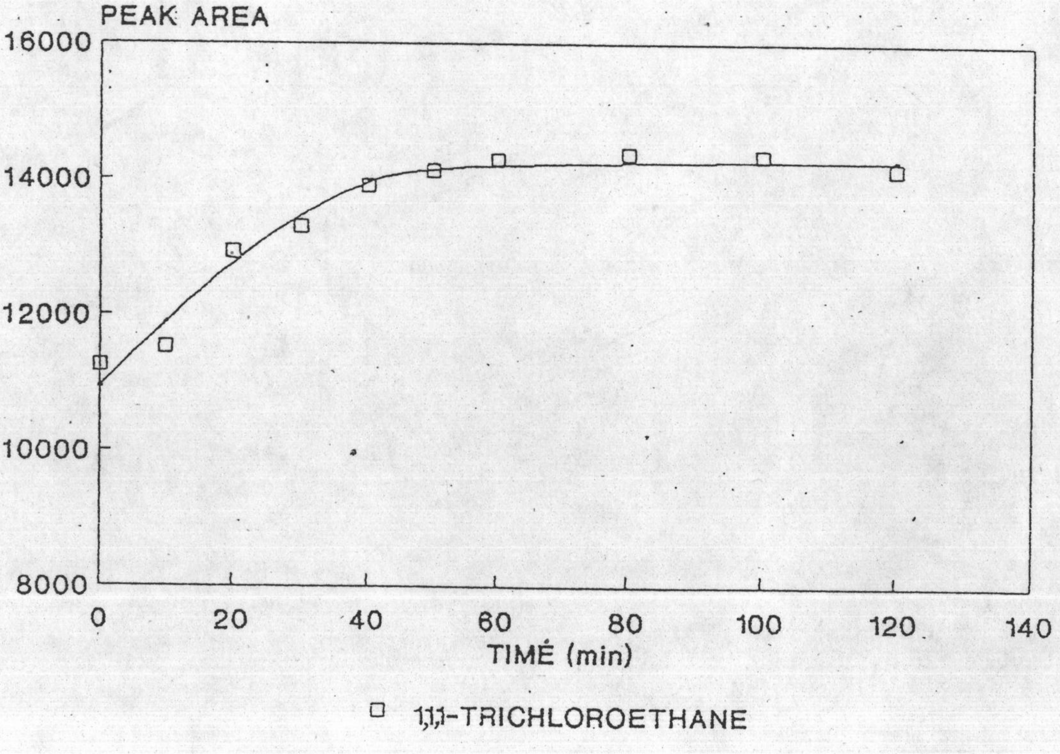


Figure 4.7 The effect of equilibration time on the peak area of 199.44 ppb 1,1,1-trichloroethane.

Table 4.8 The result of the effect of equilibration time on the peak area of 997.21 ppb 1,1,1-trichloroethane.

Time (min.)	Peak Area	% RSD
0	45544	± 3.58
10	49711	± 1.24
20	50289	± 4.60
30	50939	± 3.02
40	53384	± 1.52
50	54795	± 0.56
60	55246	± 0.15
80	54583	± 5.16
100	56084	± 4.60
120	55926	± 1.45

Triplicate analyses

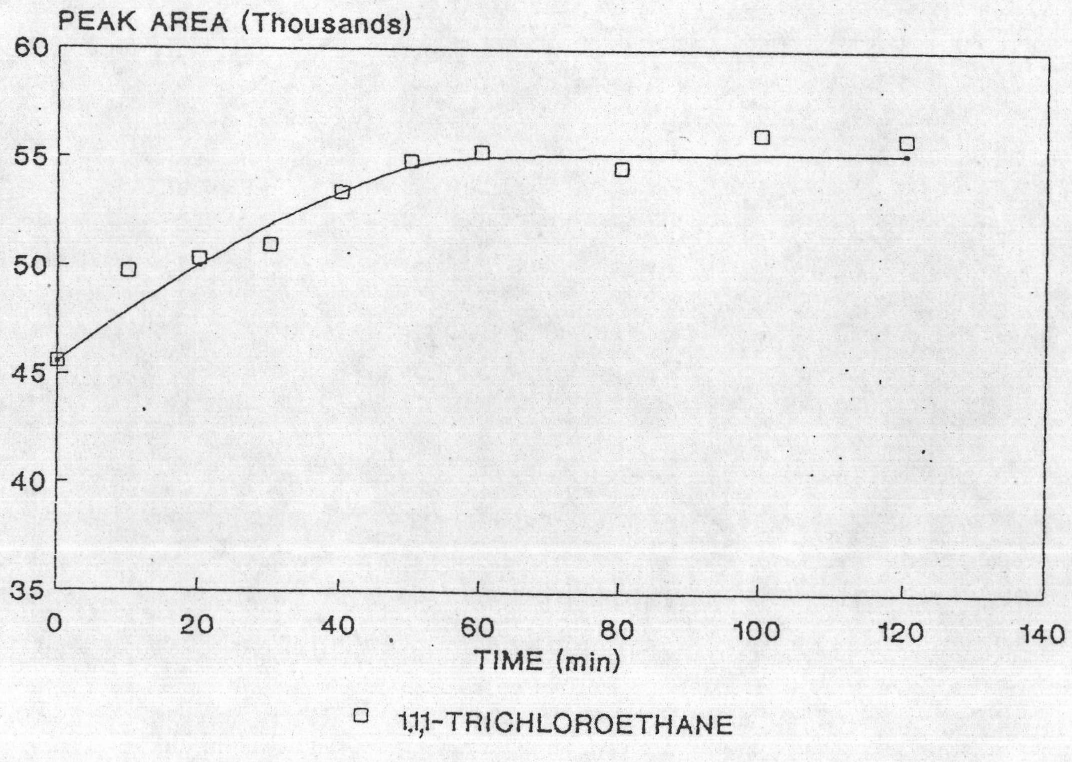


Figure 4.8 The effect of equilibration time on the peak area of 997.21 ppb 1,1,1-trichloroethane.

Table 4.9 The result of the effect of equilibration time on the peak area of 194.60 ppb trichloroethylene.

Time (min.)	Peak Area	% RSD
0	9539	± 2.38
10	13657	± 7.63
20	12724	± 4.36
30	14478	± 1.21
40	14564	± 4.20
50	15335	± 5.10
60	14517	± 2.54
80	15011	± 3.23
100	15483	± 3.23
120	15129	± 3.85

Triplicate analyses

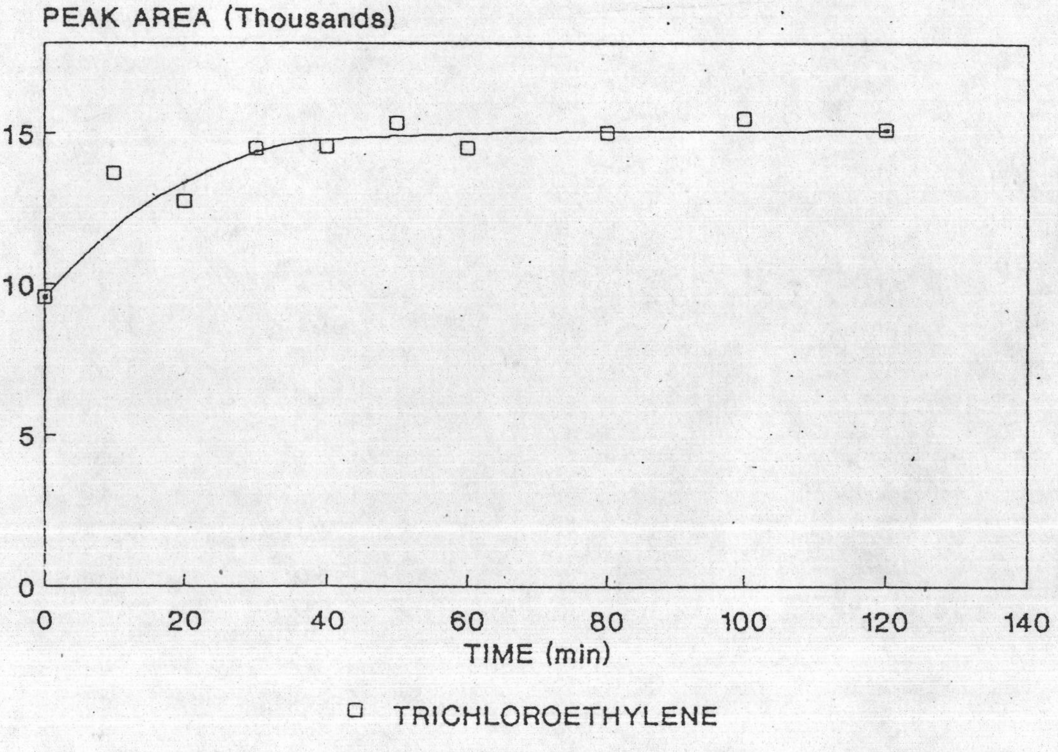


Figure 4.9 The effect of equilibration time on the peak area of 194.60 ppb trichloroethylene.

Table 4.10 The result of the effect of equilibration time on the peak area of 973.01 ppb trichloroethylene.

Time (min.)	Peak Area	% RSD
0	54023	± 5.13
10	56259	± 6.71
20	58286	±10.12
30	59078	± 5.76
40	61259	± 8.04
50	61847	± 7.53
60	60509	± 5.86
80	60407	± 1.64
100	60957	± 6.72
120	61702	± 1.04

Triplicate analyses

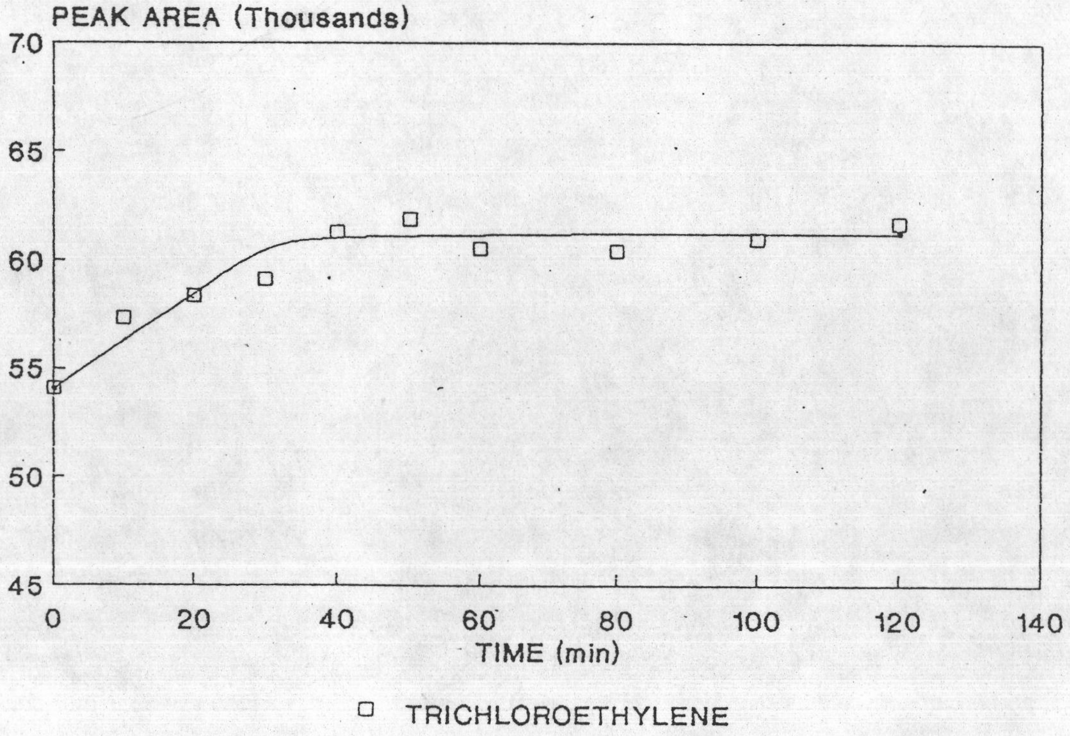


Figure 4.10 The effect of equilibration time on the peak area of 973.01 ppb trichloroethylene.

4.2 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-trichloro ethane and trichloroethylene is studied. The results of the study on the distribution coefficient (K) are presented in Tables 4.11 and 4.12 and the graphs showing the relationship of the distribution coefficient of each volatile chlorinated hydrocarbon with temperature are in Figures 4.11 and 4.12. 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 copound 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 4.11 and 4.12.

The results of the effect of the temperature on sensitivity of each volatile chlorinated hydrocarbon are shown in Tables 4.13 and 4.14 and the graphs plotted the sensitivity of each compound against temperature are shown in Figures 4.13 and 4.14. It demonstrates that the temperature has the effect on sensitivity of each volatile chlorinated hydrocarbon and therefore increasing temperature of the system will result in the enchancement of the sensitivity of headspace analysis technique. According to the results in Tables

4.13 and 4.14, it can be seen that the highest sensiitivity 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 resulting 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 4.13 and 4.14 and is a sufficient sensitivity for the determination of each volatile chlorinated hydrocarbon.

Table 4.11 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.

Compound	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 4.12 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.

Compound	Temperature (°C)	K	Cg (ppb)
	50.0	4.30	181.89
Methylene chloride	60.0	3.07	237.02
(964.75 ppb)	70.0	2.15	306.54
	80.0	1.69	359.24
	50.0	4.06	185.73
Chloroform	60.0	2.94	238.28
(940.49 ppb)	70.0	2.07	306.08
	80.0	1.52	373.90
	50.0	1.52	396.16
Carbon tetrachloride	60.0	1.04	490.77
(998.57 ppb)	70.0	0.56	640.14
	80.0	0.35	738.01
	50.0	1.69	370.35
1,1,1-Trichloroethane	60.0	1.30	433.71
(997.21 ppb)	70.0	0.99	500.07
	80.0	0.65	606.03
	50.0	2.17	307.43
Trichloroethylene	60.0	1.62	371.73
(973.01 ppb)	70.0	0.93	504.77
	80.0	0.67	582.85

Triplicate analyses

Table 4.13 The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

Compound	Temperature (°C)	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 4.14 The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

Compound	Temperature (°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

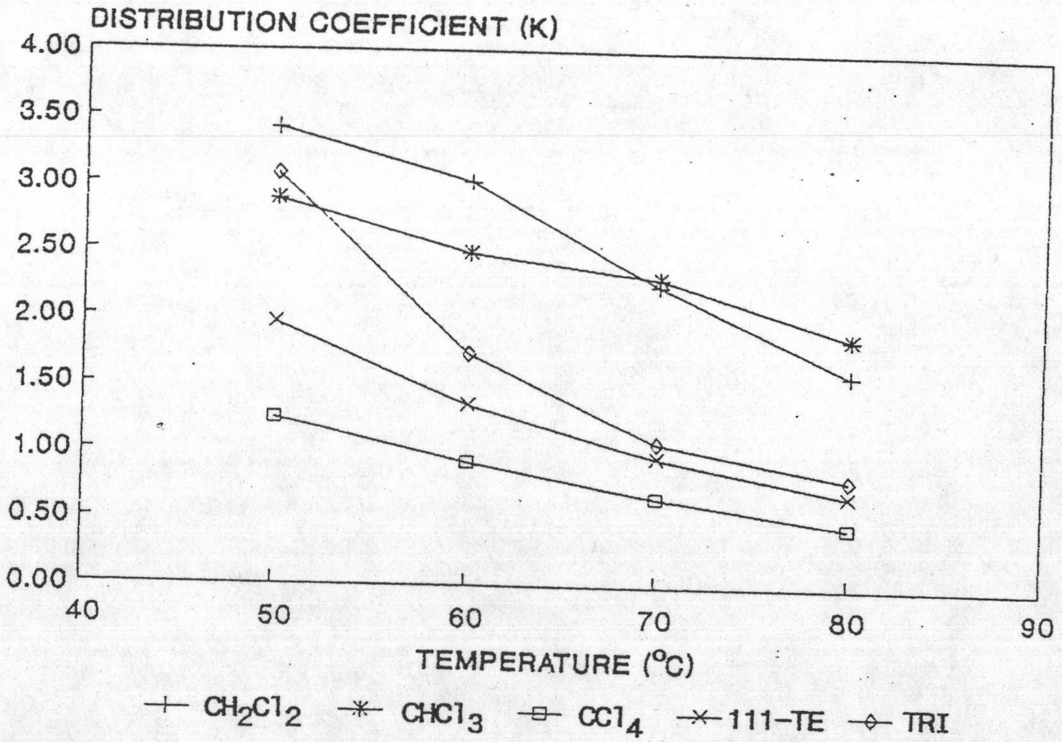


Figure 4.11 The effect of temperature on the distribution coefficient of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

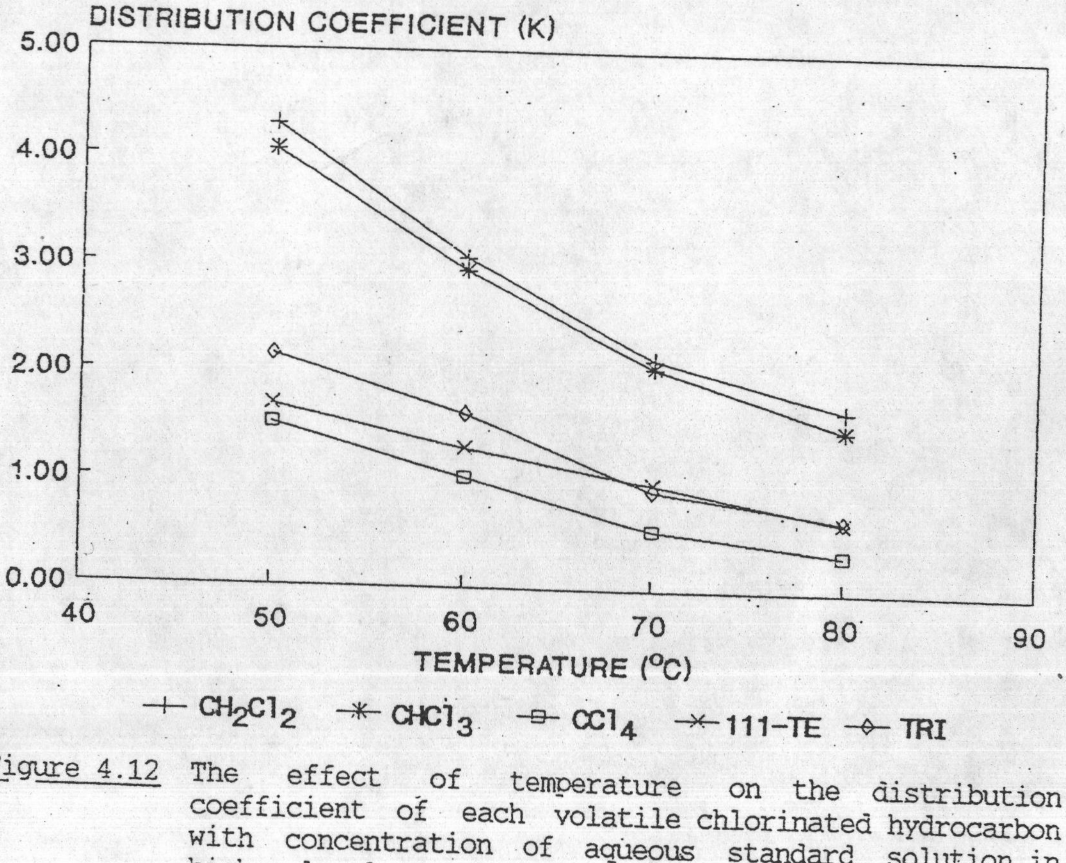


Figure 4.12 The effect of temperature on the distribution coefficient of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

* CH_2CL_2 - Methylene chloride , $CHCL_3$ - Chloroform
CCL_4 - Carbon tetrachloride , 111-TE - 1,1,1-Trichloroethane
TRI - Trichloroethylene

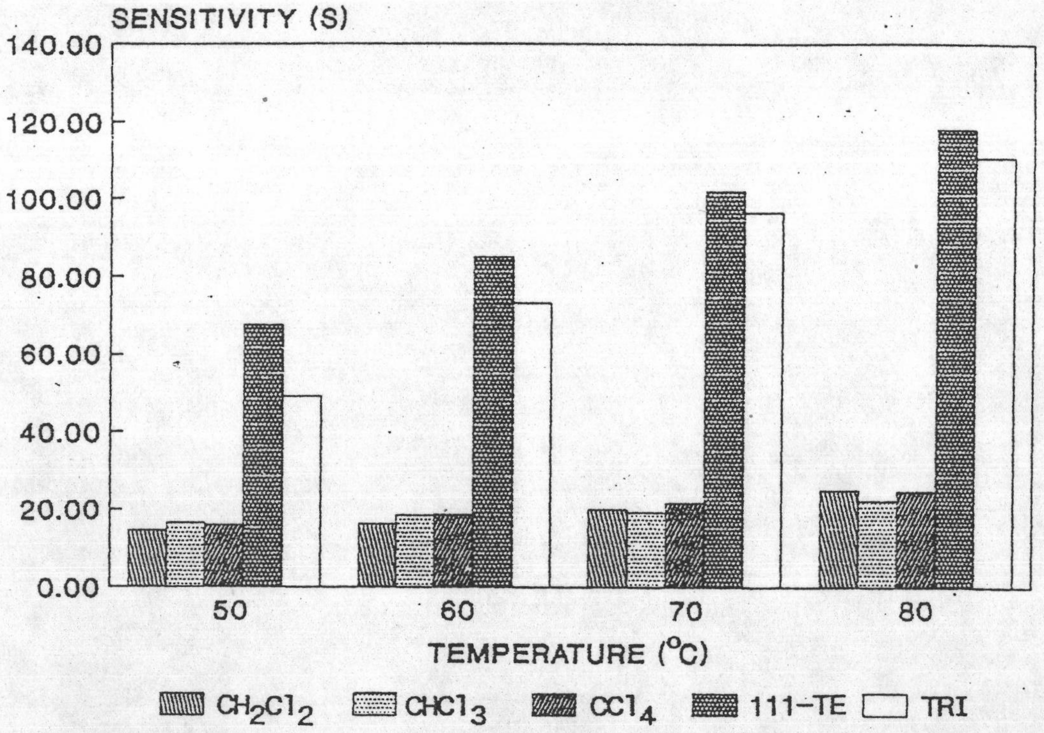


Figure 4.13 The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

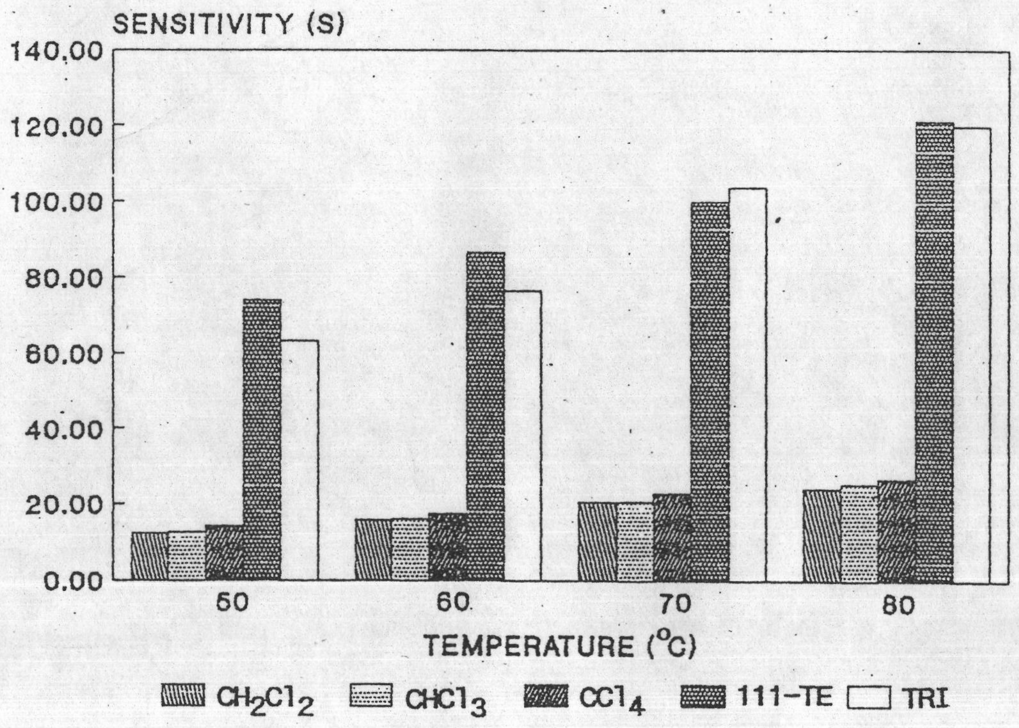


Figure 4.14 The effect of temperature on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

4.3 The Study of Liquid to Gas Phase Volume Ratio

The factor affecting the sensitivity of headspace analysis technique is also the liquid to gas phase 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 on 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 4.15 - 4.16 and 4.17 - 4.18, 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 4.15 - 4.16 and 4.17 - 4.18, 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 4.17 and 4.18 and increasing the phase volume ratio of V_l/V_g tends to decrease the precision of the analysis as shown in Tables 4.17 and 4.18 due to the high concentration of each interested compound in gas phase (C_g) as shown in Tables 4.15 and 4.16. Hence, the liquid to gas phase volume ratio of 30:30 is shosen as a suitable ratio for a headspace analysis.

Table 4.15 The effect of liguid 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	$V_l : V_g$	K	C_g (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 4.16 The effect of liguid 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.

Compound	$V_l : V_g$	K	C_g (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	1.82	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	2.17	371.14
	50 : 10	1.90	473.19

Triplicate analyses

Table 4.17 The effect of liguid to gas phase volume ratio on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

Compound	$V_l : V_g$	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 4.18 The effect of liguid to gas phase volume ratio on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

Compound	V_l : V_g	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	± 3.59
	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	± 0.78
	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 : 10	190.83	± 6.26

Triplicate analyses

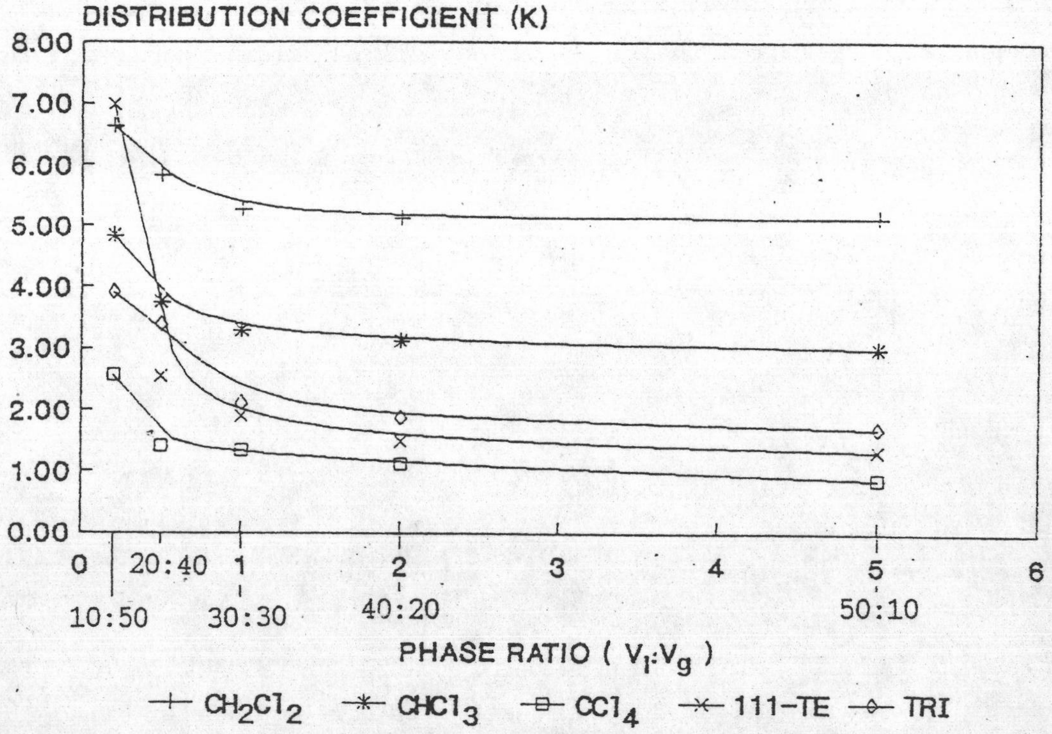


Figure 4.15 The distribution coefficient of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb versus liquid to gas phase volume ratio.

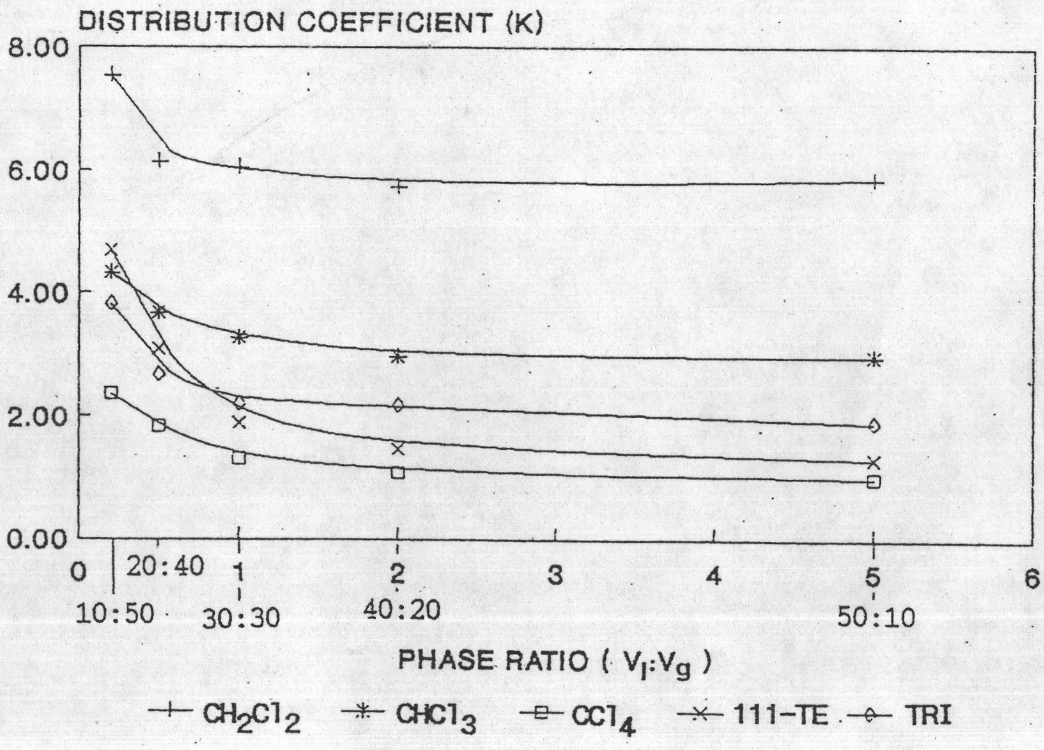


Figure 4.16 The distribution coefficient of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb versus liquid to gas phase volume ratio.

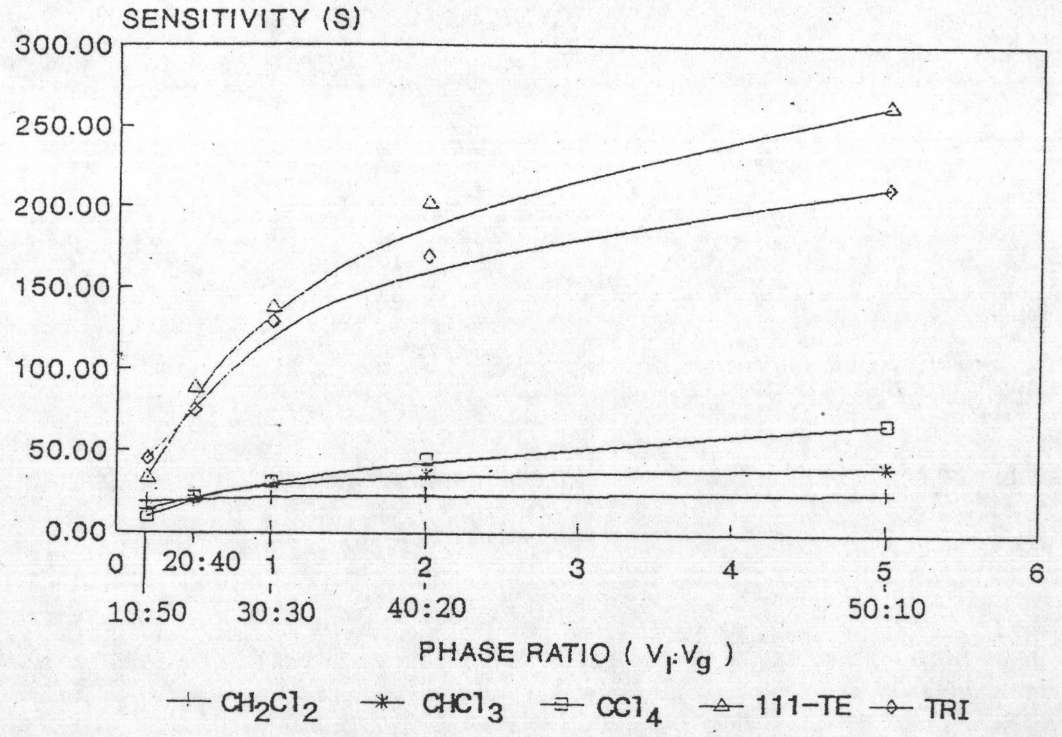


Figure 4.17 The effect of liquid to gas phase volume ratio on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

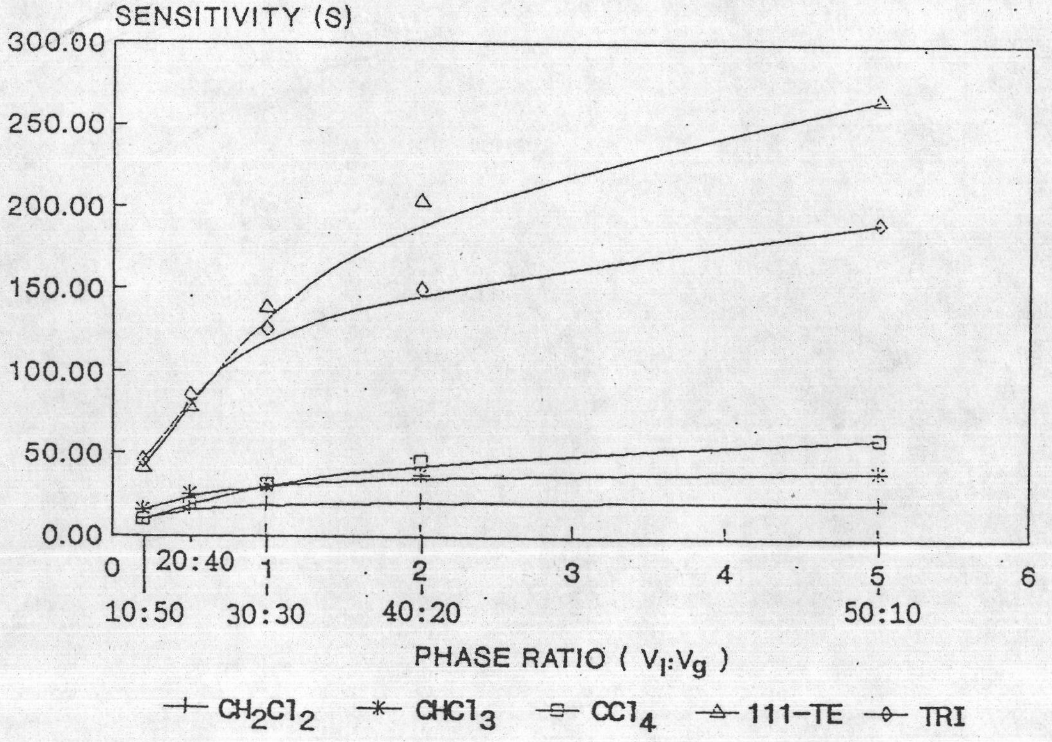


Figure 4.18 The effect of liquid to gas phase volume ratio on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

4.4 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 4.19 - 4.20 and the graphs plotted the peak area and the sensitivity against the injection volume are shown in Figures 4.19 - 4.20 and 4.21 - 4.22,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 Figures 4.21 and 4.22. However, the precisions 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 %)(29) as can be seen from Tables 4.19 and 4.20. Hence, the injection volume of 1.50 mL is selected as the optimum injection volume for this headspace analysis.

Table 4.19 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.

Compound	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	± 7.72
	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 4.20 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.

Compound	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	160608	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

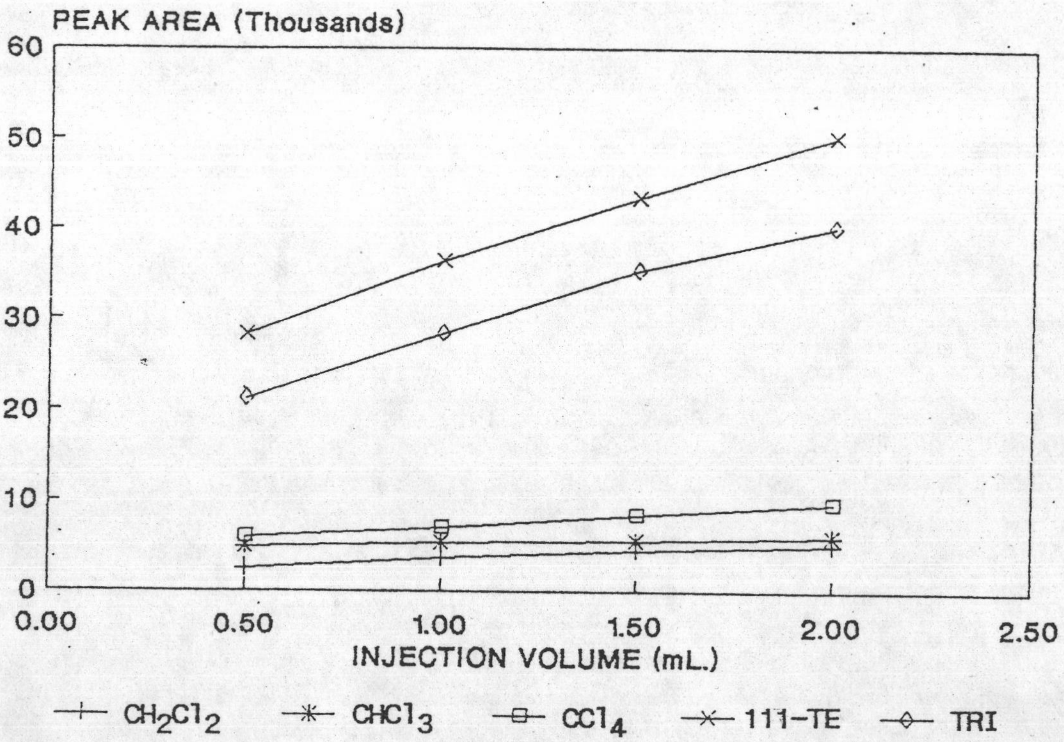


Figure 4.19 The relationship between the peak area of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb and injection volume.

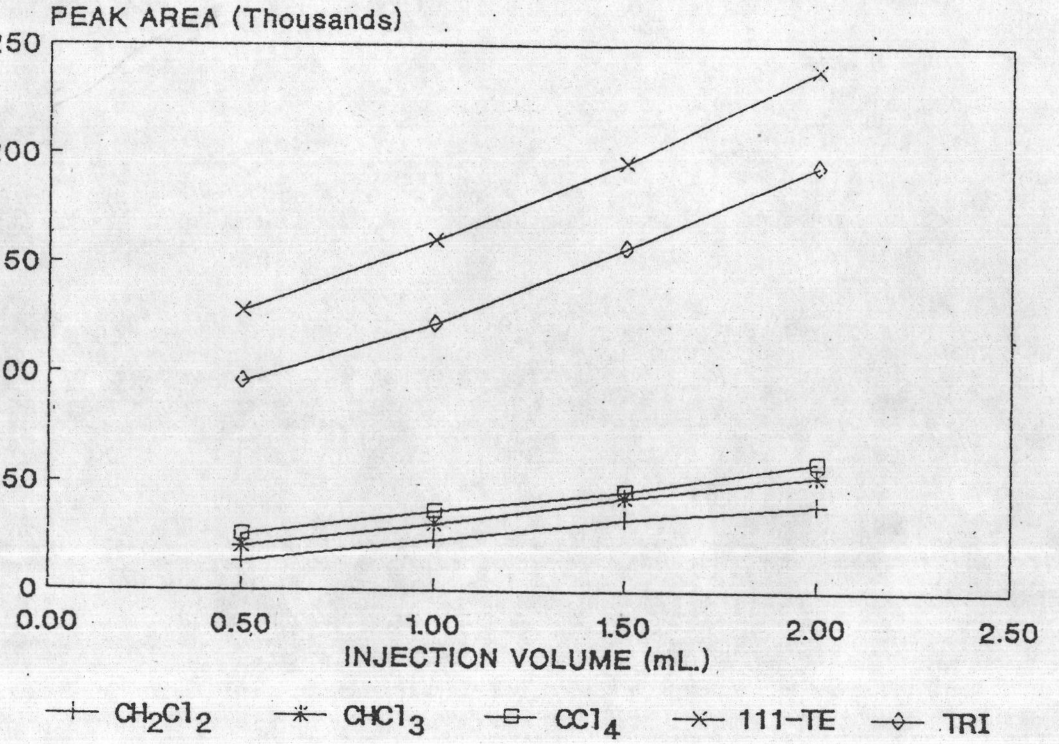


Figure 4.20 The relationship between the peak area of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb and injection volume.

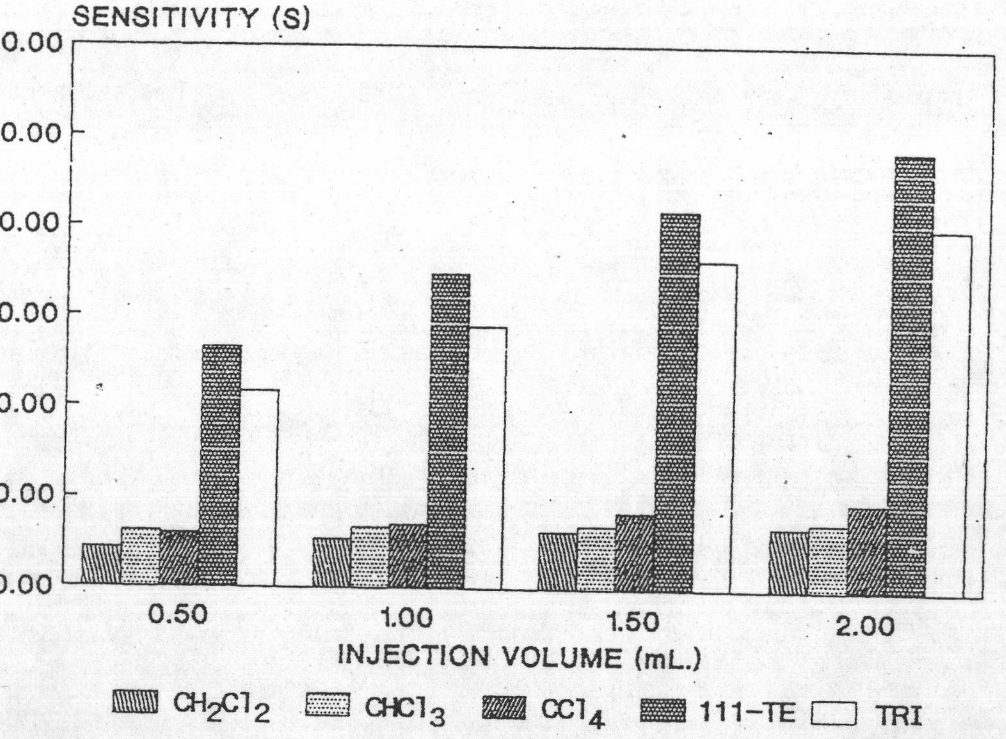


Figure 4.21 The effect of the injection volume on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in lower level of ppb.

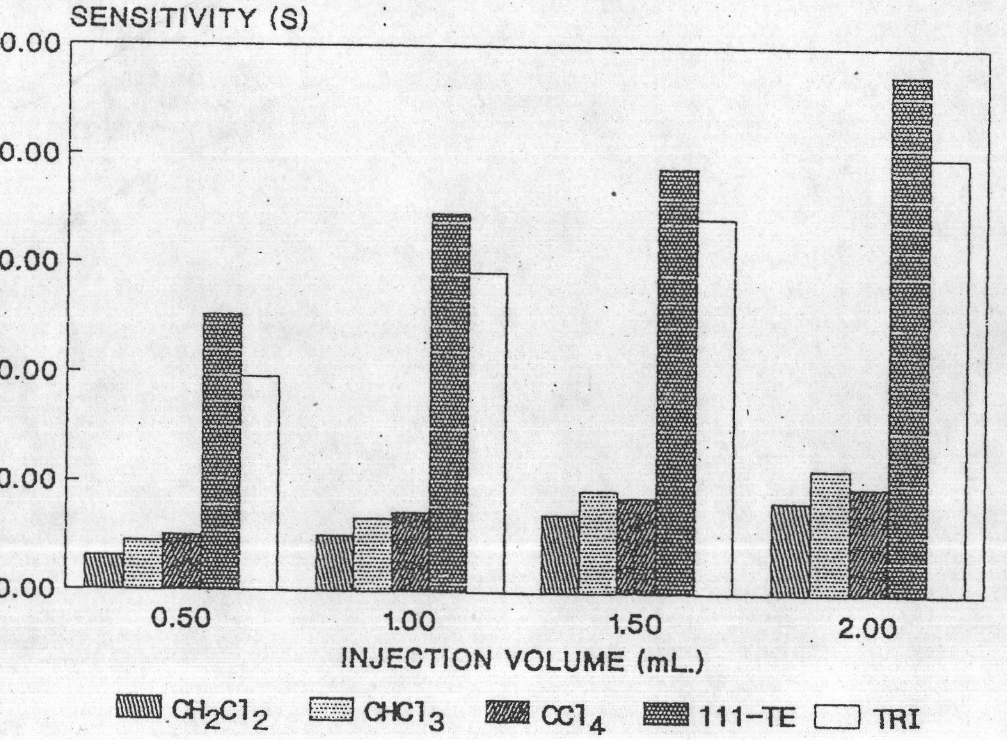


Figure 4.22 The effect of the injection volume on the sensitivity of each volatile chlorinated hydrocarbon with concentration of aqueous standard solution in higher level of ppb.

4.5 The Study of Salting Out Effect in Single Component Solution.

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 hydrocarbon i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene in single component solution is studied at two concentration levels with two detectors i.e., FID and ECD. The results of the study are shown in Tables 4.21 - 4.24. The graphs correlated to these results are shown in Figures 4.23 - 4.34. It is found that the distribution coefficient of each volatile chlorinated hydrocarbon in single component 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 distribution coefficient of all interested compounds at two concentration levels lower than sodium chloride and calcium carbonate do. Therefore, adding anhydrous sodium sulfate shows higher sensitivity and percent recovery than sodium chloride and calcium carbonate do as seen in Tables 4.21 - 4.24. 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.

Table 4.21 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in single component 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	3.46	29.37	16.95	± 4.77
	NaCl	1.69	48.60	32.67	± 3.01
	Na_2SO_4	0.75	74.95	54.22	± 1.56
	$CaCO_3$	3.40	29.75	17.26	± 4.64
Chloroform (188.10 ppb)	No salt	2.70	34.64	24.14	± 2.88
	NaCl	0.68	76.54	58.46	± 4.10
	Na_2SO_4	0.26	101.96	79.28	± 3.40
	$CaCO_3$	2.09	41.45	29.72	± 1.23
Carbon tetrachloride (199.71 ppb)	No salt	0.85	39.02	53.76	± 3.58
	NaCl	0.26	57.15	78.99	± 3.50
	Na_2SO_4	0.12	64.50	89.22	± 1.95
	$CaCO_3$	0.79	40.38	55.65	± 4.73
1,1,1-Trichloroethane (199.44 ppb)	No salt	1.30	173.50	44.66	± 2.91
	NaCl	0.40	286.18	72.30	± 2.56
	Na_2SO_4	0.22	327.28	82.38	± 2.85
	$CaCO_3$	1.00	199.46	51.03	± 3.33
Trichloroethylene (194.60 ppb)	No salt	1.61	153.52	38.48	± 6.71
	NaCl	0.56	256.64	64.19	± 2.76
	Na_2SO_4	0.32	304.01	76.00	± 2.90
	$CaCO_3$	1.51	159.15	39.88	± 3.04

Triplicate analyses

Table 4.22 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

Compound	Salt	K	S.	% E	% RSD
Methylene chloride (964.75 ppb)	No salt	4.00	26.16	18.90	± 3.33
	NaCl	2.02	43.28	32.14	± 2.93
	Na_2SO_4	0.72	76.11	57.55	± 1.56
	$CaCO_3$	4.36	24.41	17.55	± 4.16
Chloroform (940.49 ppb)	No salt	2.93	32.64	25.04	± 1.57
	NaCl	0.73	73.75	57.61	± 1.39
	Na_2SO_4	0.28	100.15	78.53	± 1.04
	$CaCO_3$	2.84	33.34	25.59	± 2.57
Carbon tetrachloride (998.57 ppb)	No salt	0.94	37.16	51.90	± 3.78
	NaCl	0.30	55.51	77.59	± 1.22
	Na_2SO_4	0.14	62.96	88.01	± 1.95
	$CaCO_3$	0.81	39.81	55.60	± 3.30
1,1,1-Trichloroethane (997.21 ppb)	No salt	1.39	166.91	42.08	± 3.81
	NaCl	0.37	291.18	73.09	± 2.26
	Na_2SO_4	0.19	333.08	83.54	± 1.48
	$CaCO_3$	1.27	175.25	44.16	± 4.20
Trichloroethylene (973.01 ppb)	No salt	1.71	147.56	36.89	± 5.35
	NaCl	0.50	266.07	66.48	± 3.72
	Na_2SO_4	0.30	307.42	76.81	± 2.50
	$CaCO_3$	1.69	148.38	37.09	± 1.44

Triplicate analyses

Table 4.23 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

Compound	Salt	K	S	% E	% RSD
Methylene chloride (4.90 ppb)	No salt	15.88	1255	22.92	± 4.93
	NaCl	3.41	4803	36.64	± 1.08
	Na_2SO_4	0.94	10905	60.22	± 2.19
	$CaCO_3$	8.68	2189	26.53	± 1.15
Chloroform (4.90 ppb)	No salt	3.91	107151	30.06	± 3.97
	NaCl	0.87	281108	59.11	± 4.00
	Na_2SO_4	0.23	428104	83.65	± 2.88
	$CaCO_3$	3.66	112755	31.00	± 2.85
Carbon tetrachloride (5.00 ppb)	No salt	1.36	1018758	56.94	± 1.16
	NaCl	0.32	1813960	81.70	± 3.93
	Na_2SO_4	0.14	2106362	90.81	± 3.69
	$CaCO_3$	1.23	1078620	58.80	± 2.98
1,1,1-Trichloroethane (4.98 ppb)	No salt	1.46	173122	44.93	± 3.50
	NaCl	0.45	294934	71.44	± 4.72
	Na_2SO_4	0.25	340403	81.33	± 3.17
	$CaCO_3$	1.17	196553	50.03	± 4.27
Trichloroethylene (4.87 ppb)	No salt	2.73	210224	32.88	± 5.54
	NaCl	0.64	478975	64.27	± 2.02
	Na_2SO_4	0.31	601265	78.55	± 3.65
	$CaCO_3$	1.74	286264	41.76	± 4.01

Triplicate analyses

Table 4.24 The results of salting out effect on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

Compound	Salt	K	S	% E	% RSD
Methylene chloride (49.01 ppb)	No salt	6.04	3007	16.04	± 2.01
	NaCl	2.02	7007	34.50	± 4.82
	Na_2SO_4	0.73	12230	58.61	± 3.16
	$CaCO_3$	4.80	3653	19.02	± 2.99
Chloroform (48.98 ppb)	No salt	2.58	146648	28.86	± 3.61
	NaCl	0.70	308627	59.24	± 5.03
	Na_2SO_4	0.18	444527	84.72	± 3.33
	$CaCO_3$	2.37	155915	30.60	± 2.16
Carbon tetrachloride (49.98 ppb)	No salt	0.85	1291601	55.29	± 5.51
	NaCl	0.24	1929125	80.97	± 4.01
	Na_2SO_4	0.12	2131358	89.12	± 4.32
	$CaCO_3$	0.80	1330110	56.84	± 3.94
1,1,1-Trichloroethane (49.75 ppb)	No salt	1.23	190268	45.07	± 6.03
	NaCl	0.36	311229	73.24	± 2.10
	Na_2SO_4	0.22	348728	81.97	± 2.04
	$CaCO_3$	1.23	190912	45.22	± 1.59
Trichloroethylene (48.65 ppb)	No salt	1.98	263011	34.10	± 4.34
	NaCl	0.55	505225	64.69	± 2.19
	Na_2SO_4	0.26	618313	78.97	± 3.31
	$CaCO_3$	1.39	327920	42.30	± 3.66

Triplicate analyses

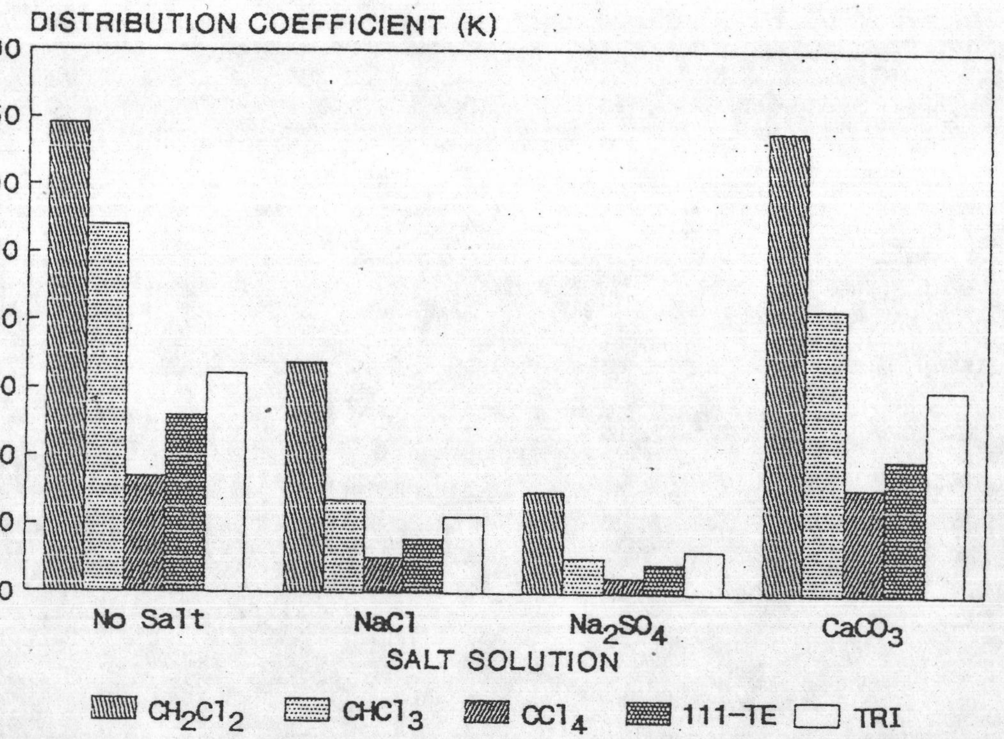


Figure 4.23 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

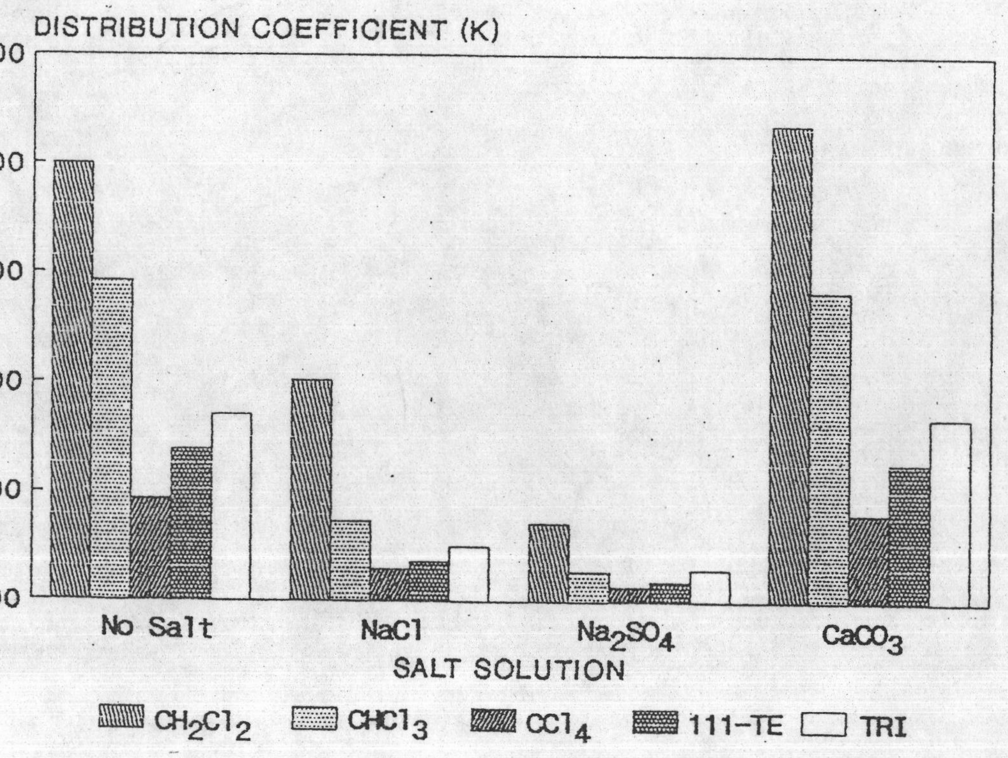


Figure 4.24 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

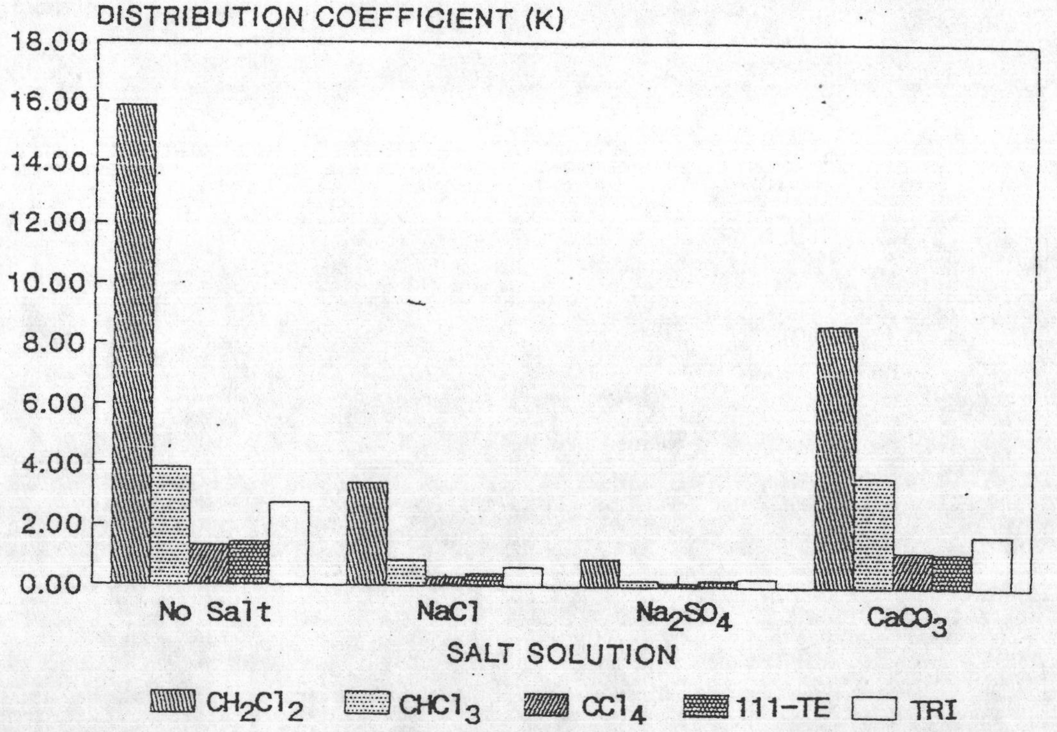


Figure 4.25 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

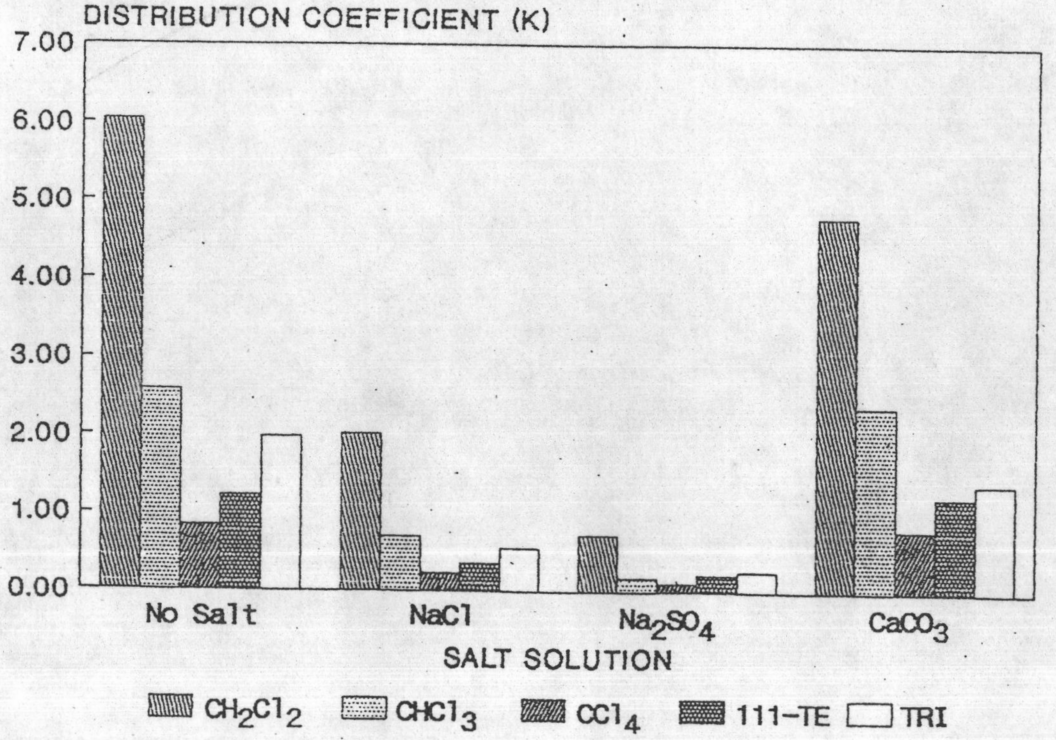


Figure 4.26 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

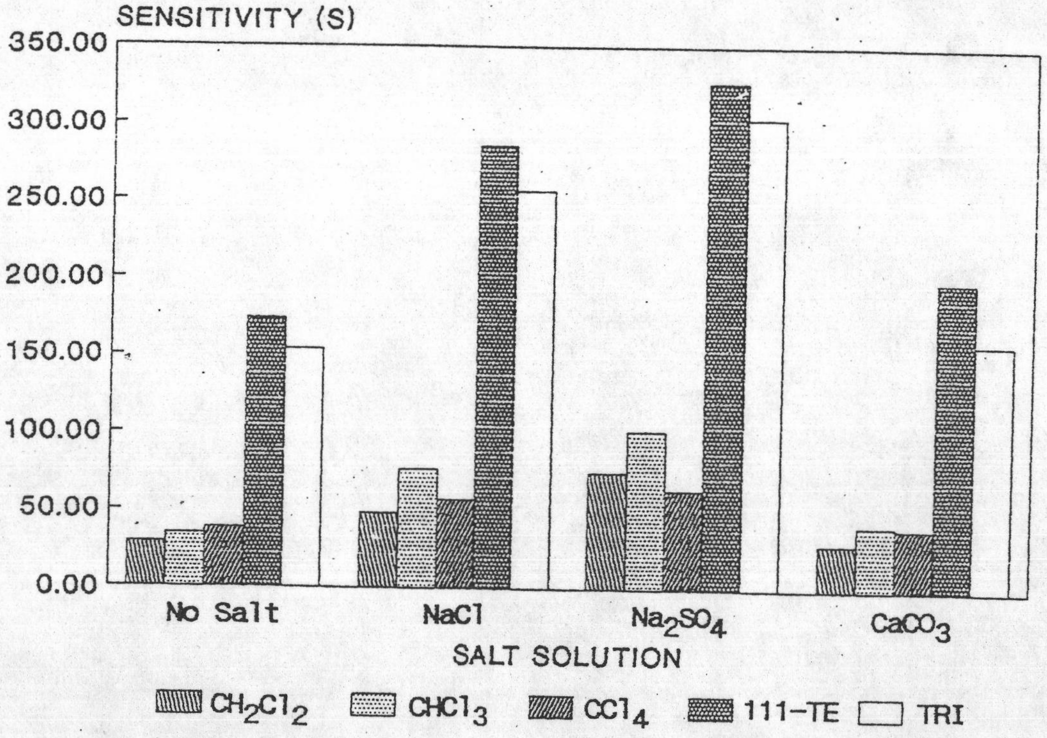


Figure 4.27 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

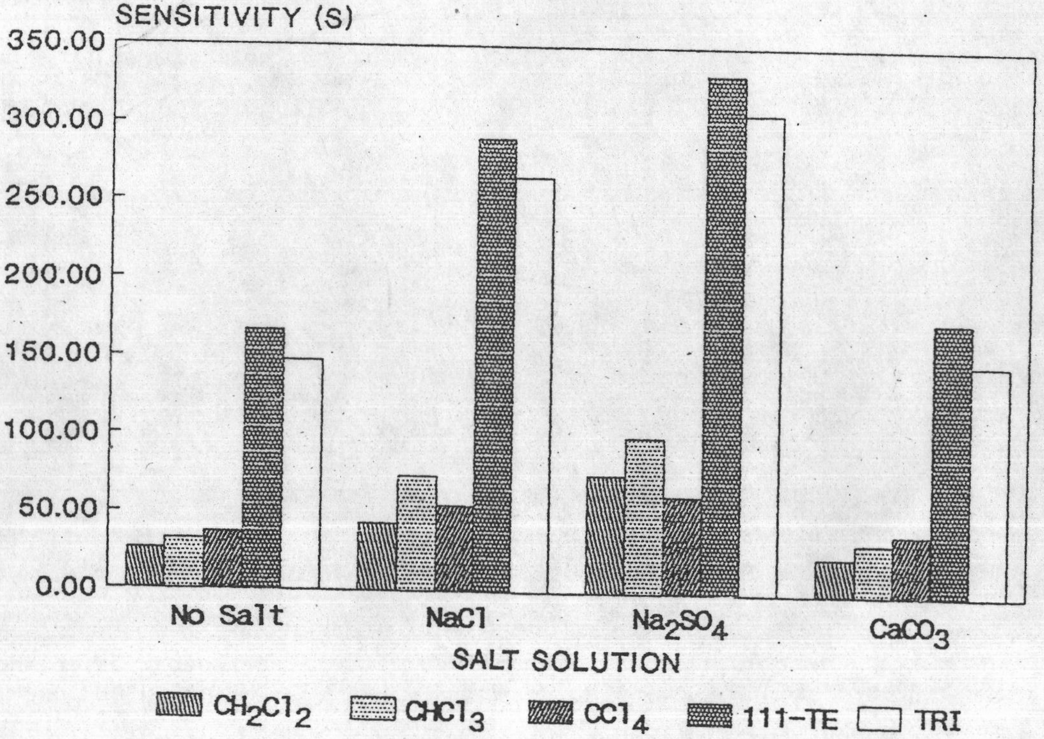


Figure 4.28 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

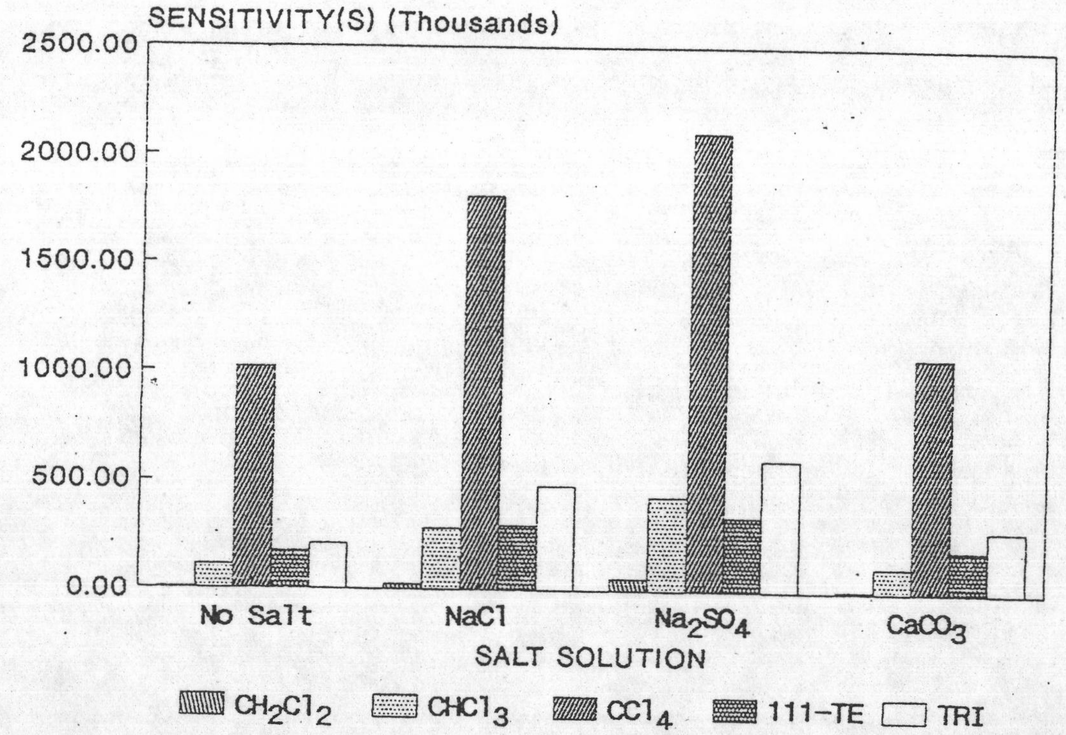


Figure 4.29 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

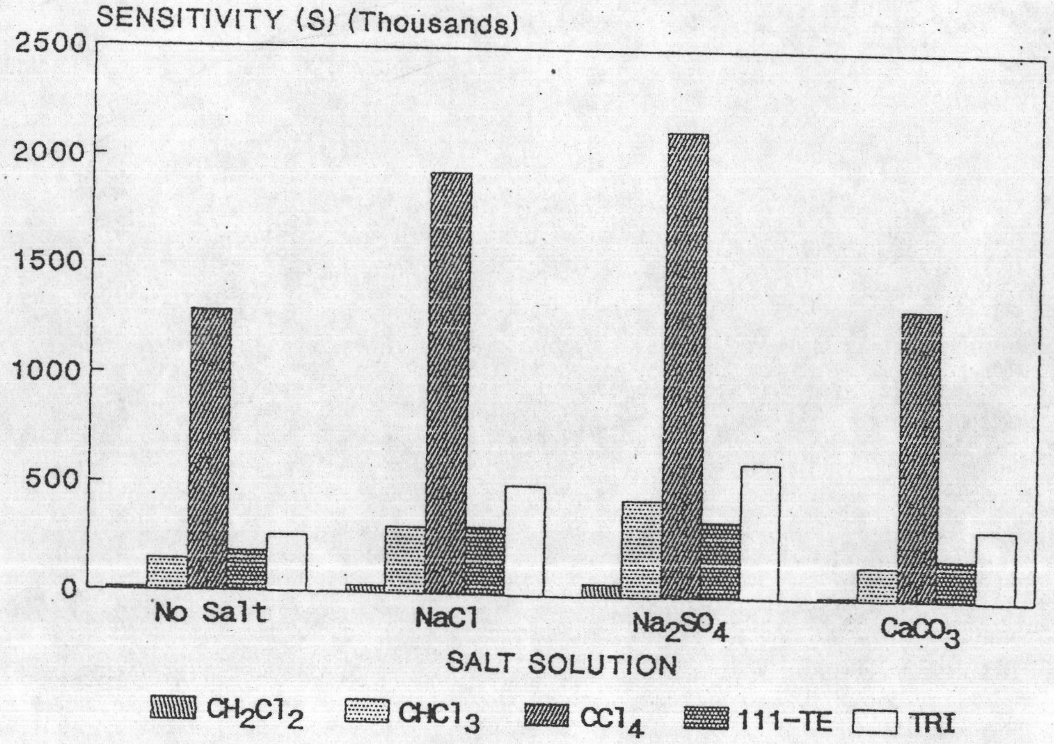


Figure 4.30 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

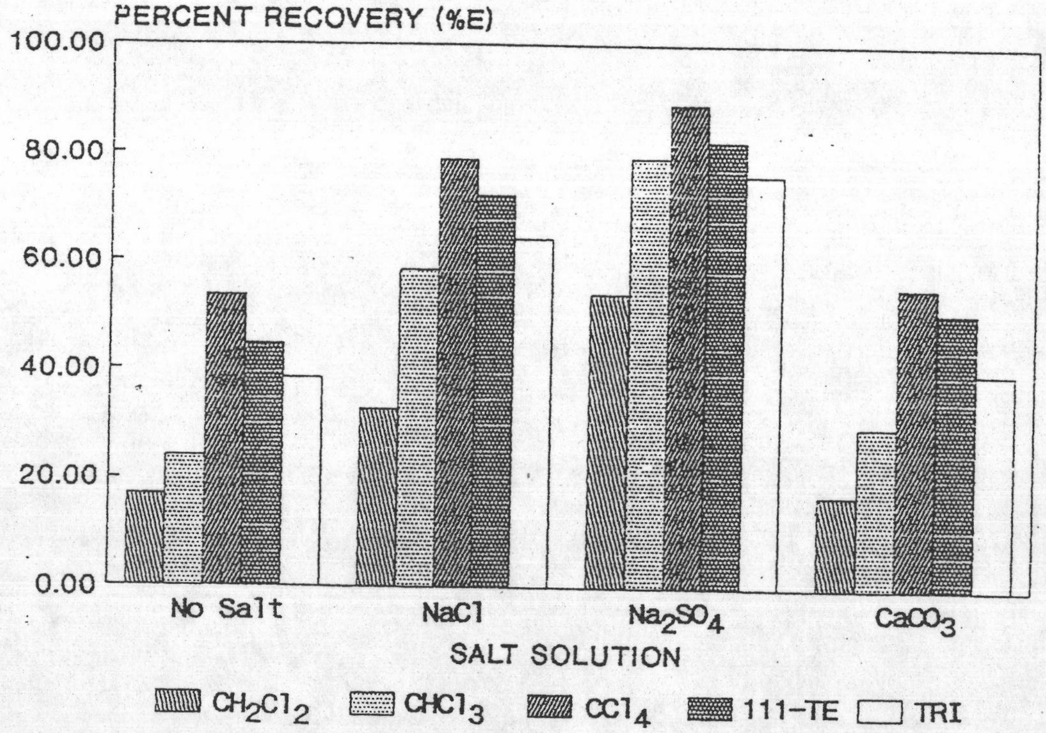


Figure 4.31 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

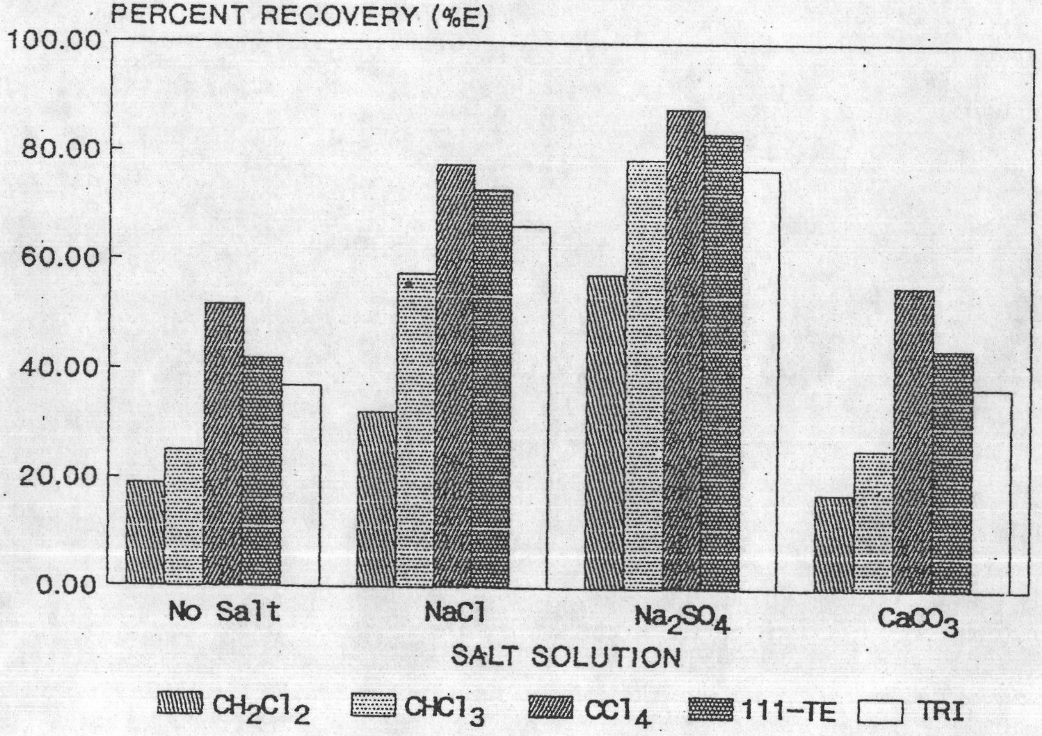


Figure 4.32 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

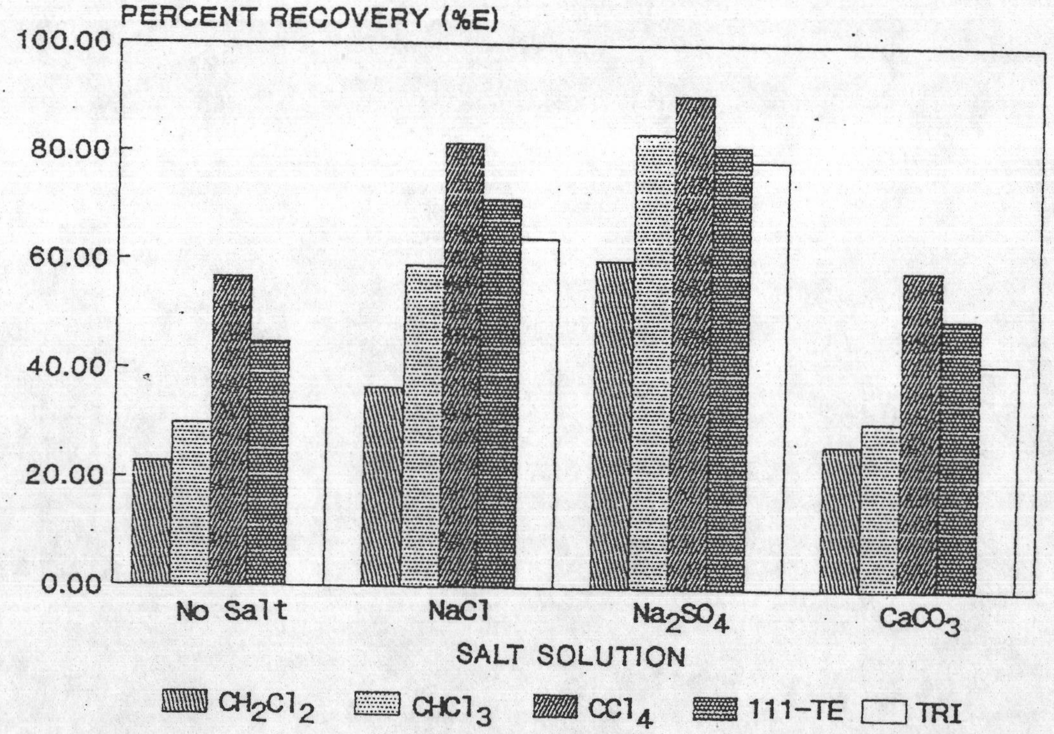


Figure 4.33 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

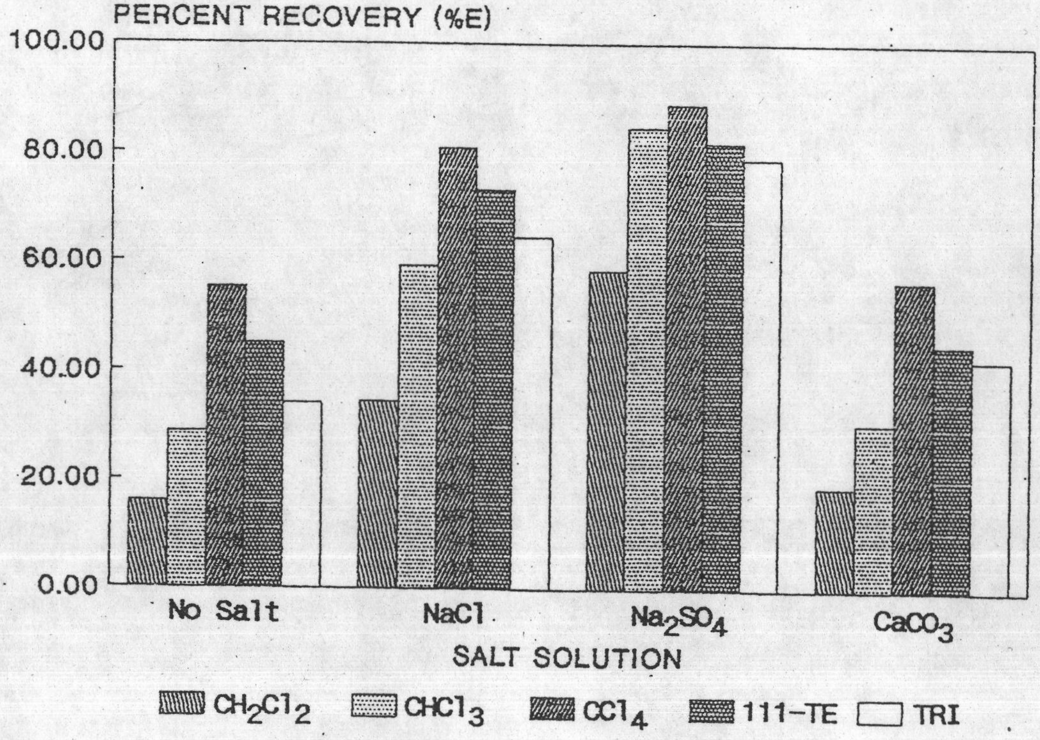


Figure 4.34 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in single component solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

4.6 The Study of Salting Out Effect in Mixture Solution.

The results of adding salts i.e., 10.50 g of sodium chloride, 13.00 g of anhydrous sodium sulfate and 0.10 g of calcium carbonate affecting on the distribution coefficient, the sensitivity and the percent recovery of each volatile chlorinated hydrocarbon i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloro ethane and trichloroethylene in mixture component solution at two concentration levels using FID and ECD as the detectors are shown in Tables 4.25 - 4.26 and 4.27 - 4.28, respectively and the graphs plotted the distribution coefficient, the sensitivity and the percent recovery against salts used are shown in Figures 3.35 - 3.38, 3.39 - 3.42 and 3.43 - 3.46,respectively. It is found that the result of the salting out effect on the distribution coefficient, the sensitivity and the percent recovery in mixture and single component solutions are similar. However, adding anhydrous sodium sulfate into the solutions gives the lower distribution coefficient and the higher sensitivity and percent recovery for each volatile chlorinated hydrocarbon than other salts. Therefore, the anhydrous sodium sulfate is considered to be the suitable salt which can be used to increase the sensitivity and the percent recovery of each interested compound in both mixture and single component solutions, and is chosen as the appropiate salt for the headspace analysis technique.

Table 4.25 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 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_2SO_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_2SO_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_2SO_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_2SO_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_2SO_4	0.32	106.30	75.47	± 3.35
	$CaCO_3$	1.61	54.07	38.75	± 5.96

Triplicate analyses

Table 4.26 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 higher level of ppb using FID as a detector.

Compound	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_2SO_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	± 3.93
	Na_2SO_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_2SO_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_2SO_4	0.22	97.44	81.96	± 2.01
	$CaCO_3$	1.12	56.07	47.22	± 3.71
Trichloroethylene (973.01 ppb)	No salt	1.90	48.60	34.52	± 2.39
	NaCl	0.47	95.85	67.94	± 3.33
	Na_2SO_4	0.26	111.28	78.85	± 3.27
	$CaCO_3$	1.58	54.72	38.84	± 2.94

Triplicate analyses

Table 4.27 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.

Compound	Salt	K	S	% E	% RSD
Methylene chloride (4.90 ppb)	No salt	13.98	1414	23.83	± 3.81
	NaCl	3.54	4663	36.34	± 5.01
	Na_2SO_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_2SO_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	± 4.78
	NaCl	0.35	1780120	80.77	± 7.31
	Na_2SO_4	0.16	2076419	89.95	± 4.40
	$CaCO_3$	1.04	1176119	62.05	± 2.79
1,1,1-Trichloroethane (4.98 ppb)	No salt	1.11	201554	51.20	± 3.01
	NaCl	0.41	301440	72.92	± 6.23
	Na_2SO_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_2SO_4	0.27	620239	80.83	± 4.44
	$CaCO_3$	1.79	281147	41.28	± 2.39

Triplicate analyses

Table 4.28 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 higher level of ppb using ECD as a detector.

Compound	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_2SO_4	0.78	11905	57.15	± 2.20
	$CaCO_3$	4.39	3934	20.36	± 3.77
Chloroform (48.98 ppb)	No salt	2.40	154760	30.42	± 5.66
	NaCl	0.66	316746	60.80	± 2.63
	Na_2SO_4	0.24	425321	81.16	± 3.70
	$CaCO_3$	2.23	162660	31.90	± 3.59
Carbon tetrachloride (49.98 ppb)	No salt	0.71	1404160	59.87	± 4.03
	NaCl	0.16	2066093	86.53	± 1.32
	Na_2SO_4	0.13	2134260	89.27	± 2.78
	$CaCO_3$	0.55	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_2SO_4	0.19	357186	84.35	± 2.02
	$CaCO_3$	1.24	190329	45.32	± 2.99
Trichloroethylene (48.65 ppb)	No salt	1.62	299862	38.79	± 5.60
	NaCl	0.46	538627	68.94	± 2.48
	Na_2SO_4	0.30	601611	76.89	± 1.45
	$CaCO_3$	1.59	303448	39.24	± 2.13

Triplicate analyses

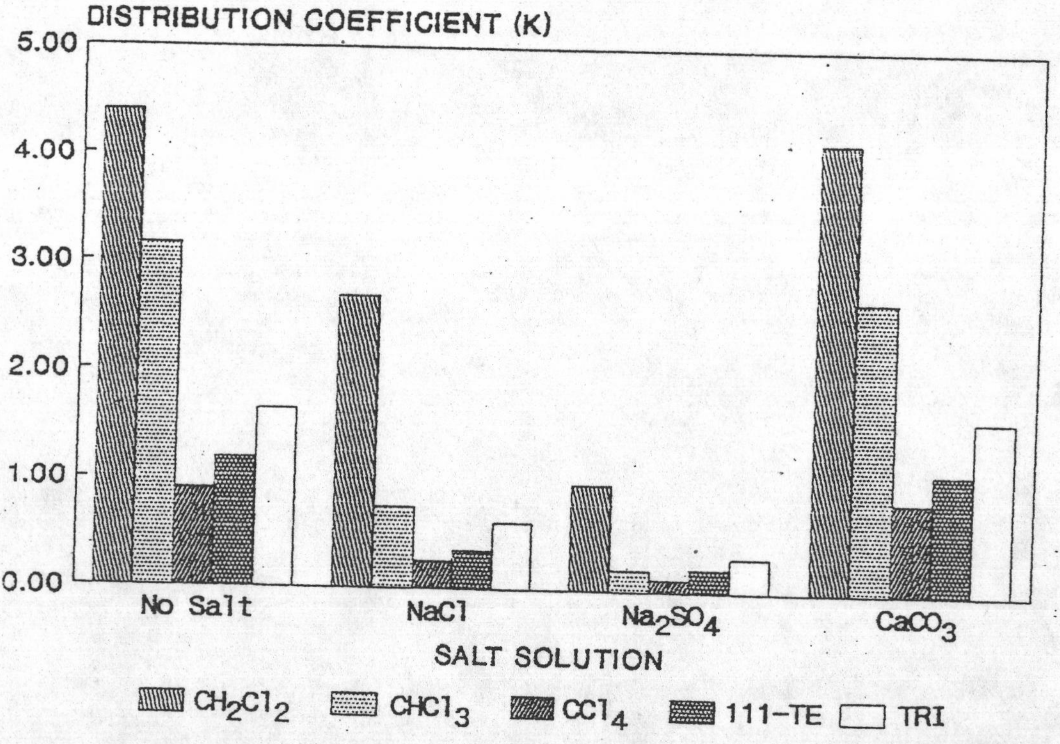


Figure 4.35 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

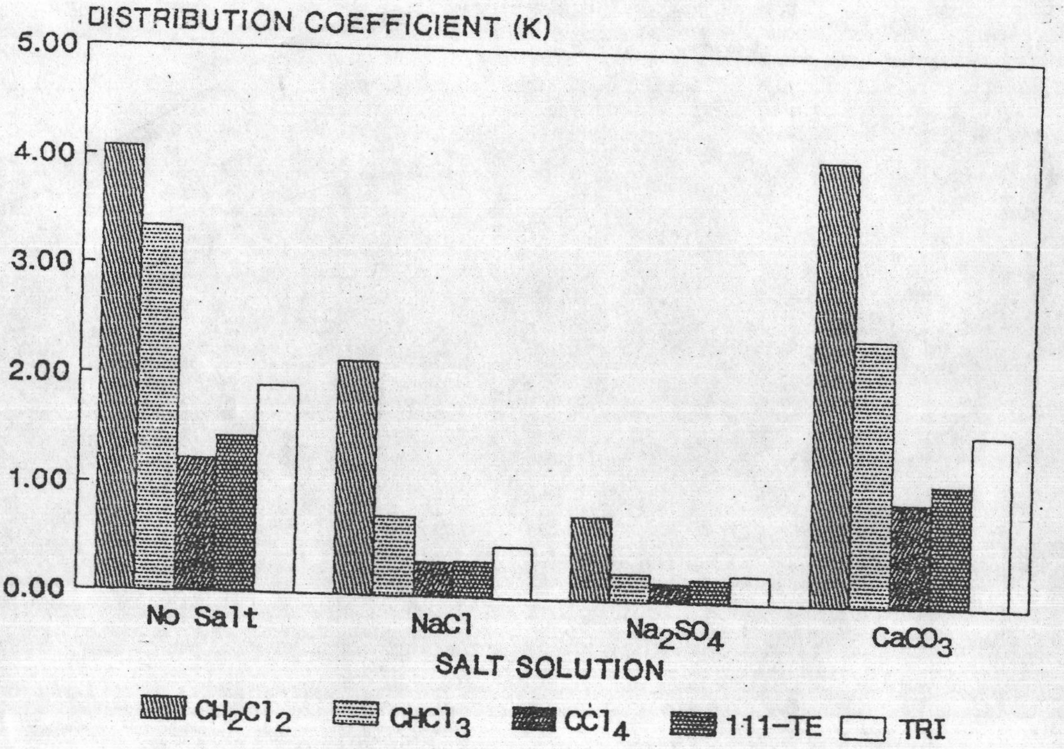


Figure 4.36 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

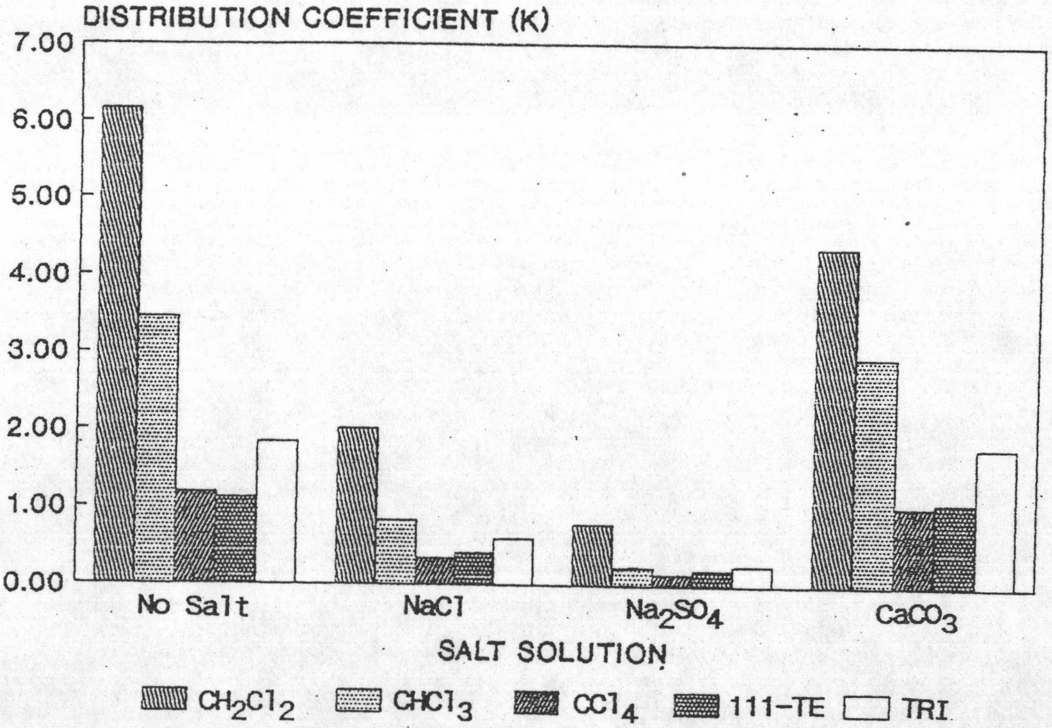


Figure 4.37 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

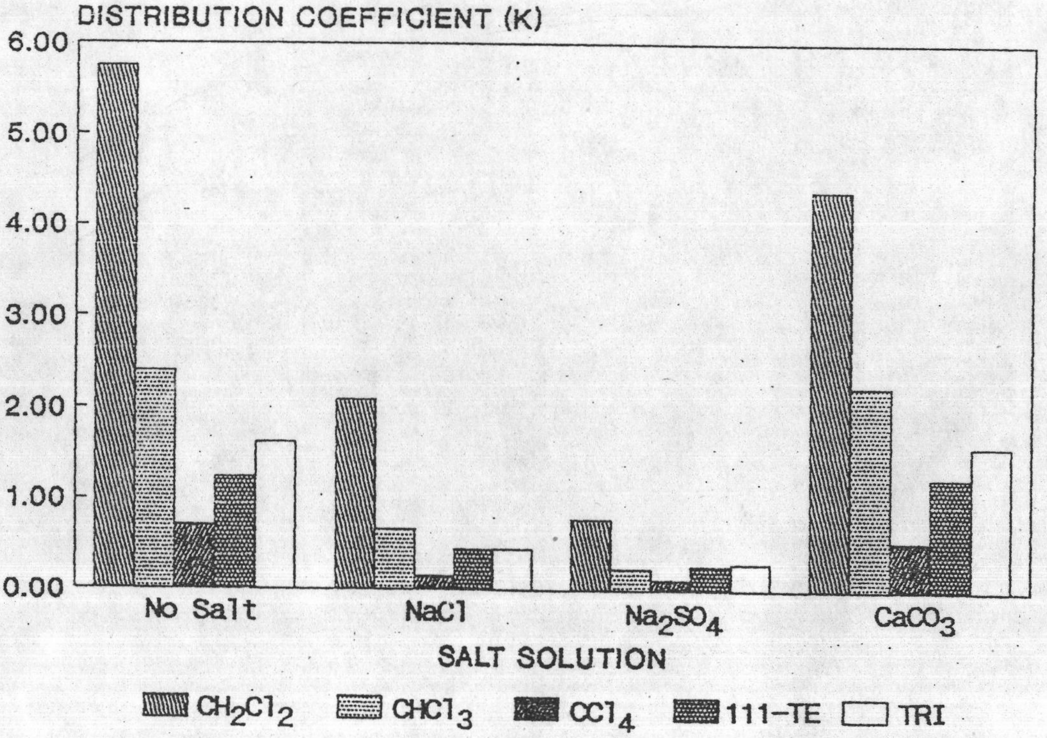


Figure 4.38 The effect of salting out on the distribution coefficient of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

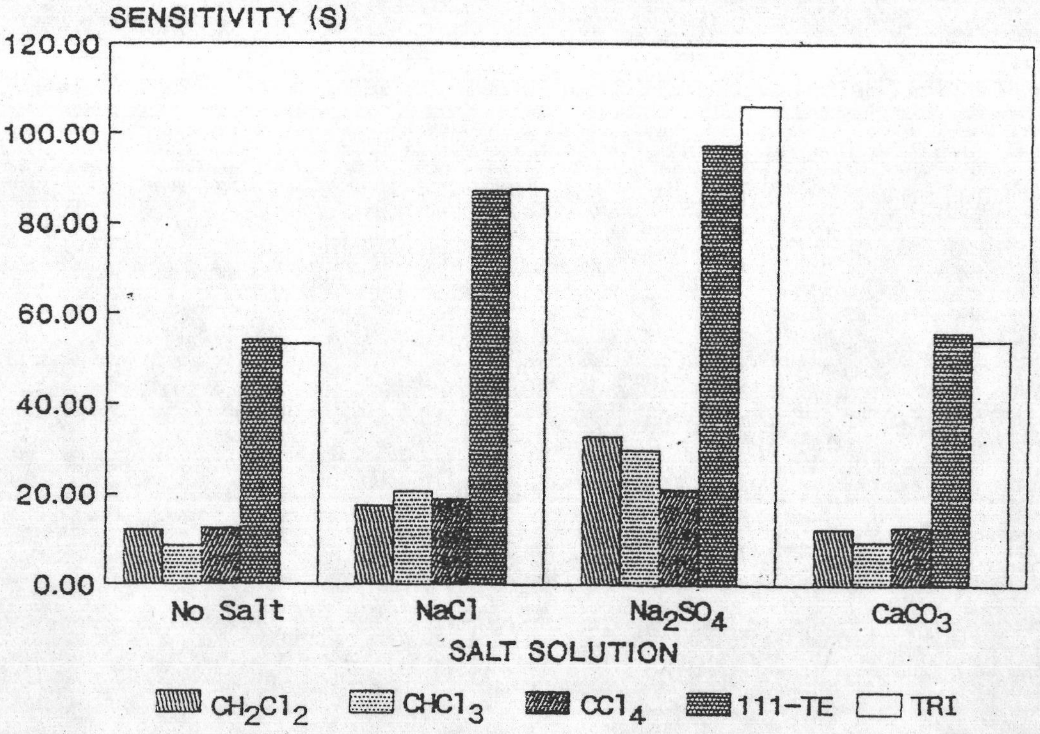


Figure 4.39 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

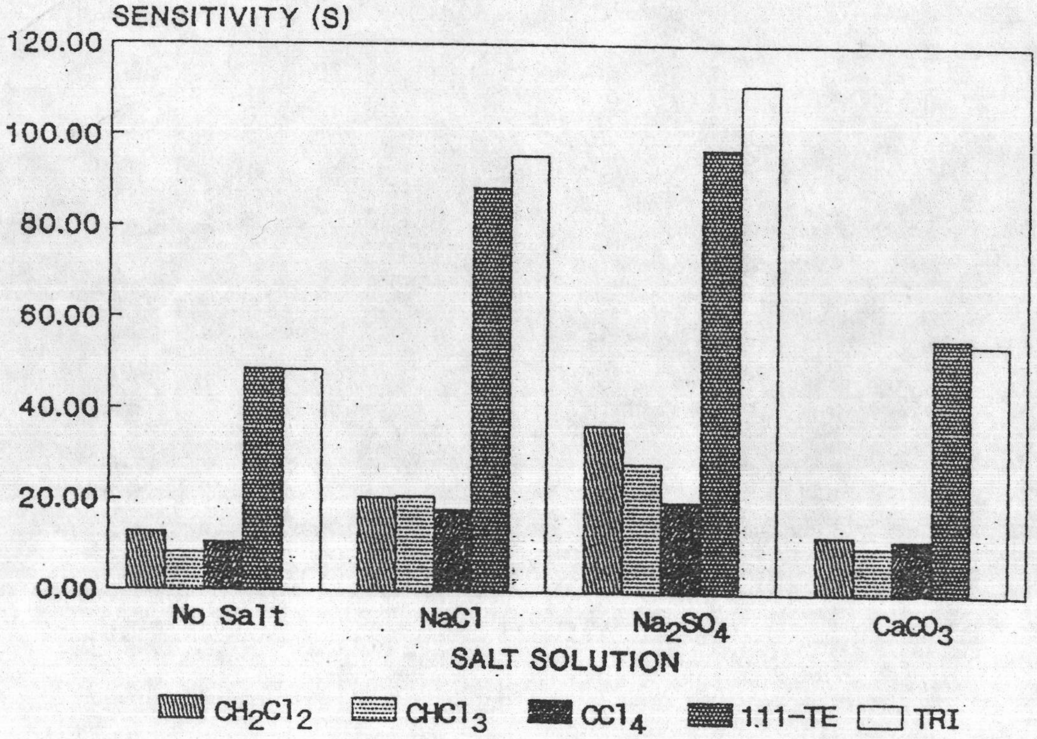


Figure 4.40 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

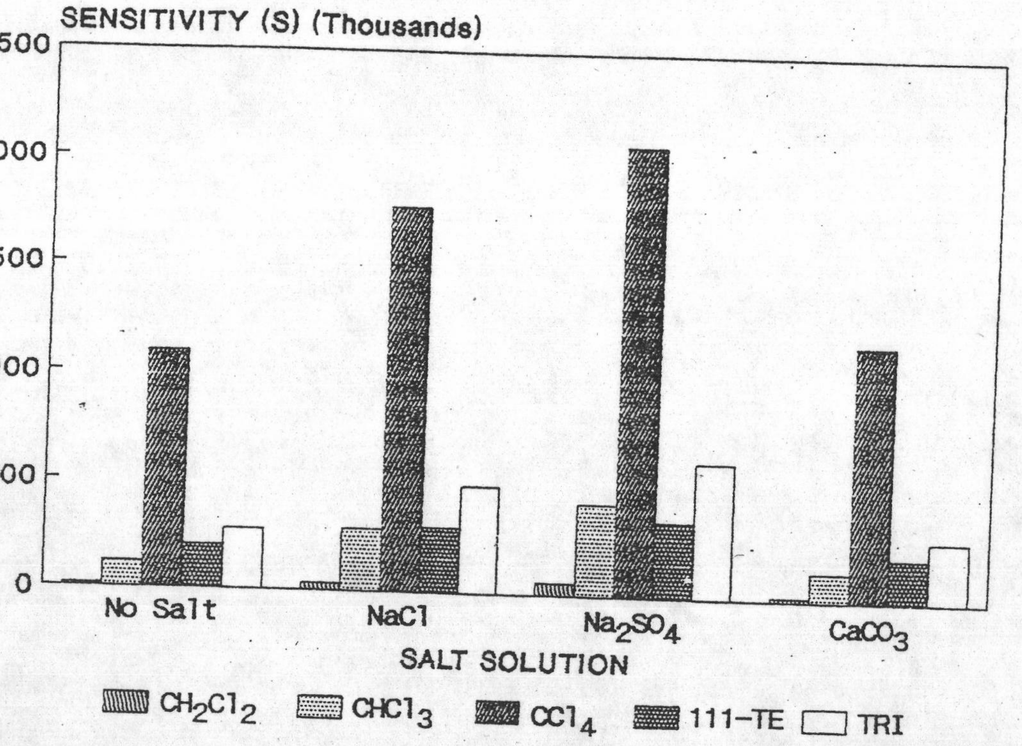


Figure 4.41 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

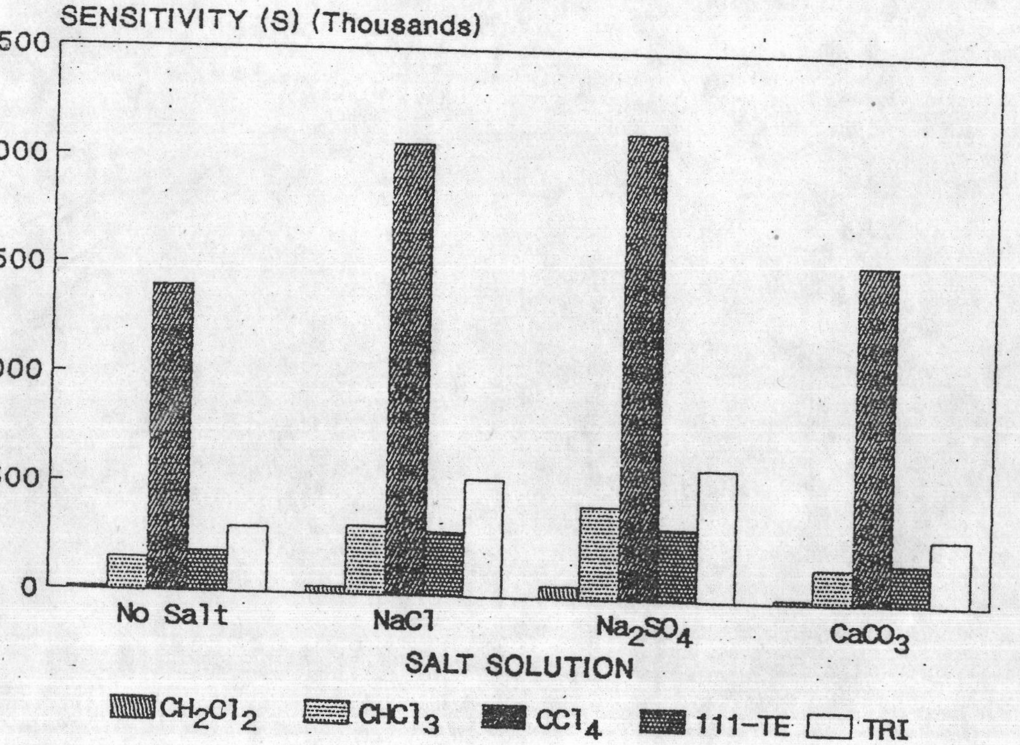


Figure 4.42 The effect of salting out on the sensitivity of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

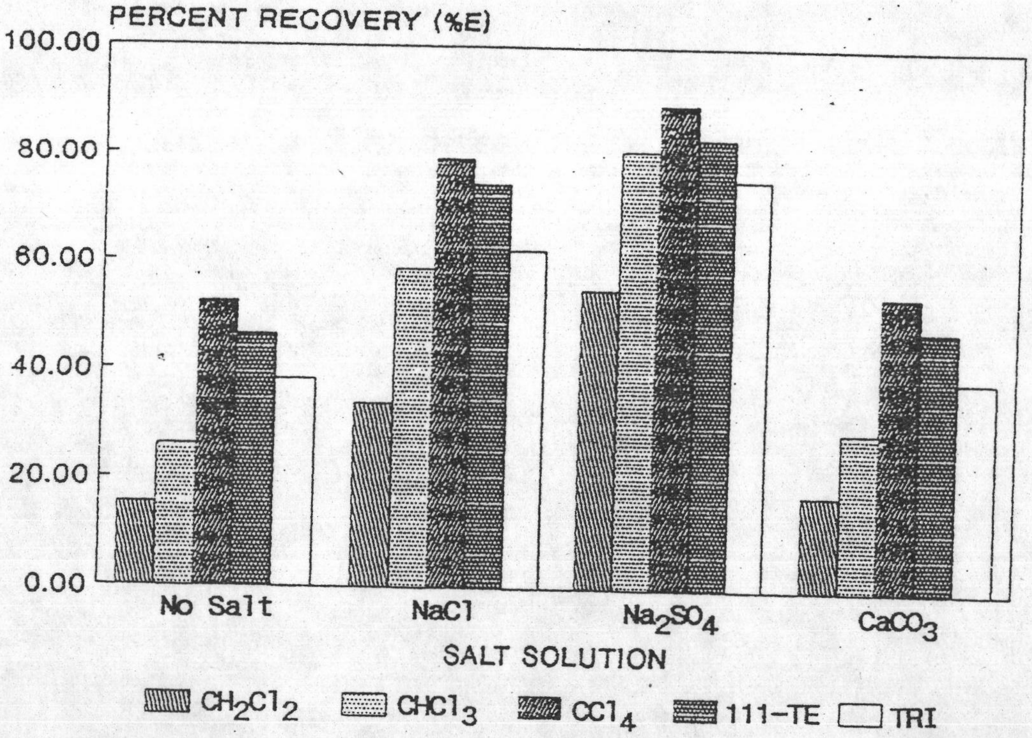


Figure 4.43 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using FID as a detector.

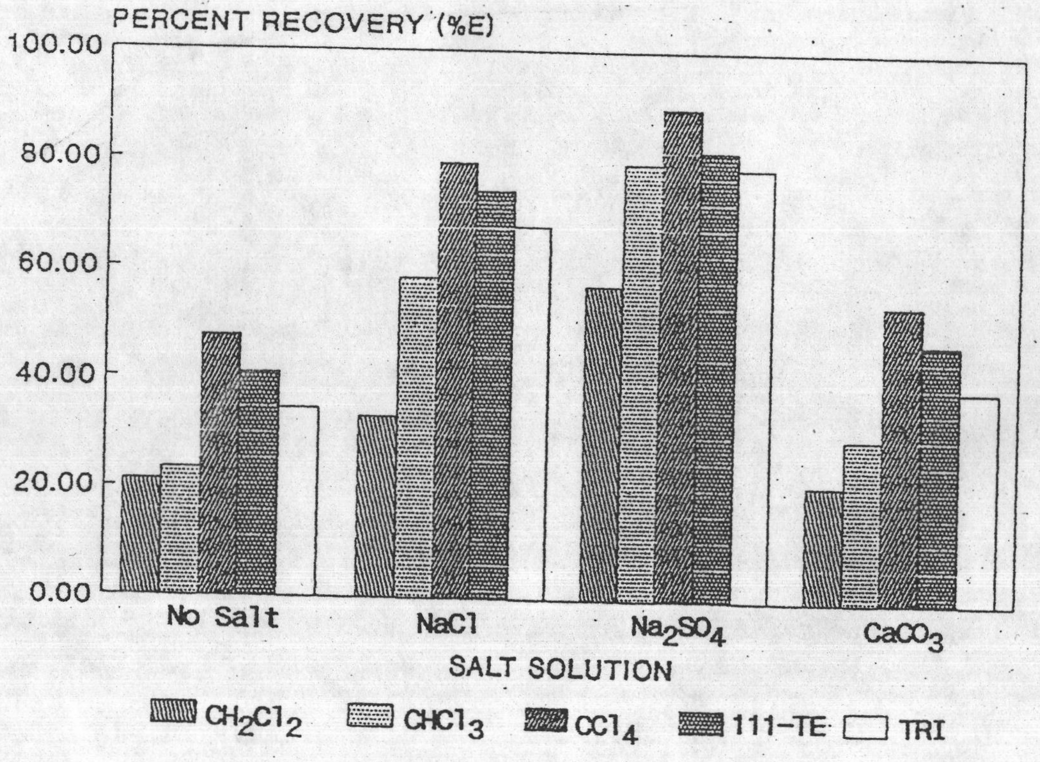


Figure 4.44 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in higher level of ppb using FID as a detector.

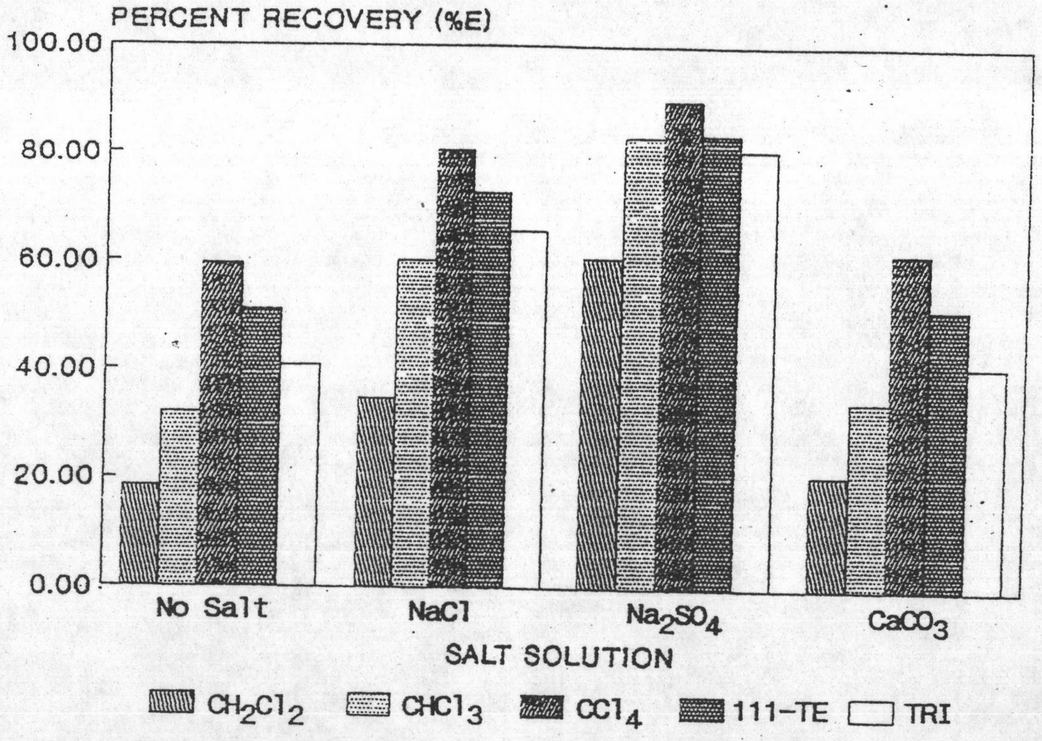


Figure 4.45 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in lower level of ppb using ECD as a detector.

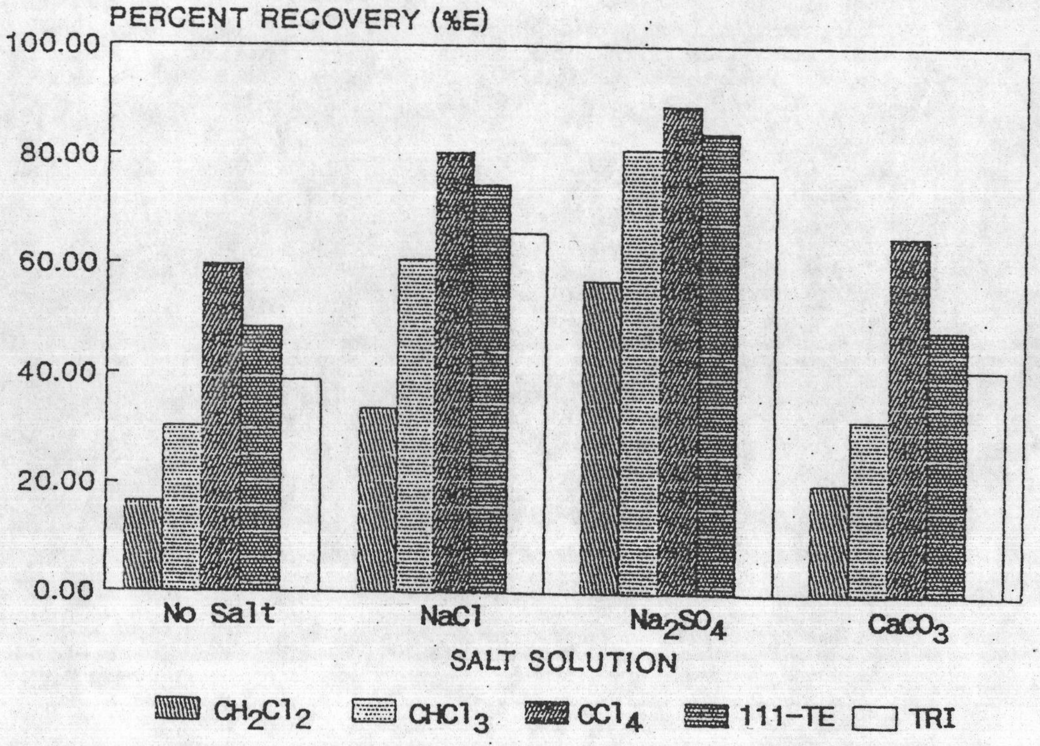


Figure 4.46 The effect of salting out on the percent recovery of each volatile chlorinated hydrocarbon in mixture solution with concentration of aqueous standard solution in higher level of ppb using ECD as a detector.

The result in Table 4.29 shows that the percent recovery of methylene chloride ranges from 54.22 to 62.43 with ± 1.56 - 4.81 % RSD, chloroform ranges from 78.53 to 84.72 with ± 1.04 - 3.70 % RSD, carbon tetrachloride ranges from 88.01 to 90.81 with ± 1.95 - 4.32 % RSD, 1,1,1-trichloroethane ranges from 81.33 to 84.35 with ± 1.48 - 3.17 % RSD and trichloroethylene ranges from 75.47 to 80.83 with ± 1.45-3.65 % %RSD. It can be summerized as follows :

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

(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.

(3) The percent recovery of each volatile chlorinated hydrocarbon in single component solution is slightly different from the percent recovery of each compound in mixture component solution.

This indicates that the percent recovery of each volatile oraganic 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 2.30. 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 on 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.

Table 4.29 The percent recovery of each volatile chlorinated hydrocarbon at two concentration levels in single and mixture solution with anhydrous sodium sulfate.

Compound	The percent recovery (% E) (% RSD)							
	Single component solution				Mixture solution			
	F I D		E C D		F I D		E C D	
	Concentration level		Concentration level		Concentration level		Concentration level	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
Methylene chloride	54.22 (±1.56)	57.55 (±1.56)	60.22 (±2.19)	58.61 (±3.16)	55.14 (±2.71)	57.33 (±2.94)	62.43 (±4.81)	57.15 (±2.20)
Chloroform	79.28 (±3.40)	78.53 (±1.04)	83.65 (±2.88)	84.72 (±3.33)	80.83 (±1.34)	79.68 (±3.64)	83.15 (±2.40)	81.16 (±3.70)
Carbon tetrachloride	89.22 (±1.95)	88.01 (±1.95)	90.81 (±3.69)	89.12 (±4.32)	89.37 (±4.10)	89.85 (±2.32)	89.95 (±4.40)	89.27 (±2.78)
1,1,1-Trichloroethane	82.38 (±2.85)	83.54 (±1.48)	81.33 (±3.17)	81.97 (±2.04)	83.20 (±1.75)	81.96 (±2.01)	83.71 (±3.49)	84.35 (±2.02)
Trichloroehylene	76.00 (±2.90)	76.81 (±2.50)	78.55 (±3.65)	78.97 (±3.31)	75.47 (±3.35)	78.85 (±3.27)	80.83 (±4.44)	76.89 (±1.45)

Triplicate analyses

Table 4.30 The sensitivity of each volatile chlorinated hydrocarbon at two concentration levels in mixture solution with anhydrous sodium sulfate.

Compound	Sensitivity (S) (% RSD)			
	F I D		E C D	
	Concentration level		Concentration level	
	Lower	Higher	Lower	Higher
Methylene chloride	33 (±2.71)	37 (±2.94)	11435 (±2.40)	11905 (±3.70)
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

4.7 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 (60). 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 3.8 is shown in Table 4.31. This condition would be used in the investigation of the accuracy and analyses of the synthetic samples. The results obtained from the minimum detectable level study of each interested compound are shown in Table 4.32.

4.8 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 described in Section 3.6.1.

The results obtained from the study are presented in Table 4.33. The percent error and the percent relative standard deviation in the determination of the concentration of each volatile orgnic compound in the synthetic unknown mixture component solution is in the range of 0.31 - 6.44 % and 0.59 - 3.34 %, respectively.

Table 4.31 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_2SO_4

Triplicate analyses

Table 4.32 The minimum detectable level of each volatile chlorinated hydrocarbon in aqueous solution.

Compound	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

Table 4.33 The result of the analysis of the synthetic unknown mixture solution.

Compound	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

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 :

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 as shown in Table 4.34. The reasons of this are that the septa, aluminum foils, aluminum caps and serum vials used in this technique can be purchased locally and also the price of a constant temperature water bath used in this study is cheaper than the one of a commercial headspace sampler used in the conventional headspace analysis technique.

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

Table 4.34 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 inn the commercial headspace sampler.

4.9 The Determination of Volatile Chlorinated Hydrocarbons in Real Water Samples.

Six water samples i.e., three samples of tap water collected from different sites, Chemistry building 3 and residence of Chulalongkorn University, and Municipal Water Authorities, and three water samples collected from Klong Prapa Samsen, Chulalongkorn University pool and the swimming pool are analyzed by the headspace analysis technique developed in this study under the optimal headspace analysis condition as shown in Table 4.31 and under GC condition as described in Table 3.8. The chromatograms of the unknown water samples after adding 2-bromo-1-chloropropane as internal standard are shown in Figure 4.48 (A) - 4.53 (A).

The retention times (t_r) of the unknown peaks obtained from the samples chromatograms are compared with the retention times of the standard mixture of the volatile chlorinated hydrocarbon peaks as shown in the chromatogram in Figure 4.47. It is found that all samples seem to have a peak with the same retention times of methylene chloride and chloroform. Morever, it seem to be that there is a small carbon tetrachloride peak appeared in all samples chromatograms and this peak however is the impurity in methanol used as solvent for the internal standard. To confirm this result, all samples are spiked with the standard mixture solution of the interested compounds in methanol and it is analyzed under the identical analysis condition. The chromatograms of the spiked samples are shown in Figures 4.48 (B) - 4.53 (B). It can be seen that all six samples having the peaks eluted at the same time as the peaks of standard methylene chloride (t_r 3.31 min.) and chloroform (t_r 4.81 min.).

Methylene chloride and chloroform in all samples are then determined by means of internal standardization methods as mentioned in section 3.6.1 and the concentration of the component are indicated in Table 4.35.

<u>Table 4.35</u> The concentration of the component in six water samples collected from several places.

No.	Sample	Concentration of the component (ppb)			
		Methylene chloride	% RSD	Chloroform	% RSD
1	Tap water from Municipal Water Authorities	78.68	± 0.66	29.58	± 0.27
2	Tap water from residence of Chulalongkorn university	67.44	± 1.72	31.86	± 1.79
3	Tab water from chemistry building 3 of Chulalongkorn university	30.53	± 1.30	29.85	± 1.35
4	Water from Klong Prapa Samsen	10.22	± 1.55	0.22	± 1.42
5	Water from Chulalongkorn university pool	50.05	± 1.11	0.32	± 1.53
6	Water from Chulalongkorn university swimming pool	448.68	± 4.57	21.15	± 4.52

Triplicate analyses

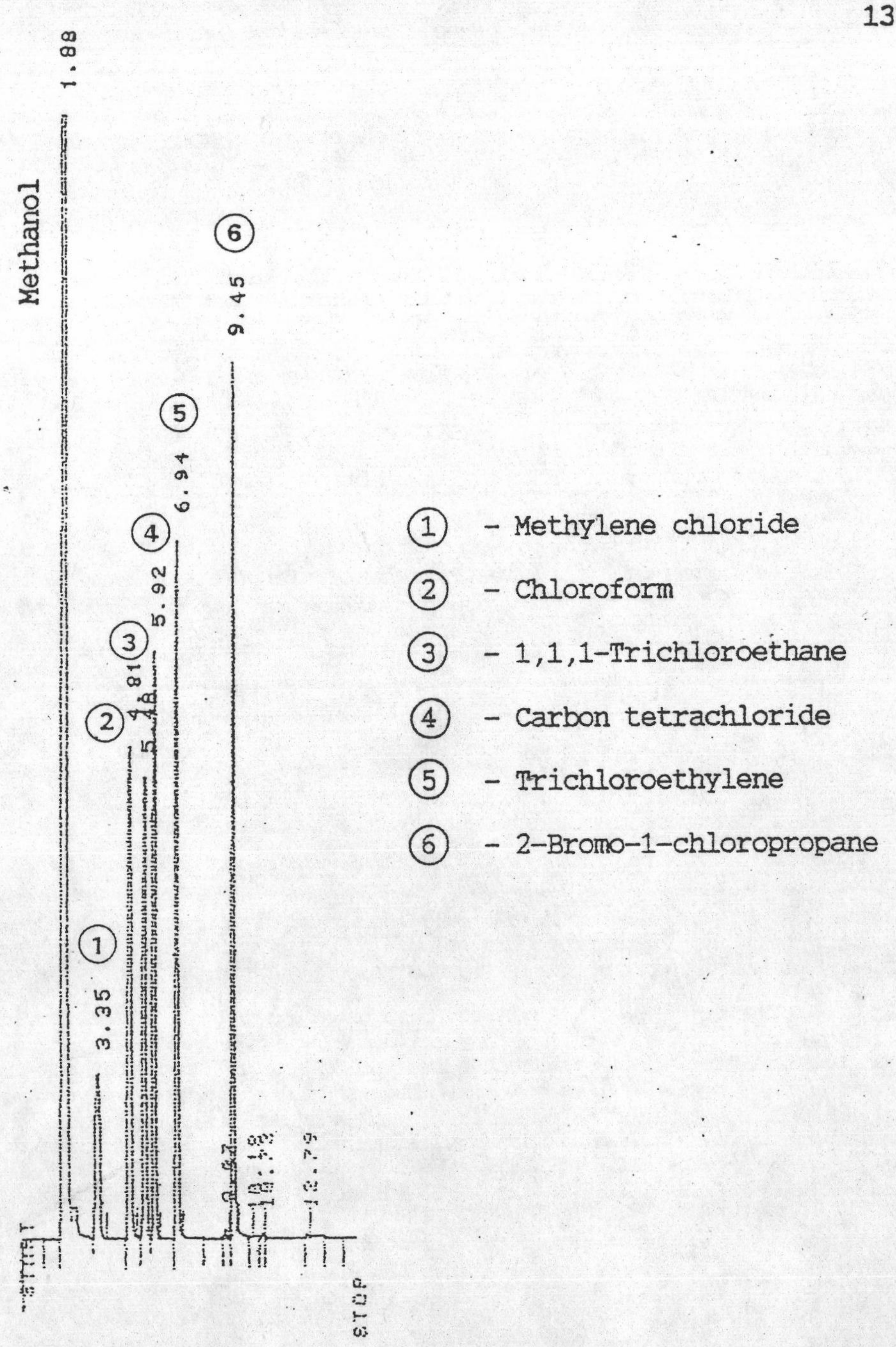
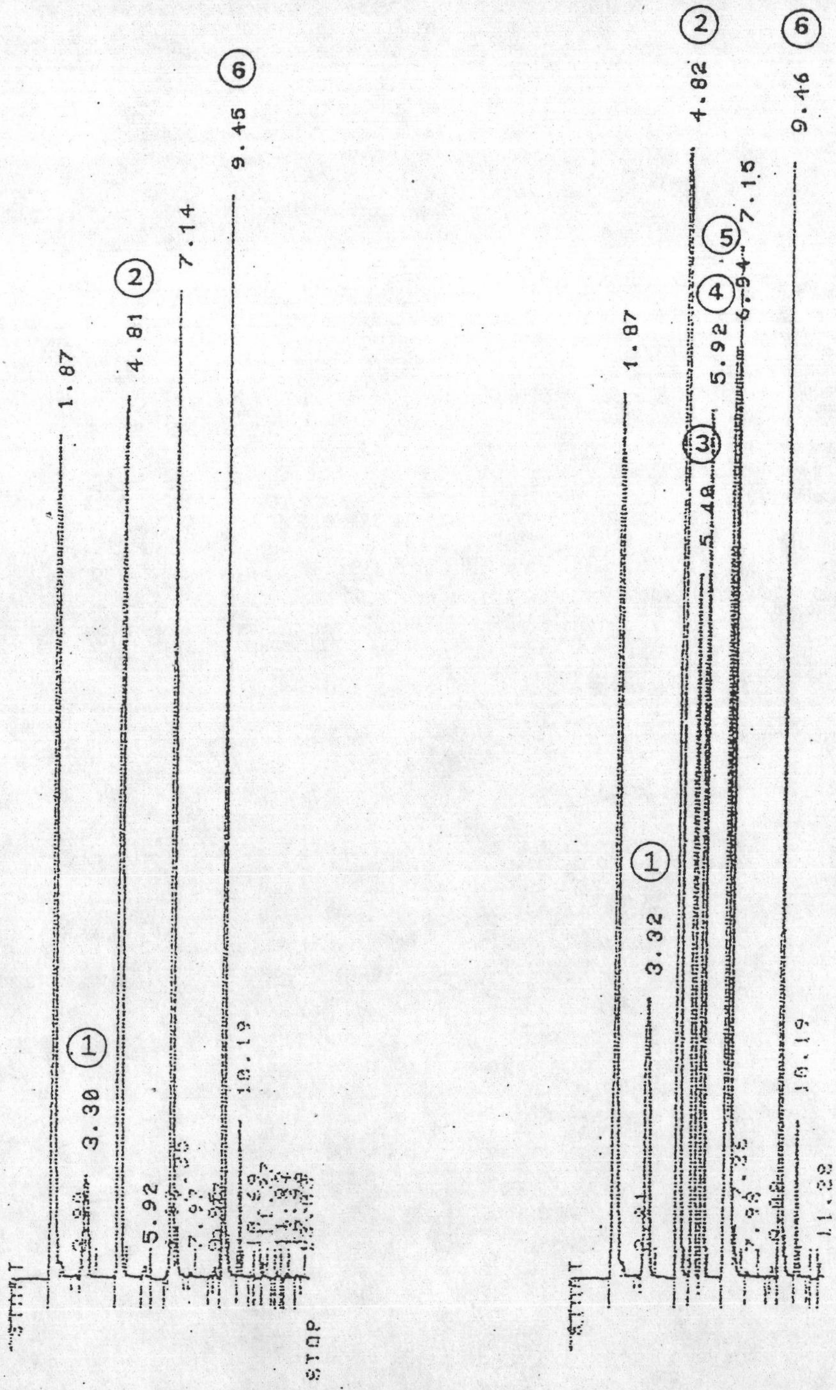


Figure 4.47 The gas chromatogram of standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 3
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.



(A)   (B)

Figure 4.48 The gas chromatogram of
(A) sample 1
(B) sample 1 + standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 5

sample 1 = tap water from Municipal Water Authorities.

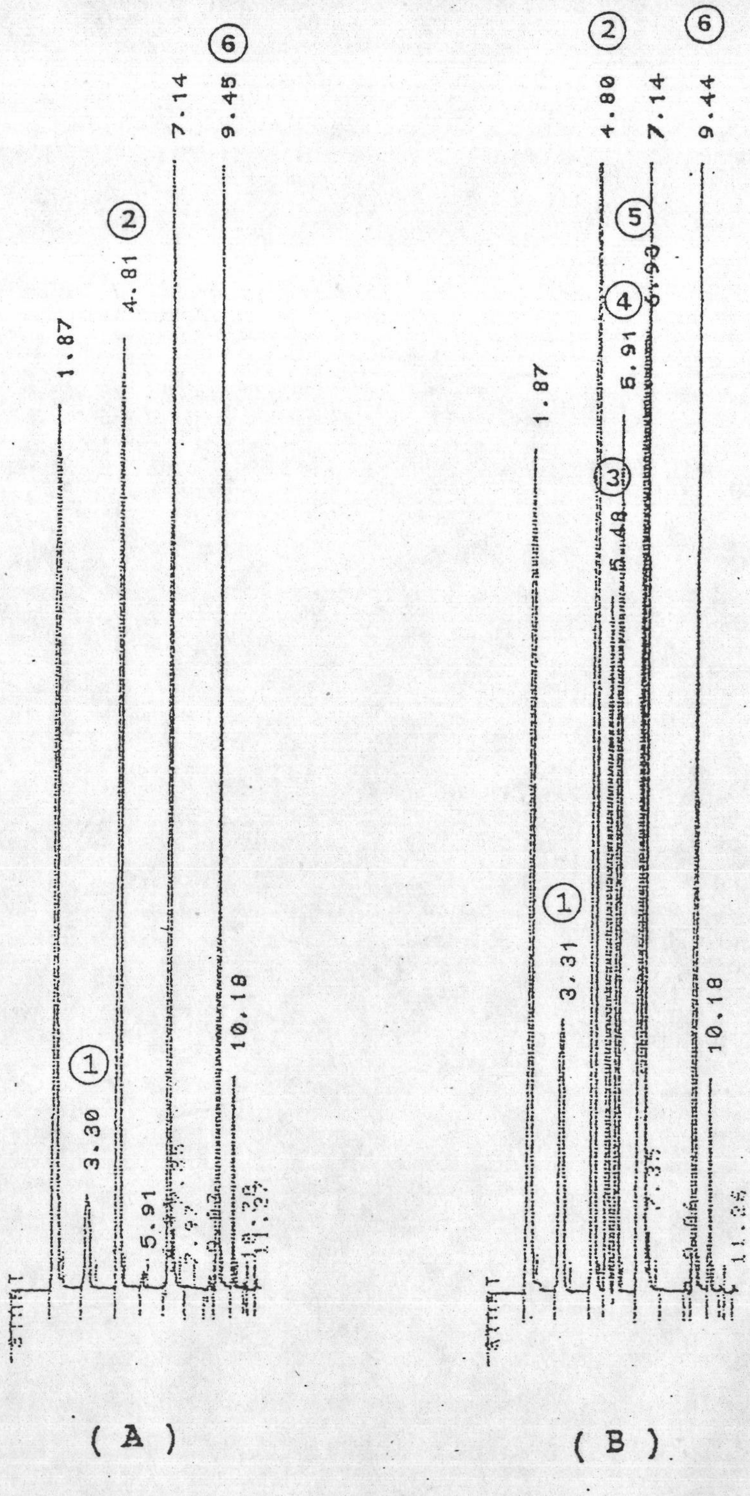
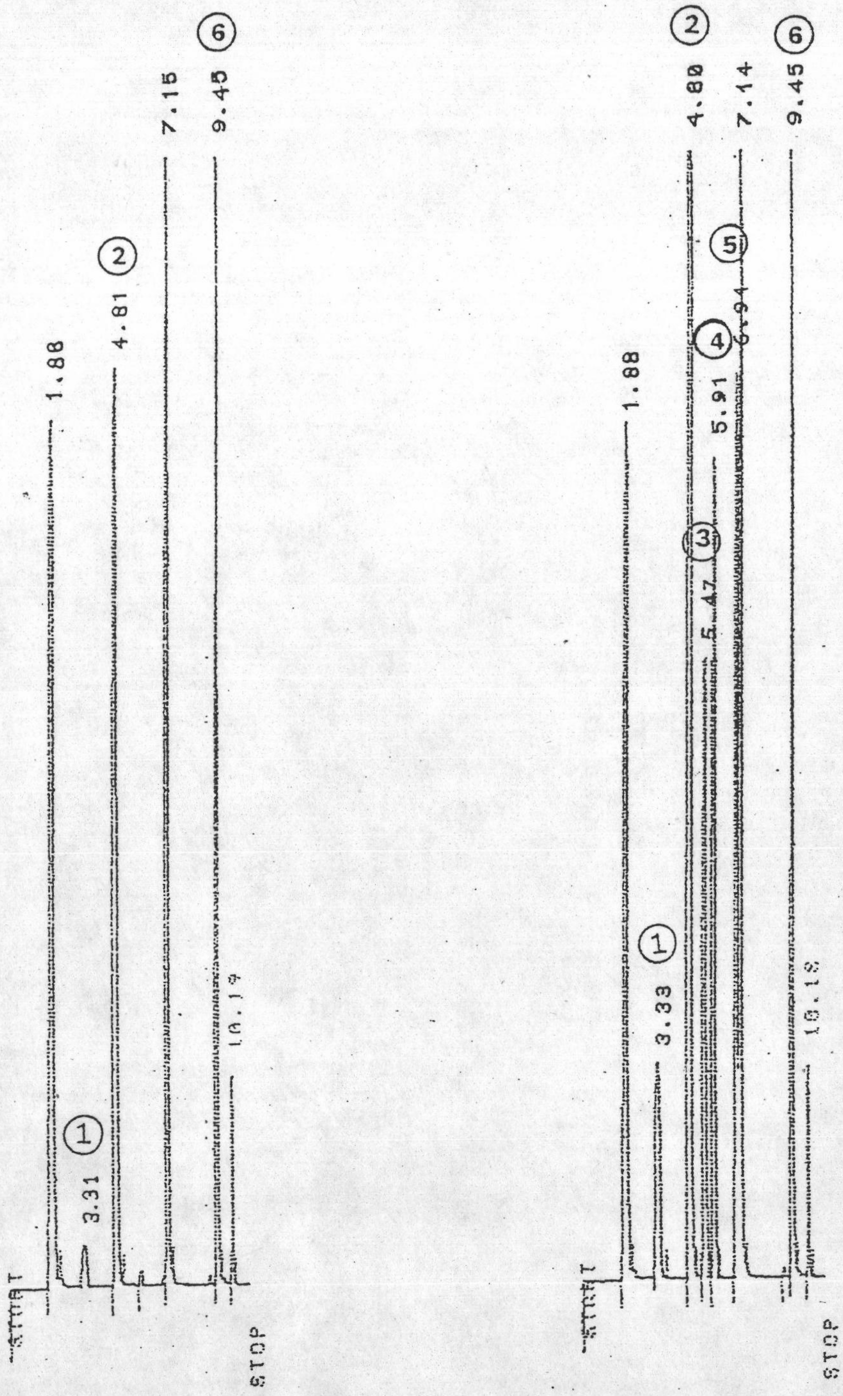


Figure 4.49 The gas chromatogram of
(A) sample 2
(B) sample 2 + standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 5

sample 2 = tap water from residence of Chulalongkorn university.



(A) (B)

Figure 4.50 The gas chromatogram of
(A) sample 3
(B) sample 3 + standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 5

sample 3 = tab water from chemistry building 3 of Chulalongkorn university.

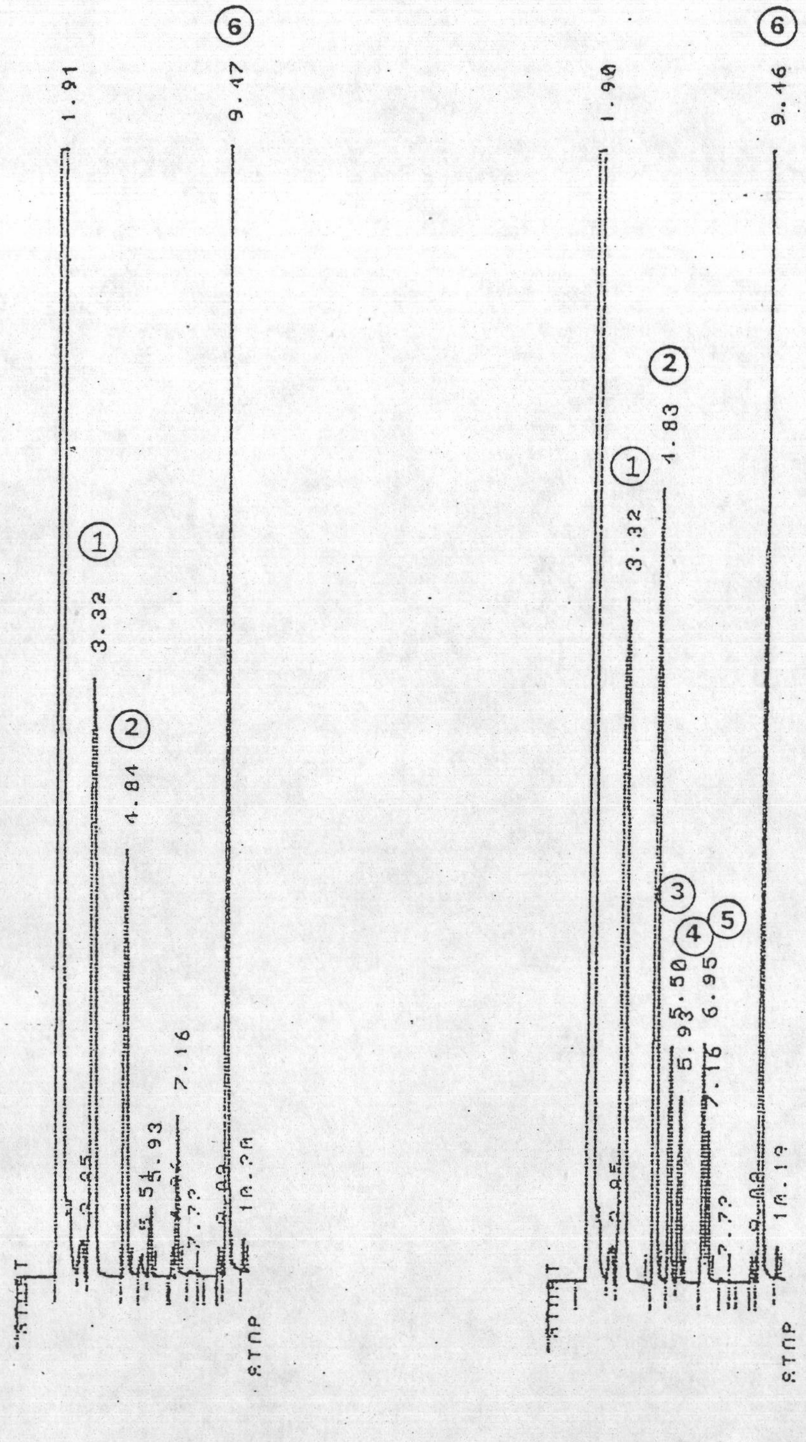
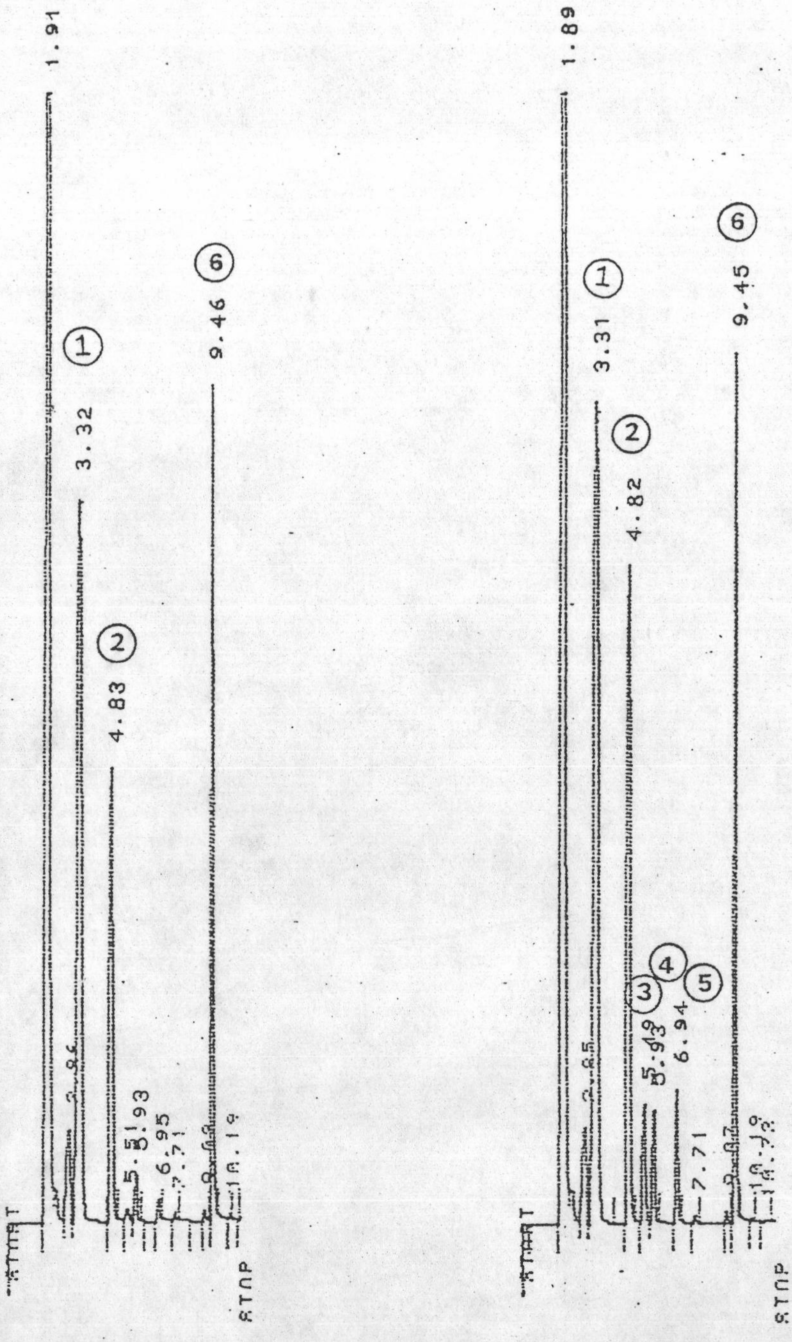


Figure 4.51 The gas chromatogram of
(A) sample 4
(B) sample 4 + standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 2

sample 4 = water from Klong Prapa Samsen



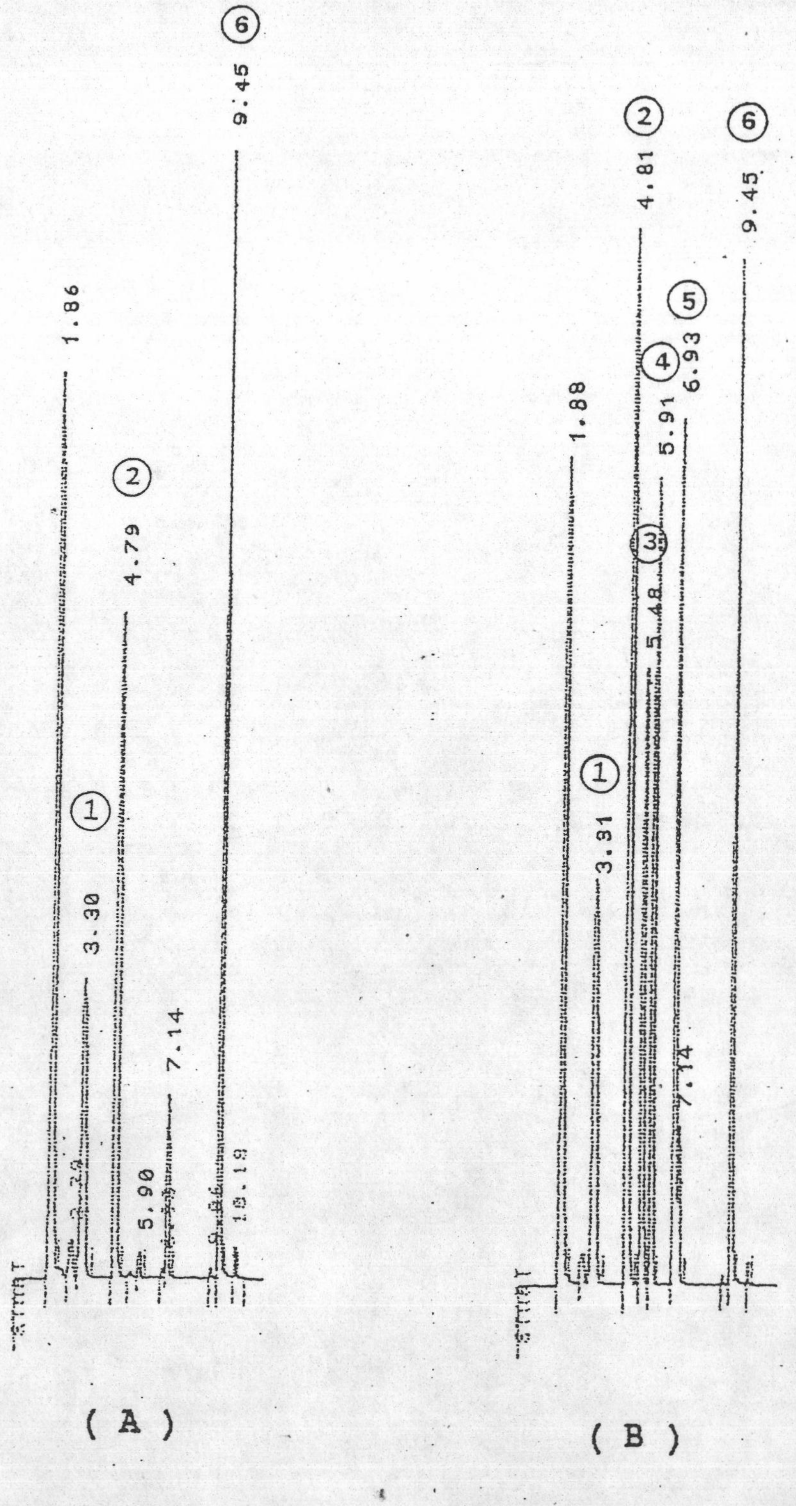
(A)

(B)

Figure 4.52 The gas chromatogram of
(A) sample 5
(B) sample 5 + standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 3

sample 5 = water from Chulalongkorn university pool.



(A)

(B)

Figure 4.53 The gas chromatogram of
(A) sample 6
(B) sample 6 + standard mixture in aqueous solution.

Condition
Headspace : described in Table 4.31
GC : described in Table 3.8
Integrator : att 5

sample 6 = water from Chulalongkorn university swimming pool.