CHAPTER 4

RESULT AND DISCUSSION

4.1 THE STUDY OF pH

The investigation of pH on % recovery of each phenolic compound ,i.e., phenol , 2-nitrophenol , 2,4-dichlorophenol , 2,4,6-trichlorophenol , and 4-chloro-3-cresol with each extracting organic solvent including methylene chloride , carbon disulfide , and hexane for the sample-to-solvent ratio of 9:1 and the concentration of 10.00 ppm of a single standard in aqueous solutions are shown in Table 4.1-4.5 and Table 4.6-4.10 are for a standard mixture in aqueous solutions. The graphs plotted between the percent recovery of each phenolic compound against the various pHs of aqueous solutions are shown in Figure 4.1 and 4.2 for the single standard in aqueous solutions and the standard mixture in aqueous solutions , respectively.

The results are shown that the optimum pH for 2-nitrophenol , 2,4-dichlorophenol , 2,4,6-trichloro-phenol is in the range of 1.0-5.0 and 1.0-9.0 is for phenol and 4-chloro-3-cresol for the single standard and standard mixture in aqueous solutions with all extracting organic solvents. Therefore, the pH of 2

would be used as the optimum pH for the microextraction studies of phenolic compounds for their highest percent recovery and to prevent certain organic compounds ,e.g. , neutral and basic organic compounds , etc. , to be extracted into the organic extract.

Table 4.1 The effect of pH on % recovery of 10.00 ppm of phenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	4.24	26.34	0.49
2	4.07	25.54	1.91
3	3.94	24.97	1.25
4	4.02	25.34	2.20
5	3.96	25.09	1.56
6	3.93	24.88	0.93
7	3.89	24.68	2.12
8	3.89	24.72	0.34
9	3.92	24.83	1.64

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	1.17	5.57	3.24
2	0.55	5.26	1.53
3	0.54	4.07	1.64
4	0.54	5.17	0.97
5	0.53	5.07	2.26
6	0.53	5.06	2.48
7	0.52	4.98	1.62
8	0.51	4.97	0.93
9	0.51	4.88	5.51

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	0.16	1.60	3.62
2	0.15	1.53	4.64
3	0.15	1.54	3.98
4	0.16	1.60	2.58
5	0.16	1.58	1.10
6	0.15	1.49	6.40
7	0.15	1.51	5.79
8	0.15	1.50	3.16
9	0.16	1.56	1.81

Triplicate analyses.

Table 4.2 The effect of pH on % recovery of 10.00 ppm of 2-nitrophenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLEME CHLORIDE

pH	K_d	%E	%RSD
1	559.41	98.13	1.39
2	386.18	96.90	1.25
3	254.38	96.90	1.11
4	201.13	94.21	1.42
5	161.27	95.88	2.28
6	629.48	97.79	1.15
7	134.72	91.89	0.84
8	23.66	66.66	1.86
9	12.21	50.81	1.24

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	43.07	81.21	2.41
2	50.65	83.69	0.21
3	52.58	83.90	3.18
4	43.82	81.60	0.82
5	45.44	82.05	1.93
6	41.54	80.76	1.23
7	33.72	77.45	0.59
8	31.99	74.15	5.15
9	2.25	18.55	4.86

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	28.64	74.37	0.47
2	29.74	75.09	4.30
3	30.57	75.62	2.55
4	29.12	74.72	6.50
5	28.95	74.58	1.53
6	26.37	72.77	0.92
7	11.95	54.58	0.96
8	9.58	49.24	3.86
9	2.45	19.87	7.69

Triplicate analyses.

Table 4.3 The effect of pH on % recovery of 10.00 ppm of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	40.21	77.25	0.81
2	39.23	76.82	1.00
3	38.19	76.34	1.08
4	39.86	77.05	1.96
5	36.16	75.35	0.86
6	33.31	73.78	1.06
7	30.76	72.19	1.52
8	18.80	61.39	0.97
9	4.51	27.61	1.07

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	69.63	23.34	0.80
2	40.75	73.23	2.50
3	26.46	72.80	1.19
4	26.40	72.78	0.75
5	26.43	72.66	2.71
6	19.90	66.32	3.87
7	20.31	67.28	0.91
8	17.76	64.26	1.19
9	5.91	37.46	0.90

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	17.72	64.23	0.31
2	17.68	64.15	1.85
3	18.82	65.60	1.92
4	17.01	63.30	0.62
5	17.51	64.07	0.91
6	16.67	62.19	2.33
7	11.39	61.12	2.80
8	7.47	53.07	0.33
9	4.52	31.39	3.36

Triplicate analyses.

Table 4.4 The effect of pH on % recovery of 10.00 ppm of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	55.73	81.88	1.63
2	48.27	79.49	3.08
3	55.35	81.72	0.61
4	48.39	79.72	0.69
5	54.67	81.46	1.90
6	21.92	64.60	8.16
7	20.73	63.18	3.67
8	27.51	42.81	6.97
9	4.10	25.66	4.25

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	42.21	78.80	2.54
2	49.99	81.12	1.24
3	50.30	81.25	0.39
4	45.68	79.80	2.59
5	44.73	79.64	0.99
6	27.43	71.71	0.31
7	13.58	56.75	2.35
8	9.77	48.83	5.05
9	4.43	29.93	2.30

(3) SOLVENT : HAXANE

pH	K_d	%E	%RSD
1	41.64	80.07	2.21
2	43.74	80.87	1.56
3	61.19	85.61	1.16
4	45.51	80.73	2.73
5	35.60	76.45	2.81
6	14.34	58.87	1.65
7	5.72	36.53	2.99
8	5.02	33.59	0.53
9	3.17	24.25	4.73

Triplicate analyses.

Table 4.5 The effect of pH on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	29.60	71.46	0.60
2	28.89	70.93	1.59
3	30.35	71.96	0.53
4	28.59	70.74	0.95
5	30.36	71.97	0.59
6	27.27	69.78	0.19
7	28.39	70.60	0.09
8	25.98	62.72	0.50
9	27.20	69.68	1.62

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	11.77	54.35	2.79
2	12.64	56.14	1.09
3	12.21	55.29	0.97
4	11.30	53.36	1.48
5	11.49	53.46	1.83
6	11.08	52.87	2.45
7	10.49	51.52	0.91
8	11.05	52.82	0.43
9	8.77	47.05	1.83

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	2.24	18.51	2.68
2	2.22	18.36	5.56
3	2.38	19.39	1.67
4	2.15	17.90	3.37
5	2.03	17.05	1.60
6	2.08	17.43	1.93
7	2.11	17.61	1.58
8	2.08	17.42	1.68
9	2.09	17.47	1.48

Triplicate analyses.

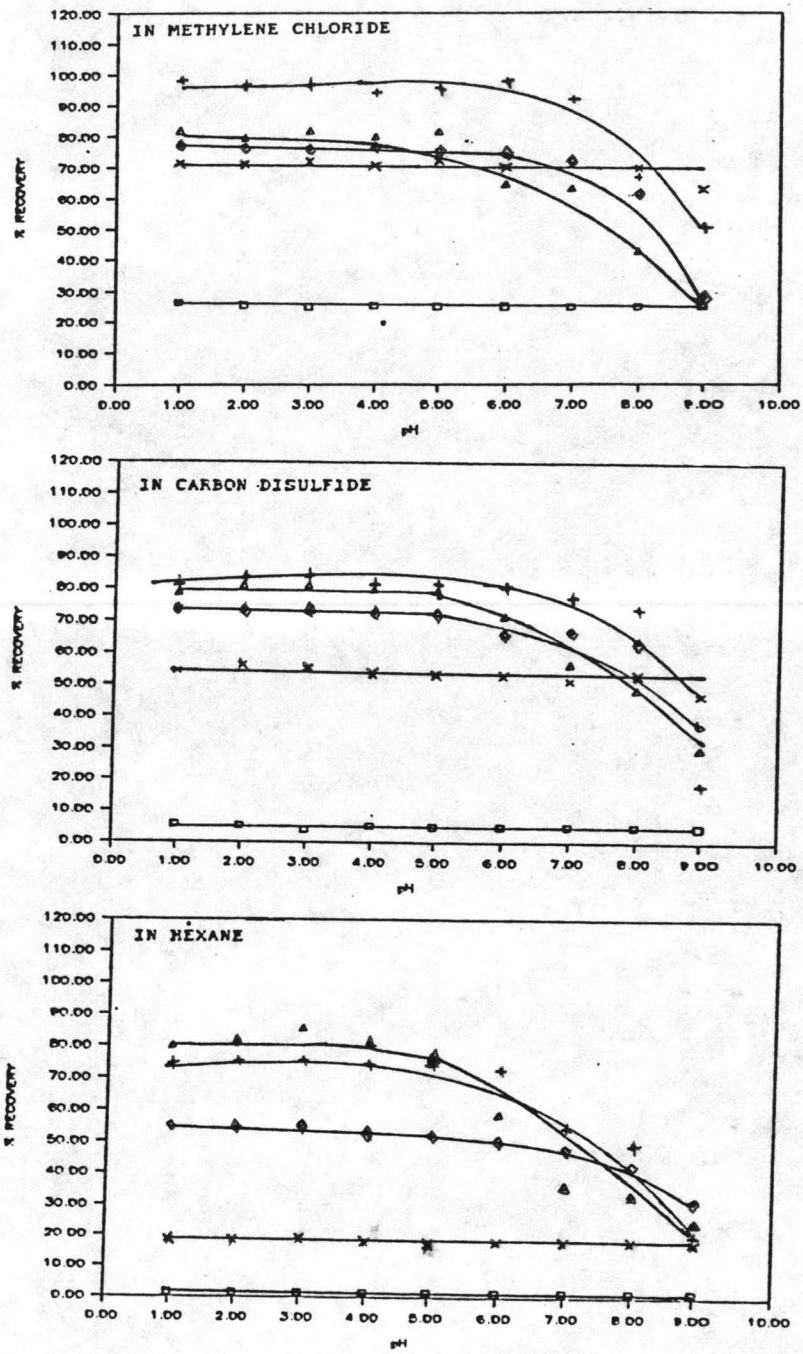


Figure 4.1 The effect of pH on % recovery of 10.00 ppm of each phenolic compounds in standard aqueous solution with the various organic solvents.

□ Phenol

\+ 2-Nitrophenol

◇ 2,4-Dichlorophenol

△ 2,4,6-Trichlorophenol

× 4-Chloro-3-cresol

Table 4.6 The effect of pH on % recovery of 10.00 ppm of phenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	4.23	26.38	1.37
2	3.88	24.73	0.20
3	3.77	24.16	0.56
4	3.54	23.05	1.51
5	3.57	23.20	1.27
6	3.46	22.66	2.64
7	3.38	22.23	0.41
8	3.30	21.81	0.66
9	3.07	20.60	1.91

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	0.88	8.14	3.11
2	0.80	7.47	1.92
3	0.80	7.47	1.66
4	0.81	7.59	2.68
5	0.81	7.56	1.83
6	0.81	7.60	2.62
7	0.78	7.33	0.36
8	0.77	7.20	1.30
9	0.78	7.35	0.54

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	0.29	2.89	3.02
2	0.29	2.81	3.48
3	0.28	2.77	1.13
4	0.28	2.72	6.64
5	0.28	2.76	0.57
6	0.27	2.70	3.07
7	0.23	2.27	5.65
8	0.26	2.54	1.85
9	0.22	2.18	2.19

Triplicate analyses.

Table 4.7 The effect of pH on % recovery of 10.00 ppm 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	196.22	94.11	1.24
2	264.17	95.96	0.33
3	185.49	93.88	0.92
4	116.12	90.20	2.65
5	107.37	89.69	2.11
6	60.86	82.03	6.16
7	28.16	70.43	0.51
8	9.75	45.17	2.34
9	3.52	22.92	5.89

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	40.80	80.50	2.60
2	40.39	80.07	3.00
3	41.67	80.61	2.65
4	40.30	80.26	1.43
5	36.58	78.42	3.52
6	24.40	71.02	3.25
7	11.38	53.54	1.75
8	5.50	35.77	1.59
9	2.99	23.21	1.83

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	34.12	77.34	2.79
2	35.83	78.22	2.58
3	33.30	77.02	2.19
4	31.56	76.17	0.59
5	28.98	74.43	2.79
6	19.33	66.14	2.13
7	10.96	52.57	2.68
8	6.22	38.64	1.98
9	1.38	12.27	4.11

Triplicate analyses.

Table 4.8 The effect of pH on % recovery of 10.00 ppm of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	53.54	81.86	1.32
2	58.19	83.06	0.18
3	50.66	81.06	0.76
4	39.55	76.92	1.59
5	40.34	77.21	2.15
6	30.63	71.42	6.14
7	24.10	67.10	0.30
8	11.83	50.03	0.67
9	4.92	29.41	5.37

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	37.33	78.85	2.75
2	43.63	81.21	3.03
3	44.78	81.68	2.61
4	46.30	82.40	0.88
5	41.16	80.43	2.64
6	35.99	78.36	2.05
7	22.94	69.90	0.97
8	13.59	57.90	1.50
9	7.87	44.34	1.29

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	19.60	66.39	2.98
2	19.68	66.55	2.02
3	18.88	65.64	1.82
4	17.87	64.40	1.12
5	17.17	63.45	2.15
6	17.03	63.21	3.12
7	12.70	56.24	1.77
8	10.40	51.28	1.74
9	3.07	23.75	0.93

Triplicate analyses.

Table 4.9 The effect of pH on % recovery of 10.00 ppm of 2,4,6-trichlorophenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	78.80	86.91	0.88
2	94.54	88.82	0.95
3	86.57	87.57	0.94
4	51.79	81.37	1.12
5	61.88	83.50	3.12
6	30.22	71.48	4.57
7	6.03	67.10	3.55
8	1.18	50.03	0.67
9	4.92	29.41	5.37

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	50.86	83.60	1.82
2	69.47	86.98	3.15
3	69.70	86.73	3.73
4	72.90	88.07	0.19
5	70.96	87.47	2.29
6	25.09	71.22	5.76
7	8.03	44.86	0.99
8	3.67	27.07	3.83
9	2.46	19.92	0.97

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	80.16	88.11	3.43
2	86.12	89.29	2.85
3	68.46	87.29	1.39
4	57.11	85.24	0.76
5	45.88	81.51	4.43
6	9.35	48.37	7.64
7	5.41	35.36	5.29
8	2.08	17.38	1.87
9	0.15	1.52	0.48

Triplicate analyses.

Table 4.10 The effect of pH on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

pH	K_d	%E	%RSD
1	46.75	79.79	0.87
2	48.54	80.41	0.51
3	45.09	79.18	1.35
4	34.16	74.22	1.79
5	37.00	75.48	3.51
6	30.68	71.81	4.72
7	31.10	72.46	0.56
8	30.69	72.18	1.04
9	27.95	70.24	1.52

(2) SOLVENT : CARBON DISULFIDE

pH	K_d	%E	%RSD
1	18.97	65.74	3.15
2	19.39	62.56	0.92
3	19.71	64.25	0.57
4	19.90	64.31	1.02
5	19.85	65.87	0.37
6	19.95	65.54	0.84
7	19.34	62.30	0.46
8	18.98	60.44	0.81
9	18.92	60.20	1.47

(3) SOLVENT : HEXANE

pH	K_d	%E	%RSD
1	2.76	21.87	3.27
2	2.56	20.56	1.60
3	2.61	20.89	2.29
4	2.48	20.05	4.56
5	2.47	20.01	4.40
6	2.42	19.66	2.99
7	2.21	18.27	2.75
8	2.33	19.10	2.36
9	2.15	17.90	3.32

Triplicate analyses.

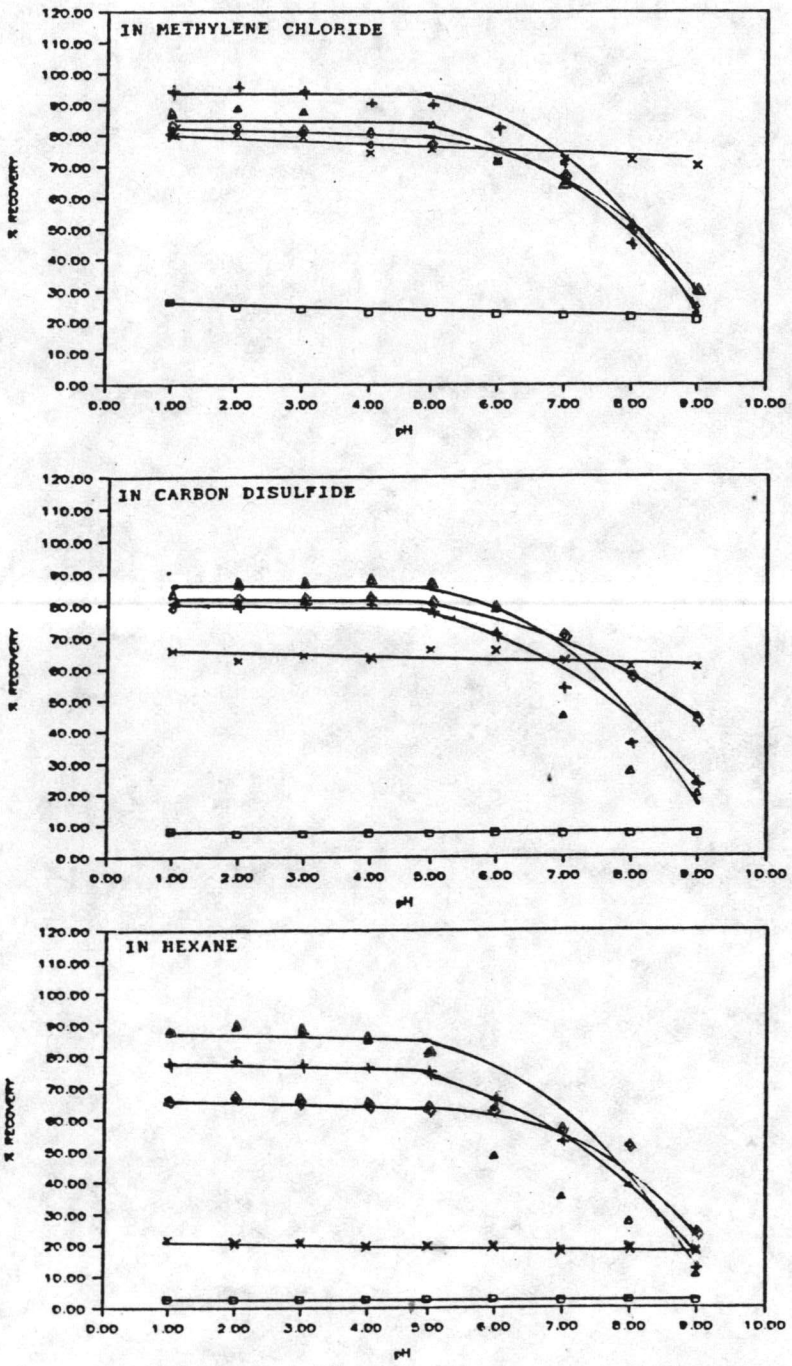


Figure 4.2 The effect of pH on % recovery of 10.00 ppm of each phenolic compounds in standard mixture aqueous solution with the various organic solvents.

□ Phenol

\+ 2-Nitrophenol

◇ 2,4-Dichlorophenol

△ 2,4,6-Trichlorophenol

× 4-Chloro-3-cresol

4.2 THE STUDY OF THE SHAKING TIME

The results of the study of the equilibration time for each phenolic compound , i.e. , phenol , 2-nitrophenol , 2,4-dichlorophenol , 2,4,6-trichlorophenol , and 4-chloro-3-cresol obtained from the procedure in the experimental section 3.3.2 are shown in Table 4.11-4.15 for the single standard in aqueous solutions and Table 4.16 - 4.20 for the standard mixture in aqueous solutions. The graphs plotted the shaking time against the percent recovery of each phenolic compound are depicted in the Figure 4.3 and Figure 4.4 ,respectively.

It is found that phenol reaches equilibrium at 5 min and 2-nitrophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol , and 4-chloro-3-cresol are in equilibrium at 15 min for methylene chloride , carbon disulfide , and hexane. Therefore , the optimum shaking time for the compounds studied would be 20 min to ensure that the system would be completely in equilibrium.

Table 4.11 The effect of shaking time on % recovery of 10.00 ppm of phenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	3.56	23.06	4.81
10	3.65	23.49	1.77
15	3.67	23.59	1.76
20	3.73	23.87	4.50
25	3.65	23.50	0.44
30	3.71	23.80	0.59

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	0.61	5.84	1.95
10	0.63	6.02	2.45
15	0.62	5.94	2.80
20	0.63	5.98	2.43
25	0.62	5.90	5.92
30	0.62	5.89	9.03

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	0.16	1.60	4.51
10	0.17	1.72	0.82
15	0.17	1.68	3.90
20	0.18	1.76	9.72
25	0.17	1.72	7.40
30	0.18	1.74	1.71

Triplicate analyses.

Table 4.12 The effect of shaking time on % recovery of 10.00 ppm of 2-nitrophenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	88.55	88.25	4.36
10	131.49	91.56	1.63
15	279.97	94.89	3.40
20	747.73	97.11	2.30
25	432.82	97.25	0.66
30	615.39	97.04	1.96

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	22.60	69.60	6.18
10	31.39	75.95	2.73
15	45.00	82.01	0.48
20	43.58	81.52	0.67
25	45.07	82.00	1.10
30	45.22	82.07	0.63

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	24.34	71.17	0.35
10	26.64	72.99	0.67
15	28.06	74.02	0.31
20	28.81	74.50	1.23
25	26.48	72.81	2.53
30	30.72	75.67	1.98

Triplicate analyses.

Table 4.13 The effect of shaking time on % recovery of 10.00 ppm of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	19.98	62.78	1.97
10	34.48	74.45	0.98
15	36.64	75.60	0.61
20	36.92	75.74	0.44
25	36.42	75.49	0.39
30	37.15	75.86	0.27

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	9.81	49.84	0.86
10	22.24	69.25	0.88
15	27.32	73.44	0.72
20	27.15	73.35	0.02
25	17.84	73.00	1.76
30	28.28	74.09	1.41

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	11.67	50.59	0.91
10	11.96	54.10	4.27
15	11.41	53.53	3.81
20	11.43	53.64	2.08
25	11.88	52.42	1.10
30	11.40	53.56	2.03

Triplicate analyses.

Table 4.14 The effect of shaking time on % recovery of 10.00 ppm of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	26.85	68.92	1.64
10	42.16	77.49	0.27
15	42.09	77.46	0.21
20	45.68	78.77	1.49
25	44.96	78.52	1.39
30	44.31	78.30	1.01

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	15.00	57.69	2.94
10	30.62	73.84	0.67
15	39.87	77.61	1.14
20	46.34	80.11	0.13
25	53.39	82.11	0.65
30	38.98	77.79	0.18

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	30.66	74.97	2.58
10	41.14	80.00	0.40
15	45.04	81.34	0.94
20	48.05	82.05	3.08
25	44.35	80.94	2.95
30	41.73	80.23	0.26

Triplicate analyses.

Table 4.15 The effect of shaking time on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	19.61	62.39	0.78
10	30.38	71.79	1.14
15	32.55	73.60	0.42
20	32.48	73.32	0.38
25	30.60	72.84	2.11
30	30.87	73.41	0.51

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	6.37	39.20	1.09
10	9.40	48.75	2.74
15	10.21	50.84	3.46
20	15.03	53.52	0.49
25	10.53	51.61	1.34
30	10.57	51.72	0.81

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	2.09	17.40	0.33
10	2.17	17.99	1.45
15	2.24	18.54	1.83
20	2.27	18.68	1.35
25	2.21	18.61	1.56
30	2.26	18.61	1.56

Triplicate analyses.

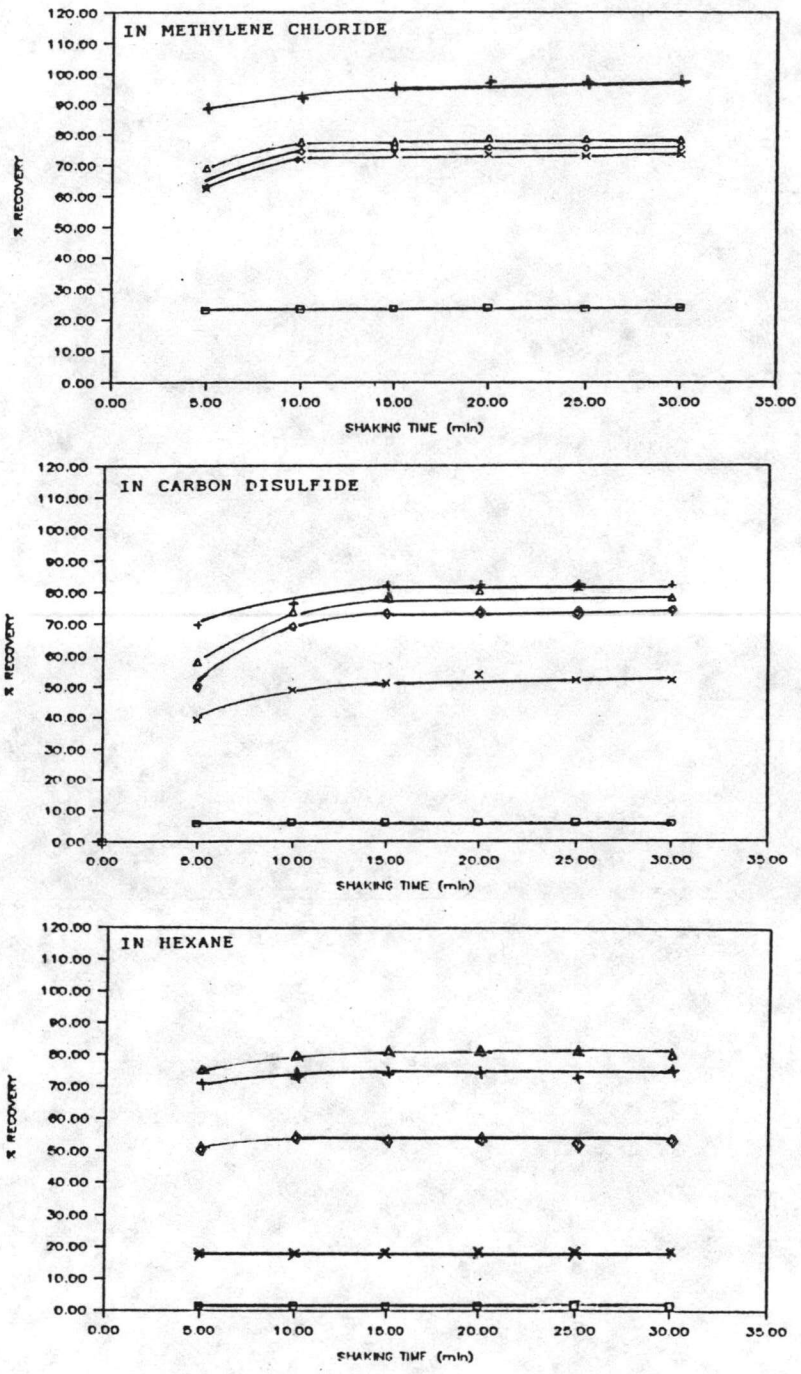


Figure 4.3 The effect of shaking time on % recovery of 10.00 ppm of each phenolic compounds in standard aqueous solution with the various organic solvents.

□ Phenol

\+ 2-Nitrophenol

◇ 2,4-Dichlorophenol

△ 2,4,6-Trichlorophenol

× 4-Chloro-3-cresol

Table 4.16 The effect of shaking time on % recovery of 10.00 ppm of phenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	4.15	25.99	3.71
10	4.47	27.46	3.34
15	4.39	27.10	3.10
20	4.43	27.26	3.04
25	4.26	26.50	1.90
30	4.59	27.94	1.35

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	0.81	7.57	7.37
10	0.87	8.09	9.67
15	0.85	7.89	7.79
20	0.86	8.01	6.99
25	0.85	7.96	2.11
30	0.87	8.08	1.49

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	0.27	2.70	7.04
10	0.31	3.08	6.05
15	0.28	2.75	1.65
20	0.26	2.59	5.36
25	0.26	2.60	2.91
30	0.29	2.83	8.87

Triplicate analyses.

Table 4.17 The effect of shaking time on % recovery of 10.00 ppm of 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	282.00	95.06	2.61
10	2946.67	99.60	5.67
15	*	100.62	2.92
20	*	101.54	2.09
25	236.14	94.55	2.02
30	*	101.10	0.95

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	22.23	69.04	3.77
10	24.35	75.05	4.17
15	29.85	79.87	2.07
20	43.04	81.35	2.50
25	44.48	81.84	5.84
30	56.29	83.50	1.91

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	23.99	70.80	1.72
10	27.79	73.76	1.16
15	29.85	75.05	2.07
20	30.88	75.72	1.52
25	33.23	77.00	1.99
30	31.55	76.14	1.18

Triplicate analyses.

Table 4.18 The effect of shaking time on % recovery of 10.00 ppm of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	49.17	80.40	2.55
10	86.52	87.45	3.02
15	80.41	86.54	3.29
20	83.16	87.19	2.39
25	52.43	81.45	2.07
30	81.91	87.33	0.99

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	42.80	80.45	4.24
10	52.06	83.16	5.01
15	49.22	83.09	2.27
20	54.11	84.30	2.56
25	65.52	84.88	7.03
30	68.27	87.19	1.67

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	15.26	60.72	0.95
10	16.74	62.90	0.92
15	17.92	64.45	1.54
20	17.60	64.05	1.31
25	18.37	62.90	2.44
30	17.83	64.33	1.61

Triplicate analyses.

Table 4.19 The effect of shaking time on % recovery of 10.00 ppm of 2,4,6 - trichlorophenol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	76.79	86.25	2.78
10	166.42	92.46	3.91
15	195.90	91.83	4.30
20	137.62	91.57	2.25
25	76.01	86.29	2.05
30	145.33	92.41	0.78

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	62.54	85.68	3.96
10	84.57	88.45	4.49
15	84.93	89.55	0.74
20	87.58	88.68	4.65
25	180.05	91.10	1.78
30	127.99	92.52	1.81

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	43.19	81.22	2.27
10	51.91	83.57	1.70
15	70.63	87.58	1.64
20	65.61	86.74	1.76
25	74.47	88.11	1.78
30	69.47	87.37	1.81

Triplicate analyses.

Table 4.20 The effect of shaking time on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

(1) SOLVENT : METHYLENE CHLORIDE

Time (min)	K_d	%E	%RSD
5	46.11	79.46	2.12
10	61.69	83.60	3.02
15	61.95	83.35	3.69
20	59.45	83.24	2.10
25	43.61	83.56	1.94
30	67.12	84.64	2.80

(2) SOLVENT : CARBON DISULFIDE

Time (min)	K_d	%E	%RSD
5	17.46	63.56	5.34
10	20.34	64.53	8.17
15	18.27	66.33	5.94
20	22.23	69.22	1.50
25	22.09	68.91	3.67
30	22.60	69.58	1.06

(3) SOLVENT : HEXANE

Time (min)	K_d	%E	%RSD
5	2.85	22.38	5.22
10	3.20	24.72	0.67
15	2.99	23.30	1.68
20	2.88	22.58	1.61
25	2.81	22.14	3.83
30	3.22	24.60	5.96

Triplicate analyses.

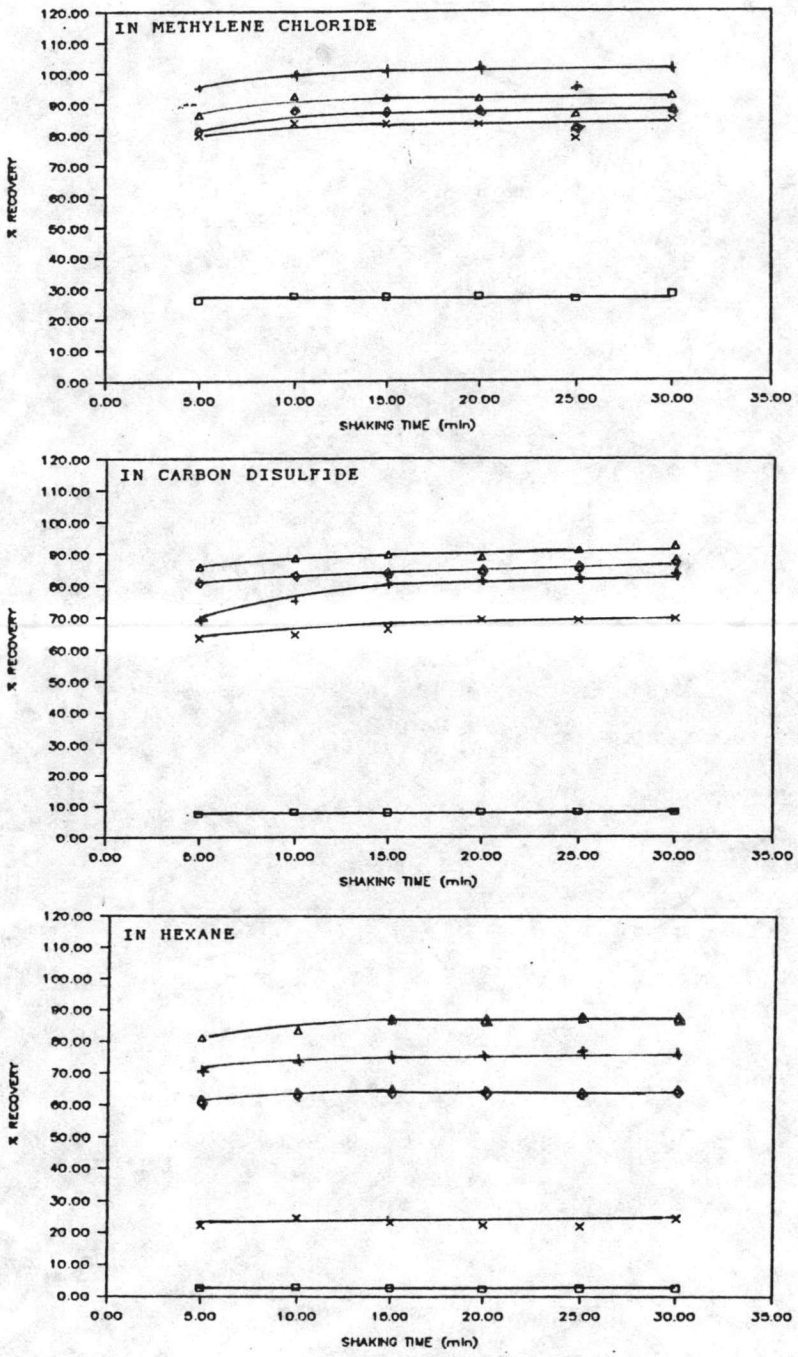


Figure 4.4 The effect of shaking time on % recovery of 10.00 ppm of each phenolic compounds in standard mixture aqueous solution with the various organic solvents.

- ▭ Phenol
- \+ 2-Nitrophenol
- ◇ 2,4-Dichlorophenol
- △ 2,4,6-Trichlorophenol
- × 4-Chloro-3-cresol

4.3 THE SALTING OUT EFFECT

The salting out effect on the percent recovery of each phenolic compound ,i.e., phenol , 2-nitrophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-chloro-3-cresol by adding 2.00 g of sodium chloride and 2.00 g of anhydrous sodium sulfate at the two different concentration ,i.e. , 1.00 and 10.00 ppm. The results obtained from the studies of salting out effect are compared with non salting out for each extracting organic solvent ,i.e., methylene chloride, carbon disulfide , and hexane and for each sample-to-solvent ratio ,i.e., 9:1 , 5:5 , 2:8 as can be seen from Table 4.21-4.25 and Table 4.26-4.30. The graphs correlated to these results are shown in Figure 4.5A-4.9B and Figure 4.10A-4.14B for the single standard and standard mixture in aqueous solutions , respectively.

It is found that the percent recovery , %E , of each phenolic compound for the sample-to-solvent ratios of 9:1 , 5:5 , 2:8 and for each organic solvent, i.e. , methylene chloride , carbon disulfide , and hexane is increased by adding sodium chloride or anhydrous sodium sulfate. This means that the salting out with sodium chloride and anhydrous sodium sulfate has the effect on percent recovery of each phenolic compound in each extracting organic solvent and each sample-to-solvent ratio. However , the addition of

anhydrous sodium sulfate yields the highest percent recovery of each phenolic compound for the single standard and standard mixture in aqueous solutions , especially phenol and 4-chloro-3-cresol than sodium chloride and non salting out do , respectively , as can be seen from Table 4.21-4.30. The reason is that anhydrous sodium sulfate added into the solutions results in higher ionic strength than the sodium chloride and non salting out do. Therefore , anhydrous sodium sulfate would be the most appropriated salt for the microextraction of these compounds in water samples.

Table 4.21 The effect of salting out on % recovery of phenol in standard aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	4.33	25.89	2.88
		NaCl	11.62	54.73	0.83
		Na_2SO_4	16.39	62.58	0.25
	5:5	No salt	2.79	71.03	1.10
		NaCl	10.80	88.34	3.56
		Na_2SO_4	20.03	92.95	2.22
	2:8	No salt	3.85	92.45	7.47
		NaCl	23.55	97.62	5.79
		Na_2SO_4	*	101.00	6.38
CS_2	9:1	No salt	0.64	6.03	2.48
		NaCl	2.51	21.61	0.85
		Na_2SO_4	7.58	43.44	3.38
	5:5	No salt	0.59	35.72	2.13
		NaCl	6.34	83.69	0.73
		Na_2SO_4	9.20	87.17	2.56
	2:8	No salt	0.84	75.36	8.94
		NaCl	1.34	81.19	7.31
		Na_2SO_4	5.20	92.63	7.10
HEXANE	9:1	No salt	0.17	1.66	2.76
		NaCl	0.66	6.82	4.79
		Na_2SO_4	2.13	17.74	2.19
	5:5	No salt	0.19	15.11	4.72
		NaCl	2.82	73.18	5.81
		Na_2SO_4	4.51	87.40	2.74
	2:8	No salt	0.22	45.88	5.19
		NaCl	1.35	84.40	4.58
		Na_2SO_4	2.15	89.90	8.85

Note : 1. * can not be calculated due to the experimental concentration of phenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	3.71	23.67	0.38
		NaCl	12.44	57.74	1.54
		Na_2SO_4	15.65	62.03	1.09
	5:5	No salt	2.71	69.53	0.68
		NaCl	10.35	87.85	2.92
		Na_2SO_4	14.38	92.49	4.40
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	0.53	5.04	3.23
		NaCl	1.94	17.39	2.21
		Na_2SO_4	5.73	38.87	2.36
	5:5	No salt	0.80	42.52	7.83
		NaCl	3.61	75.52	5.87
		Na_2SO_4	6.35	83.43	2.79
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
	5:5	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.22 The effect of salting out on % recovery of 2-nitrophenol in standard aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	243.66	95.37	0.16
		NaCl	324.22	97.23	1.34
		Na_2SO_4	1276.29	99.84	0.17
	5:5	No salt	54.01	97.65	1.09
		NaCl	*	100.12	0.49
		Na_2SO_4	*	100.44	0.20
	2:8	Na salt	*	100.51	1.38
		NaCl	*	100.23	2.57
		Na_2SO_4	*	101.93	3.15
CS_2	9:1	No salt	48.52	83.07	1.00
		NaCl	117.55	92.70	1.25
		Na_2SO_4	219.77	95.86	1.13
	5:5	No salt	9.15	89.65	1.16
		NaCl	19.14	95.19	2.66
		Na_2SO_4	*	102.04	0.08
	2:8	No salt	3.78	93.19	1.62
		NaCl	*	100.42	6.39
		Na_2SO_4	*	101.78	6.91
HEXANE	9:1	No salt	28.04	73.95	2.84
		NaCl	34.76	79.43	0.10
		Na_2SO_4	42.37	82.47	0.64
	5:5	No salt	9.49	89.57	1.58
		NaCl	18.23	92.34	1.86
		Na_2SO_4	*	94.25	0.72
	2:8	No salt	4.81	97.92	7.51
		NaCl	20.58	98.97	1.33
		Na_2SO_4	*	101.53	5.06

Note : 1. * can not be calculated due to the experimental concentration of 2-nitrophenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	211.63	94.71	0.26
		NaCl	216.00	96.01	1.57
		Na_2SO_4	464.74	98.00	2.33
	5:5	No salt	29.58	96.39	0.69
		NaCl	42.57	97.33	1.94
		Na_2SO_4	51.63	99.39	1.42
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	91.30	89.24	5.02
		NaCl	93.30	91.22	0.13
		Na_2SO_4	147.37	93.30	1.09
	5:5	No salt	25.13	96.37	0.80
		NaCl	27.57	98.17	4.18
		Na_2SO_4	81.30	98.85	3.26
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	28.05	73.97	0.58
		NaCl	47.61	84.61	3.59
		Na_2SO_4	64.15	87.71	5.27
	5:5	No salt	16.02	91.37	5.74
		NaCl	88.08	97.55	2.97
		Na_2SO_4	*	103.52	0.31
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2-nitrophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.23 The effect of salting out on % recovery of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	36.63	75.59	0.75
		NaCl	88.65	90.60	1.40
		Na_2SO_4	109.39	92.38	2.95
	5:5	No salt	10.74	90.68	2.47
		NaCl	89.16	96.54	3.49
		Na_2SO_4	84.40	97.78	2.51
	2:8	No salt	14.14	97.45	4.47
		NaCl	4.02	98.99	3.44
		Na_2SO_4	19.40	99.57	2.29
CS_2	9:1	No salt	25.01	71.58	2.53
		NaCl	68.86	88.23	1.71
		Na_2SO_4	135.61	89.17	5.65
	5:5	Na salt	5.00	86.24	1.03
		NaCl	7.87	88.66	1.00
		Na_2SO_4	11.37	91.91	0.27
	2:8	No salt	5.53	95.29	0.77
		NaCl	*	100.49	3.22
		Na_2SO_4	*	101.85	0.19
HEXANE	9:1	No salt	12.33	55.46	3.43
		NaCl	33.53	78.45	3.61
		Na_2SO_4	55.17	84.65	4.81
	5:5	No salt	2.93	73.76	2.03
		NaCl	6.45	86.32	2.20
		Na_2SO_4	7.95	88.55	1.92
	2:8	No salt	2.16	88.88	1.52
		NaCl	3.45	96.93	5.46
		Na_2SO_4	6.29	97.98	5.45

Note : 1. * can not be calculated due to the experimental concentration of 2,4-dichlorophenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	45.86	79.38	2.14
		NaCl	88.80	90.77	1.09
		Na_2SO_4	136.13	93.79	4.37
	5:5	No salt	23.14	95.52	5.53
		NaCl	31.26	96.89	2.24
		Na_2SO_4	51.63	98.08	6.37
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	30.45	75.50	0.78
		NaCl	43.71	82.53	3.90
		Na_2SO_4	50.87	84.84	2.96
	5:5	Na salt	4.63	80.89	4.34
		NaCl	5.54	88.66	5.12
		Na_2SO_4	10.11	91.48	8.06
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	18.39	65.05	2.53
		NaCl	49.07	83.50	4.47
		Na_2SO_4	93.24	88.98	4.74
	5:5	No salt	3.81	80.16	4.61
		NaCl	5.73	86.04	6.72
		Na_2SO_4	9.20	92.97	4.21
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.24 The effect of salting out on % recovery of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	45.83	78.82	1.42
		NaCl	67.99	87.50	0.84
		Na_2SO_4	105.80	91.28	0.74
	5:5	No salt	12.08	91.75	0.86
		NaCl	14.38	93.46	0.99
		Na_2SO_4	34.67	97.10	3.10
	2:8	No salt	2.07	96.05	1.38
		NaCl	*	100.94	2.57
		Na_2SO_4	*	101.38	3.15
CS_2	9:1	No salt	39.90	78.11	0.57
		NaCl	74.49	88.42	0.49
		Na_2SO_4	1272.06	94.02	4.38
	5:5	No salt	42.23	95.78	1.74
		NaCl	61.94	98.00	0.87
		Na_2SO_4	85.92	99.84	0.14
	2:8	No salt	*	100.23	1.24
		NaCl	*	100.43	2.30
		Na_2SO_4	*	101.37	2.27
HEXANE	9:1	No salt	43.88	80.92	1.51
		NaCl	108.10	89.98	3.26
		Na_2SO_4	95.74	90.39	1.86
	5:5	No salt	87.33	87.99	2.21
		NaCl	22.61	94.83	2.28
		Na_2SO_4	16.91	95.70	5.94
	2:8	No salt	4.10	90.45	2.78
		NaCl	8.09	93.39	1.33
		Na_2SO_4	38.15	96.02	5.06

Note : 1. * can not calculated due to the experimental concentration of 2,4,6-trichlorophenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	79.10	86.35	2.45
		NaCl	228.01	97.65	3.41
		Na_2SO_4	890.79	98.65	1.29
	5:5	No salt	343.16	97.13	4.14
		NaCl	*	101.88	3.67
		Na_2SO_4	*	103.57	1.98
CS_2	9:1	No salt	47.45	82.82	2.10
		NaCl	165.65	91.43	2.88
		Na_2SO_4	276.00	94.39	1.83
	5:5	No salt	54.85	90.36	2.88
		NaCl	16.51	94.93	1.83
		Na_2SO_4	59.63	96.51	0.99
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	46.20	79.50	5.81
		NaCl	44.06	83.24	3.59
		Na_2SO_4	70.72	88.65	5.27
	5:5	No salt	8.55	85.93	2.25
		NaCl	11.80	89.14	0.87
		Na_2SO_4	16.93	90.21	3.38
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2,4,6-trichlorophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.25 The effect of salting out on % recovery of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	32.47	73.27	1.15
		NaCl	73.72	89.10	0.63
		Na_2SO_4	98.50	91.41	1.75
	5:5	No salt	5.23	82.88	1.65
		NaCl	18.25	98.44	6.54
		Na_2SO_4	29.87	99.11	4.11
	2:8	No salt	7.74	97.10	1.28
		NaCl	*	100.56	3.03
		Na_2SO_4	*	101.00	2.14
CS_2	9:1	No salt	11.20	53.14	1.56
		NaCl	66.21	87.94	1.41
		Na_2SO_4	112.35	91.94	3.34
	5:5	No salt	29.56	75.91	1.51
		NaCl	9.20	90.22	1.28
		Na_2SO_4	16.86	94.43	1.34
	2:8	No salt	6.48	98.29	2.23
		NaCl	29.51	99.76	1.38
		Na_2SO_4	*	100.80	2.98
HEXANE	9:1	No salt	2.26	18.64	2.02
		NaCl	10.33	53.39	3.03
		Na_2SO_4	15.87	63.81	0.59
	5:5	No salt	1.87	64.16	1.58
		NaCl	30.00	96.34	1.79
		Na_2SO_4	*	101.24	0.72
	2:8	No salt	1.16	81.02	2.77
		NaCl	*	95.91	1.95
		Na_2SO_4	*	100.01	0.85

Note : 1. * can not be calculated due to the experimental concentration of 4-chloro-3-cresol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	27.14	69.62	0.23
		NaCl	230.80	95.93	1.41
		Na_2SO_4	125.48	96.39	4.50
	5:5	No salt	7.73	90.85	7.62
		NaCl	24.02	99.24	5.65
		Na_2SO_4	*	102.28	4.15
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	12.17	55.08	5.86
		NaCl	78.65	89.67	1.12
		Na_2SO_4	271.57	96.77	0.36
	5:5	No salt	3.21	75.55	7.38
		NaCl	10.11	90.72	3.83
		Na_2SO_4	13.29	92.81	1.22
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	1.86	15.87	7.89
		NaCl	7.66	45.96	1.45
		Na_2SO_4	9.90	52.37	1.26
	5:5	No salt	1.64	61.02	3.49
		NaCl	2.46	71.10	1.41
		Na_2SO_4	5.31	84.10	1.19
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 4-chloro-3-cresol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

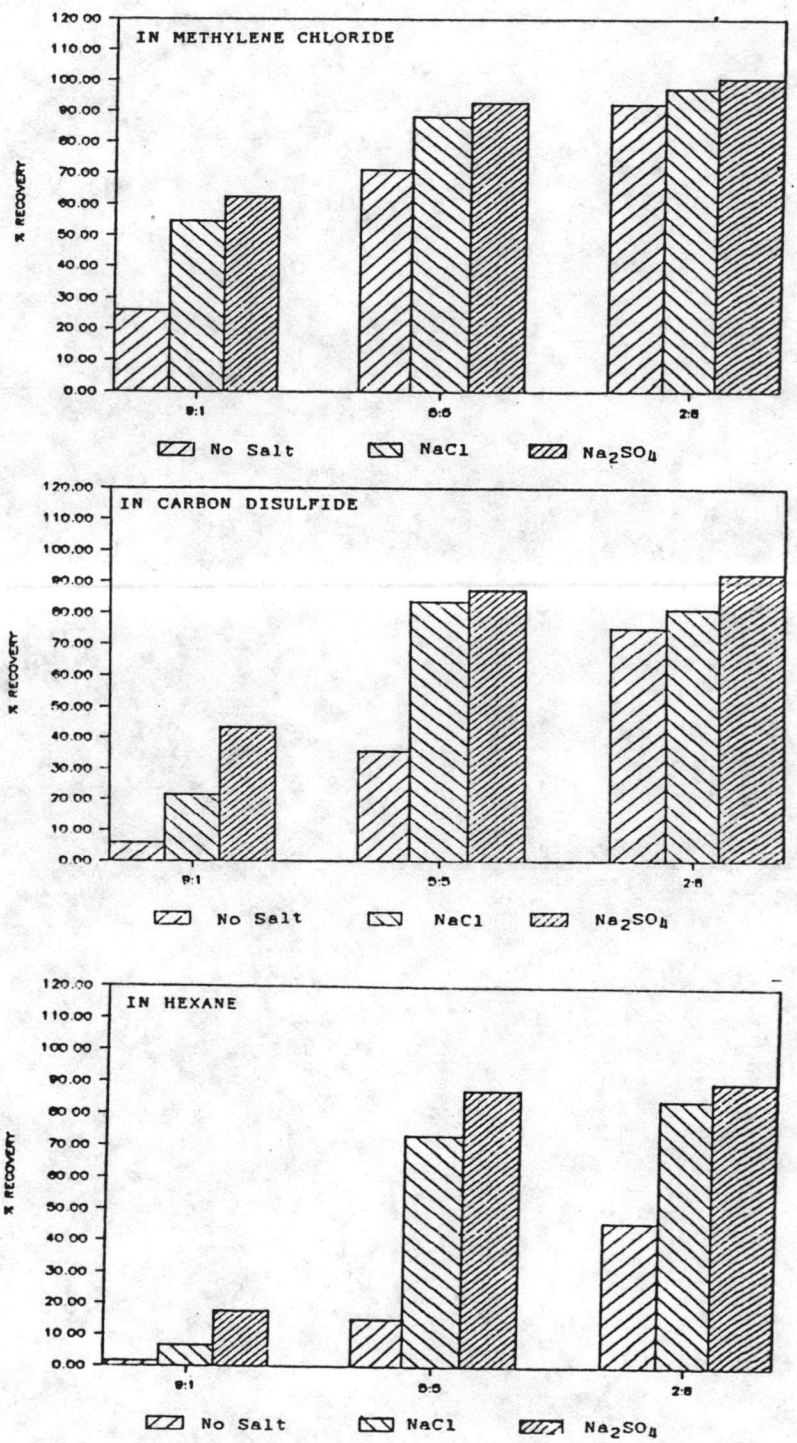


Figure 4.5A The effect of salting out on % recovery of 10.00 ppm of phenol in standard aqueous solution with the various organic solvents.

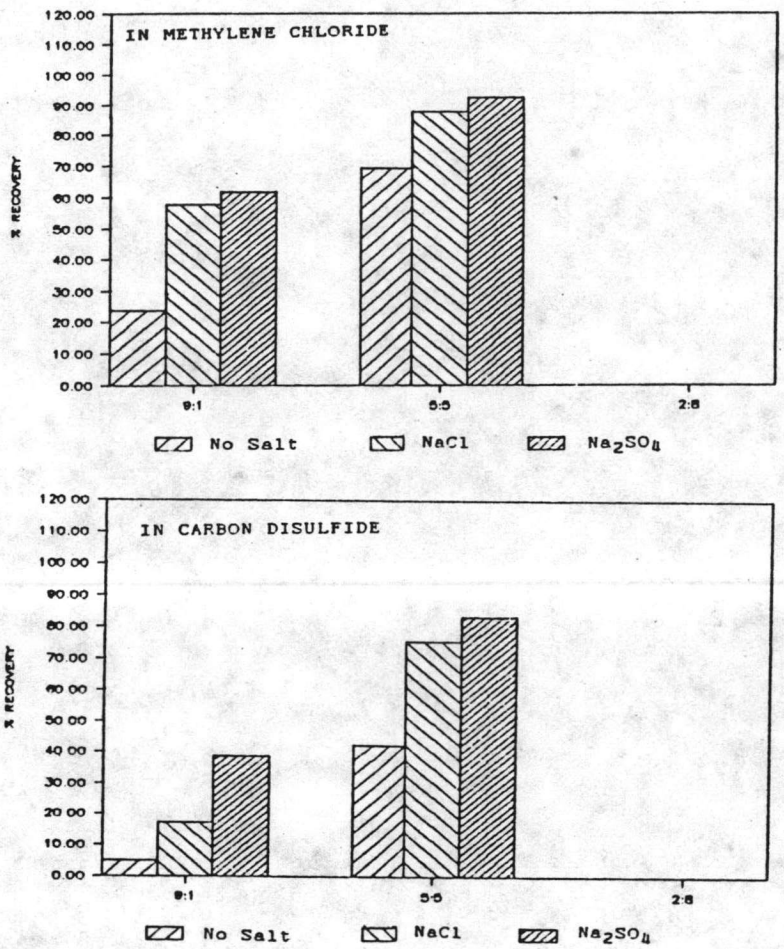


Figure 4.5B The effect of salting out on % recovery of 1.00 ppm of phenol in standard aqueous solution with the various organic solvents.

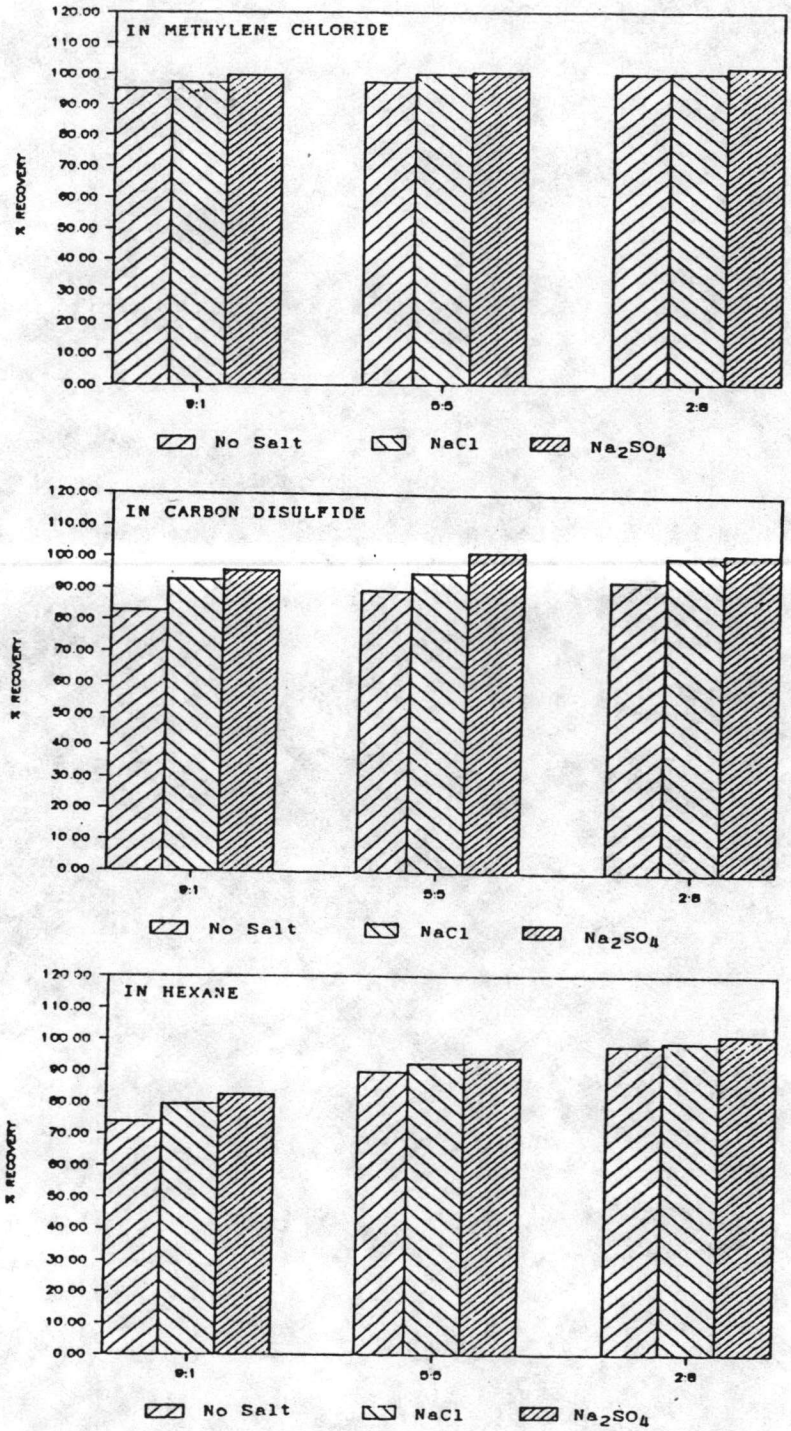


Figure 4.6A The effect of salting out on % recovery of 10.00 ppm of 2-nitrophenol in standard aqueous solution with the various organic solvents.

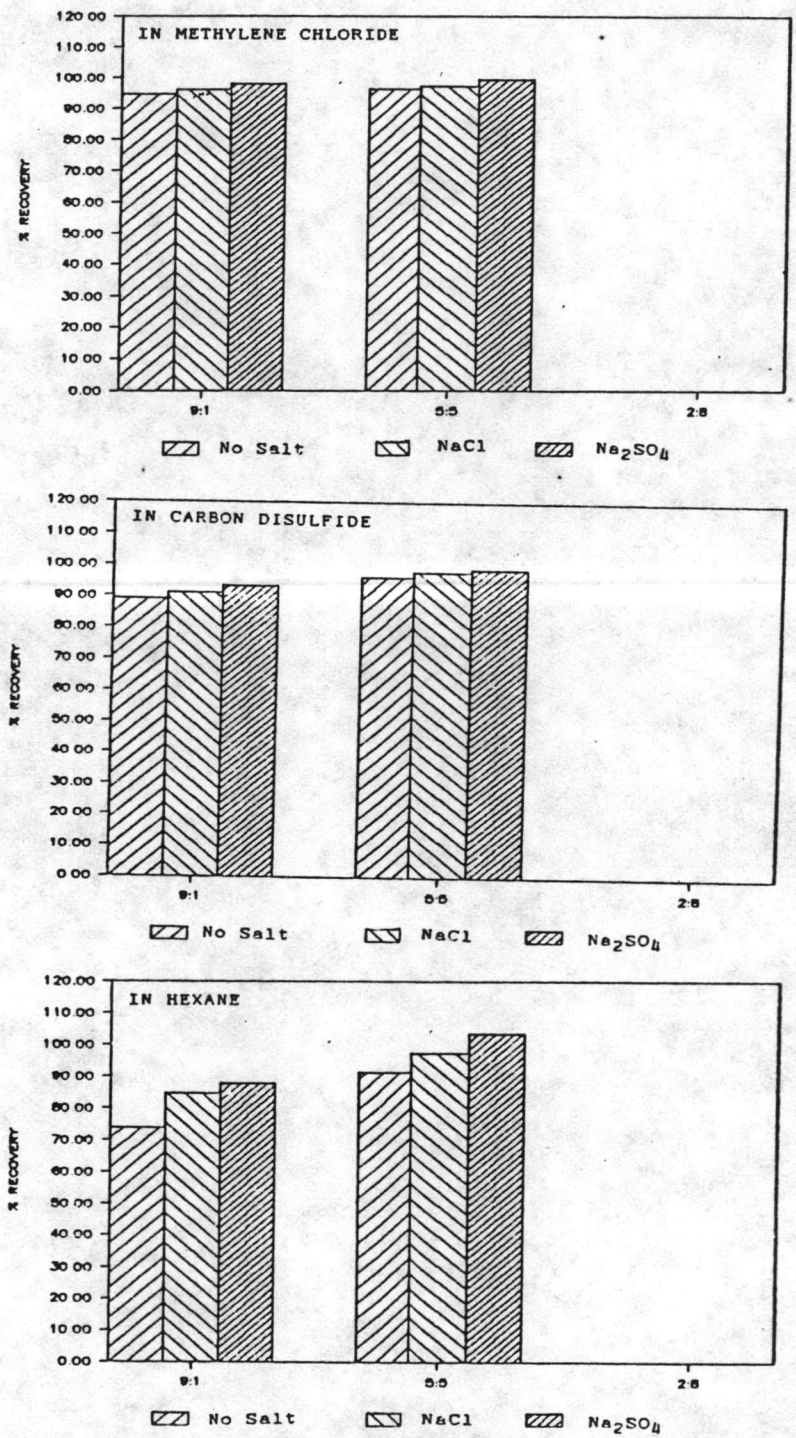


Figure 4.6B The effect of salting out on % recovery of 1.00 ppm of 2-nitrophenol in standard aqueous solution with the various organic solvents.

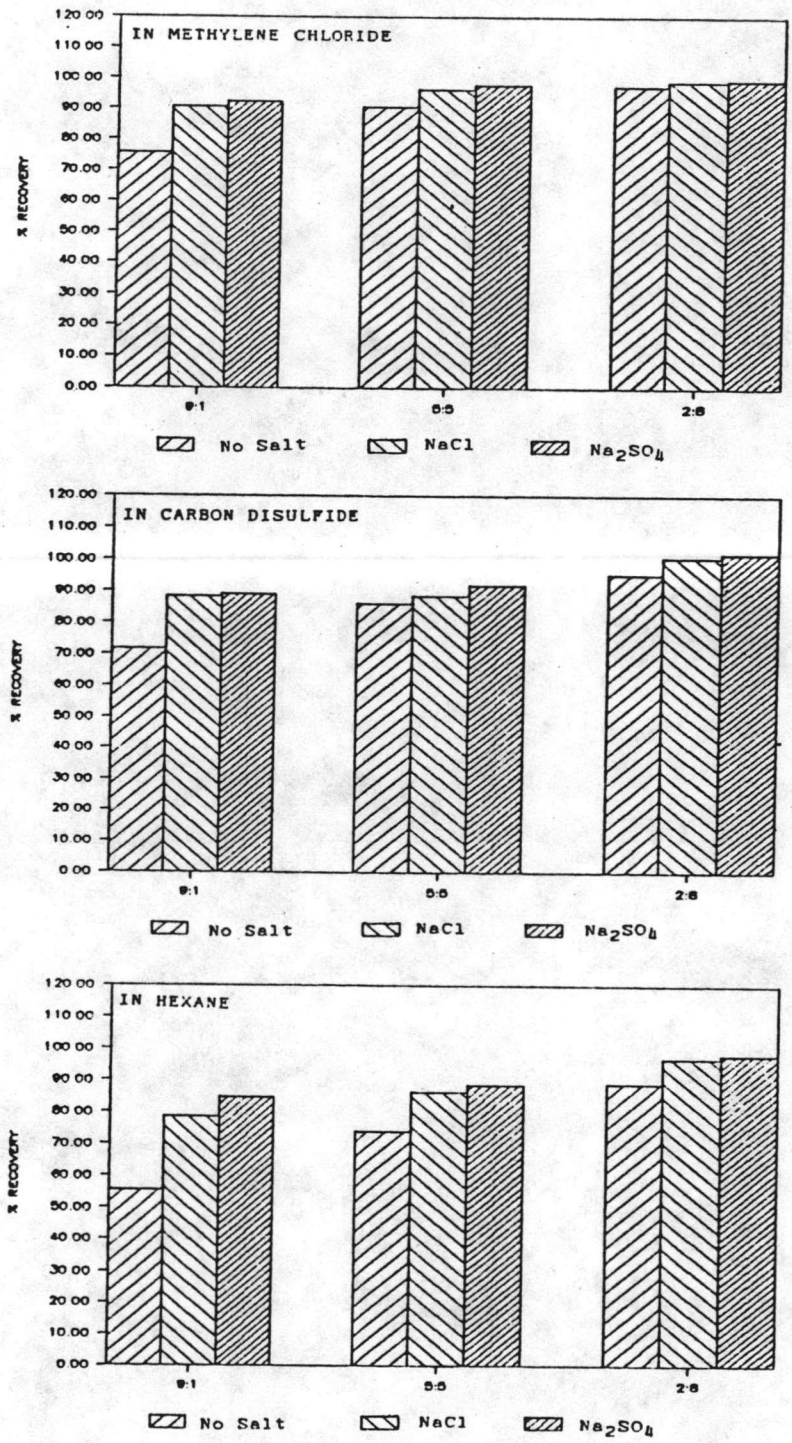


Figure 4.7A The effect of salting out on % recovery of 10.00 ppm of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.

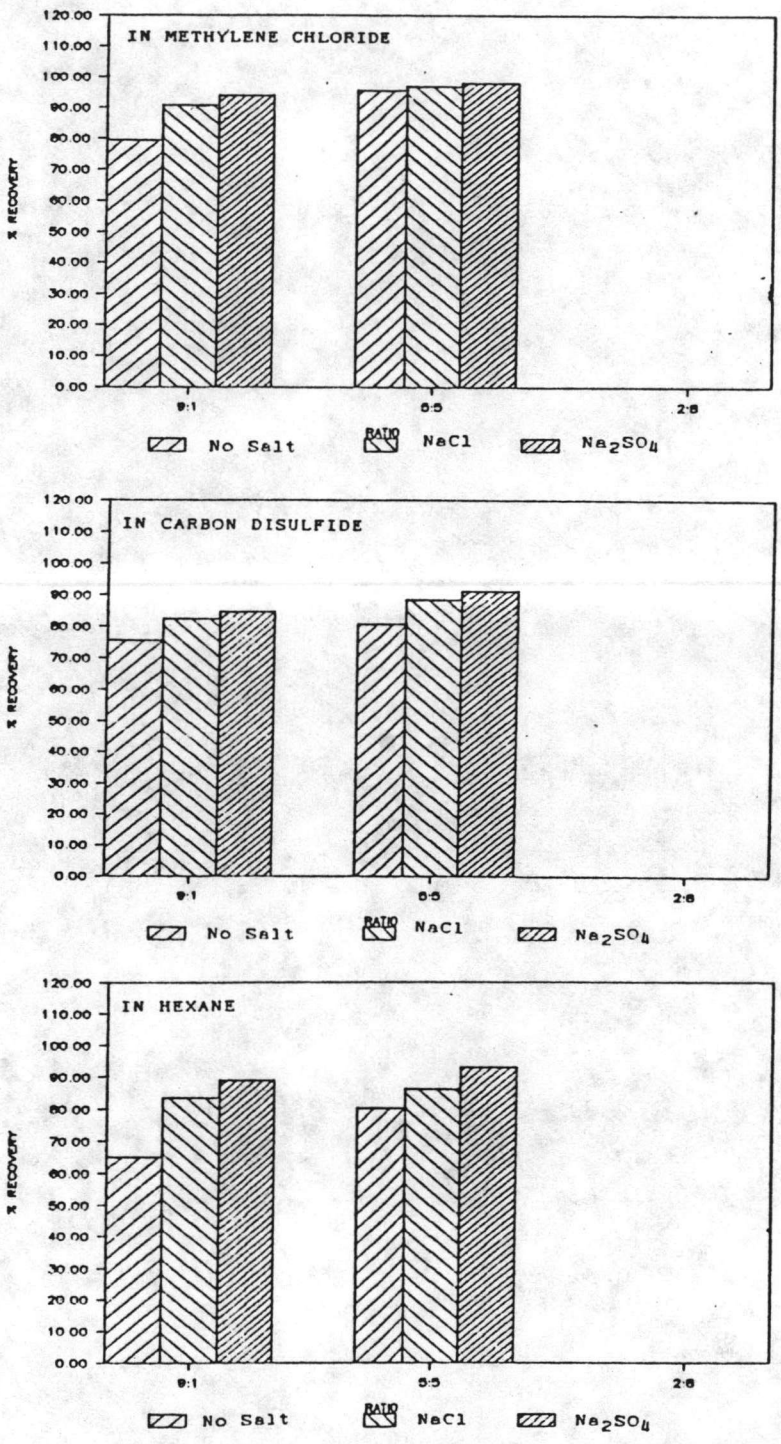


Figure 4.7B The effect of salting out on % recovery of 1.00 ppm of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.

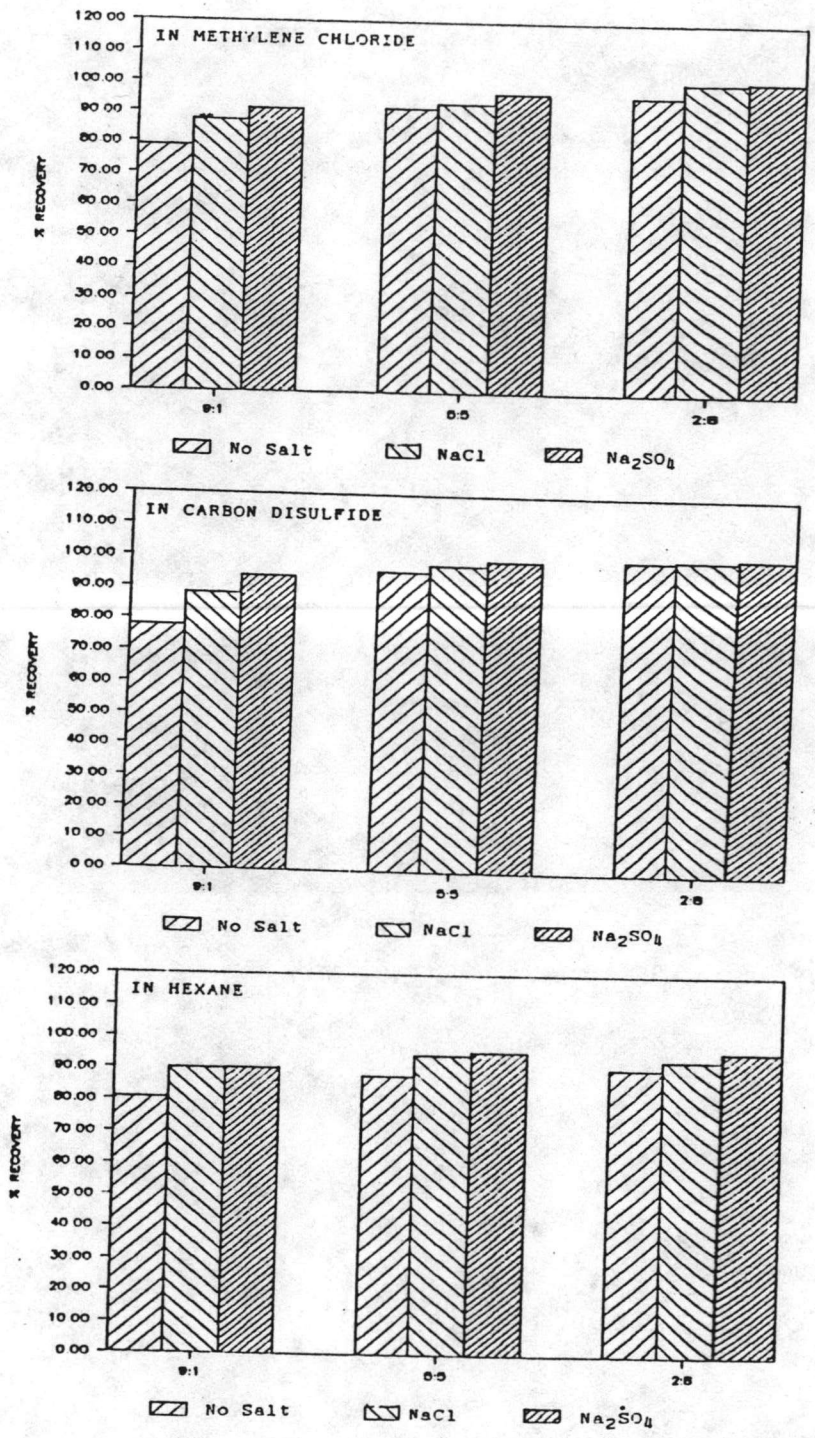


Figure 4.8A The effect of salting out on % recovery of 10.00 ppm of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

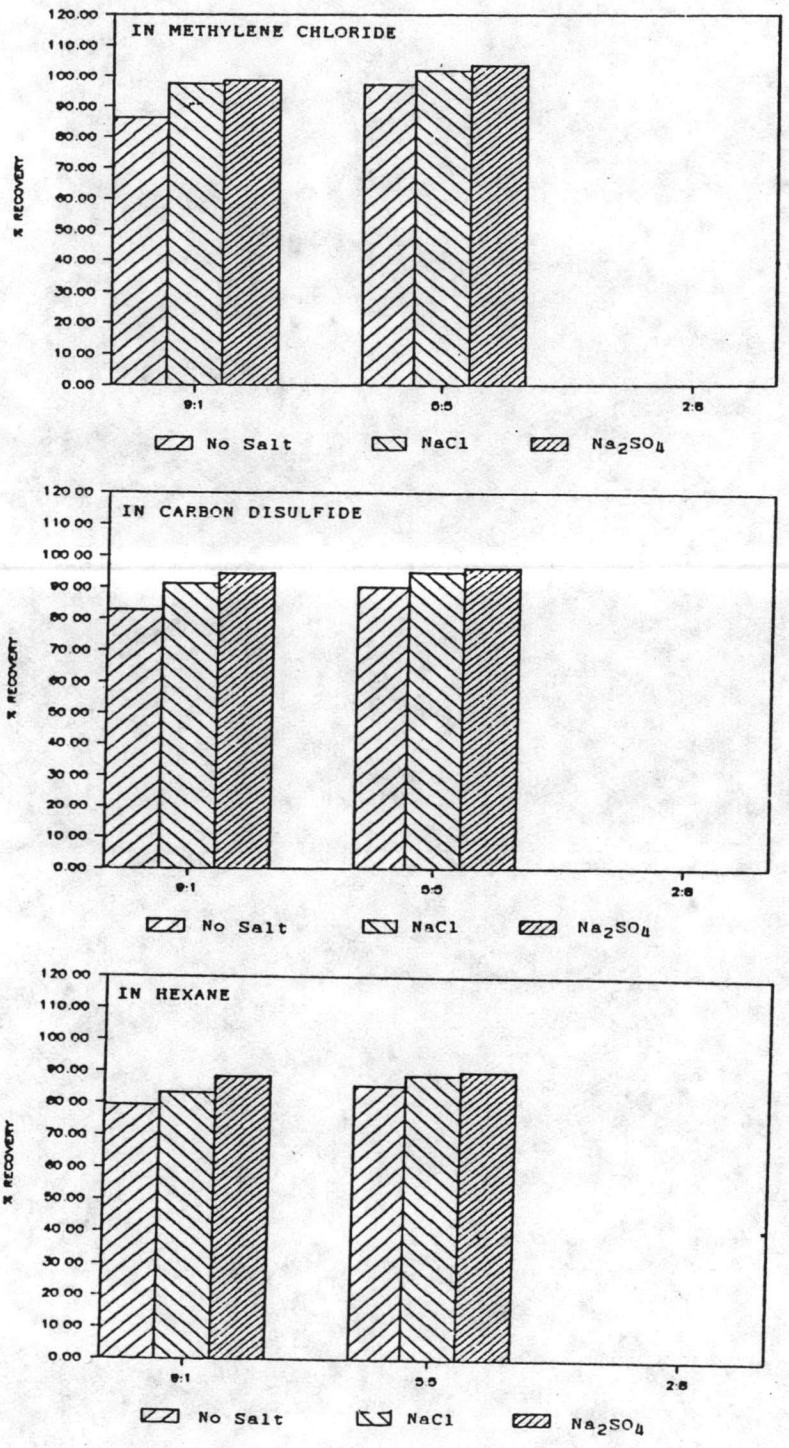


Figure 4.8B The effect of salting out on % recovery of 1.00 ppm of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

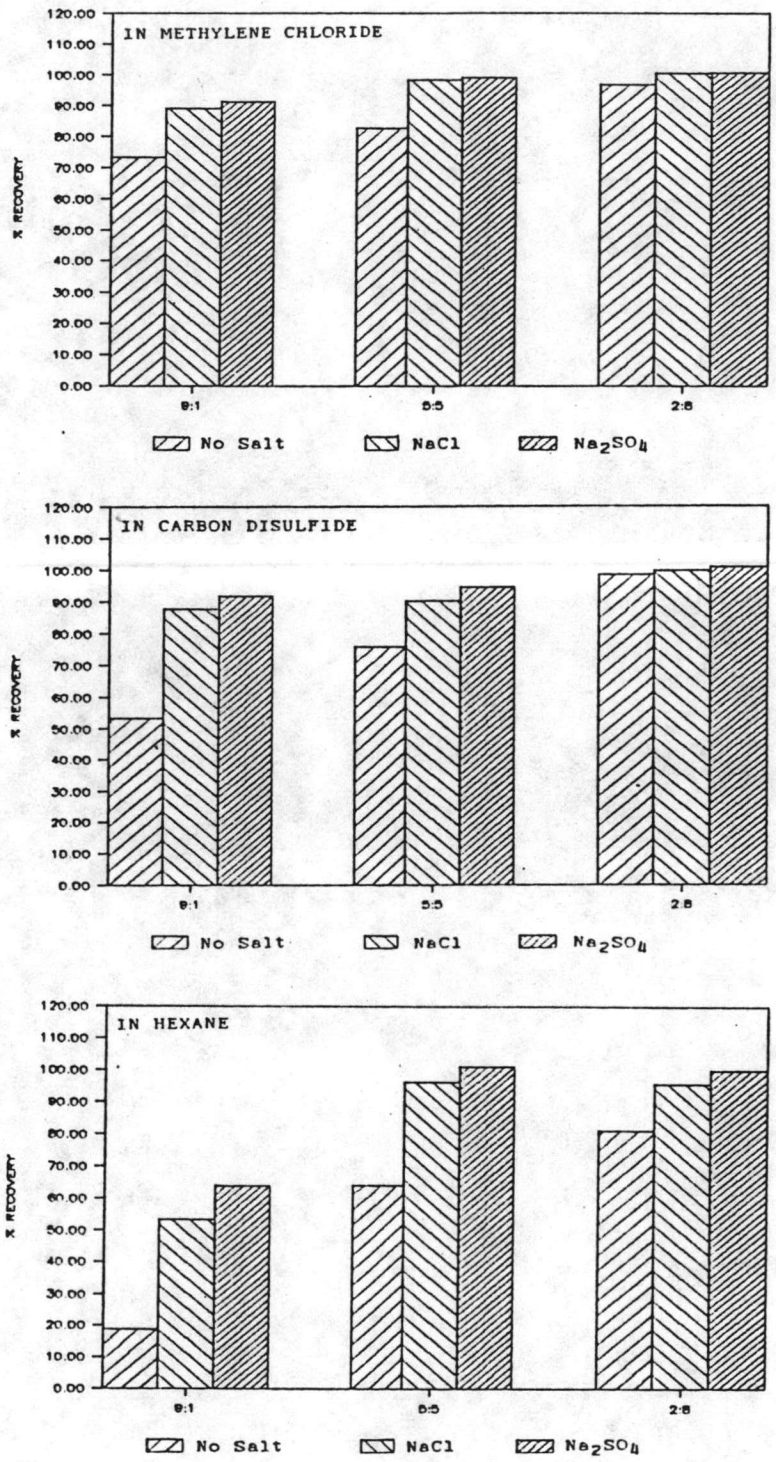


Figure 4.9A The effect of salting out on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

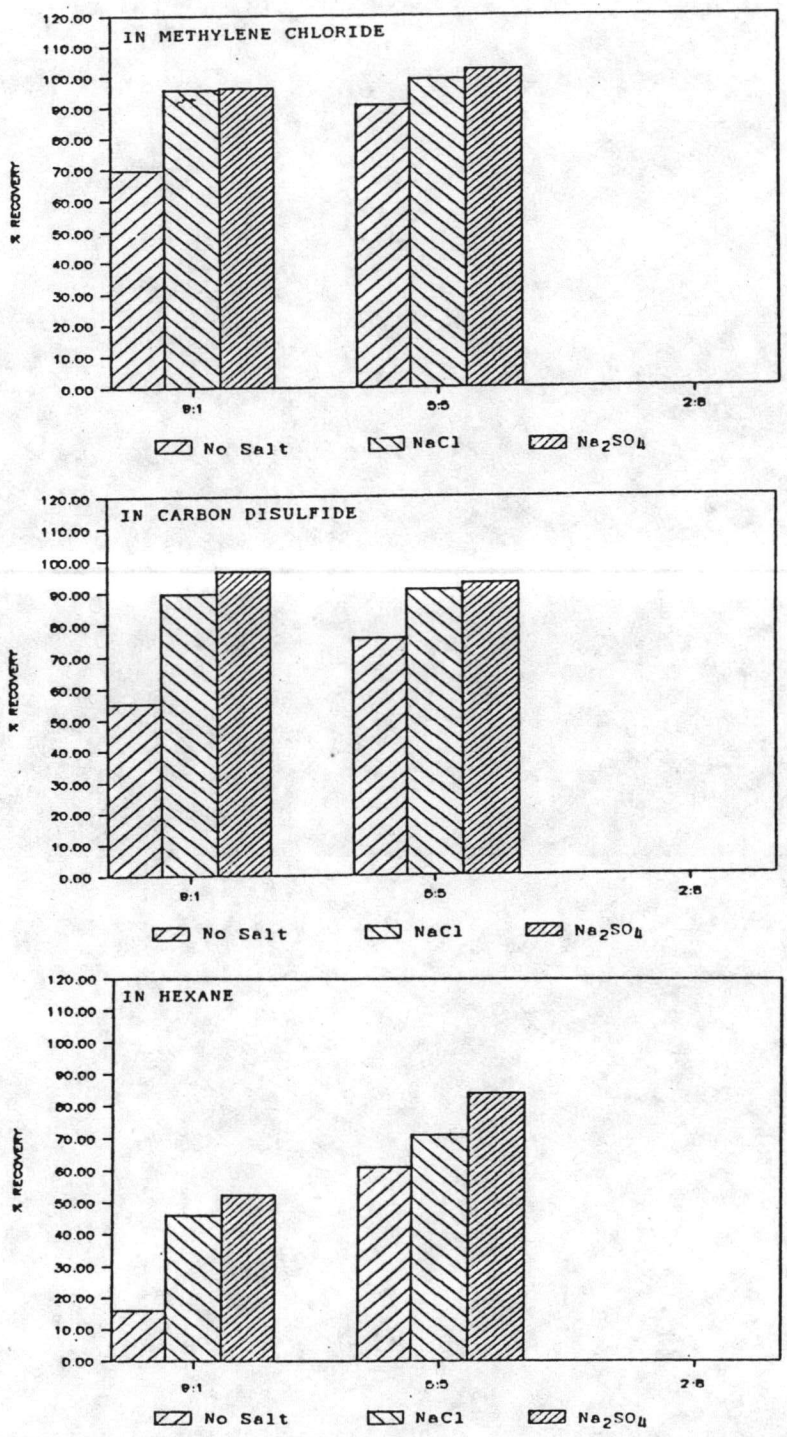


Figure 4.9B The effect of salting out on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

Table 4.26 The effect of salting out on % recovery of phenol in standard mixture aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	3.69	23.77	2.13
		NaCl	36.84	80.35	0.67
		Na_2SO_4	43.78	82.81	1.81
	5:5	No salt	2.74	71.60	1.97
		NaCl	27.47	96.17	1.12
		Na_2SO_4	*	101.06	2.06
	2:8	No salt	8.73	95.03	3.62
		NaCl	27.06	97.97	1.51
		Na_2SO_4	*	102.14	4.89
CS_2	9:1	No salt	0.88	8.18	4.93
		NaCl	5.28	36.88	7.21
		Na_2SO_4	10.21	53.01	4.87
	5:5	No salt	0.75	41.74	4.28
		NaCl	7.65	87.98	2.62
		Na_2SO_4	19.52	91.67	4.28
	2:8	No salt	1.81	85.23	5.88
		NaCl	2.03	93.14	6.24
		Na_2SO_4	3.84	96.28	6.79
HEXANE	9:1	No salt	0.27	2.68	3.97
		NaCl	1.84	16.94	5.70
		Na_2SO_4	3.20	26.19	6.51
	5:5	No salt	0.13	12.63	1.38
		NaCl	1.83	64.59	2.26
		Na_2SO_4	4.64	82.12	2.12
	2:8	No salt	0.30	52.81	8.65
		NaCl	3.06	89.19	5.87
		Na_2SO_4	3.45	90.13	7.42

Note : 1. * can not be calculated due to the experimental concentration of phenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	3.78	22.08	3.83
		NaCl	13.27	59.56	1.63
		Na_2SO_4	17.41	65.82	1.63
	5:5	No salt	2.57	69.95	2.87
		NaCl	6.09	85.86	5.34
		Na_2SO_4	29.30	96.67	4.19
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	0.84	7.84	4.68
		NaCl	4.78	34.10	2.79
		Na_2SO_4	8.24	47.81	6.28
	5:5	No salt	0.86	45.02	6.73
		NaCl	2.95	74.15	4.98
		Na_2SO_4	3.81	87.59	7.27
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
	5:5	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.27 The effect of salting out on % recovery of 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	285.50	93.15	3.89
		NaCl	771.65	96.50	2.33
		Na_2SO_4	212.90	98.65	4.54
	5:5	No salt	*	101.63	3.02
		NaCl	*	106.37	4.28
		Na_2SO_4	*	108.18	4.13
	2:8	No salt	*	103.17	1.25
		NaCl	*	105.45	1.59
		Na_2SO_4	*	106.07	2.88
CS_2	9:1	No salt	34.93	79.14	2.59
		NaCl	80.39	89.35	2.64
		Na_2SO_4	183.54	92.91	3.88
	5:5	Na salt	7.28	86.74	3.95
		NaCl	31.06	93.94	3.53
		Na_2SO_4	18.75	99.01	2.07
	2:8	No salt	1.56	97.01	8.44
		NaCl	4.62	98.96	3.16
		Na_2SO_4	*	101.26	4.34
HEXANE	9:1	No salt	31.41	76.04	1.49
		NaCl	42.83	82.81	2.39
		Na_2SO_4	69.29	88.53	2.64
	5:5	No salt	16.47	92.45	4.43
		NaCl	34.91	95.67	2.39
		Na_2SO_4	22.61	99.46	4.22
	2:8	No salt	3.60	98.81	4.26
		NaCl	16.57	99.76	4.22
		Na_2SO_4	*	101.26	3.45

Note : 1. * can not be calculated due to the experimental concentration of 2-nitrophenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	463.36	96.39	2.09
		NaCl	350.00	98.88	3.83
		Na_2SO_4	*	100.48	3.40
	5:5	No salt	58.36	98.10	1.38
		NaCl	*	102.52	1.74
		Na_2SO_4	*	104.95	2.13
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	69.54	86.90	3.67
		NaCl	270.59	87.85	1.50
		Na_2SO_4	111.95	90.16	4.59
	5:5	No salt	20.21	93.28	5.61
		NaCl	24.00	96.32	2.89
		Na_2SO_4	49.00	98.00	4.12
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	26.79	72.88	3.29
		NaCl	53.51	84.88	3.67
		Na_2SO_4	65.98	87.71	2.16
	5:5	No salt	6.40	97.40	4.18
		NaCl	20.83	99.02	1.63
		Na_2SO_4	*	100.13	1.89
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2-nitrophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.28 The effect of salting out on % recovery of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	49.53	80.02	4.46
		NaCl	61.65	86.90	2.60
		Na_2SO_4	108.73	92.34	1.35
	5:5	No salt	16.18	93.36	1.99
		NaCl	15.23	98.90	3.44
		Na_2SO_4	*	103.64	3.12
	2:8	No salt	*	100.70	3.82
		NaCl	*	102.73	2.52
		Na_2SO_4	*	106.30	2.85
CS_2	9:1	No salt	37.26	78.85	2.54
		NaCl	85.69	90.46	2.19
		Na_2SO_4	104.89	92.07	2.06
	5:5	No salt	7.00	86.40	3.51
		NaCl	38.36	94.16	3.63
		Na_2SO_4	109.94	97.66	2.35
	2:8	No salt	6.99	98.70	3.74
		NaCl	*	101.09	2.56
		Na_2SO_4	*	102.82	5.30
HEXANE	9:1	No salt	18.40	65.70	2.88
		NaCl	49.83	84.71	2.25
		Na_2SO_4	70.65	88.70	2.85
	5:5	No salt	3.54	76.96	3.28
		NaCl	6.13	84.74	4.64
		Na_2SO_4	5.47	90.11	3.27
	2:8	No salt	3.07	91.96	2.92
		NaCl	13.80	95.77	3.90
		Na_2SO_4	12.90	99.48	3.85

Note : 1. * can not be calculated due to the experimental concentration of 2,4-dichlorophenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	70.94	85.27	3.10
		NaCl	94.10	91.42	6.05
		Na_2SO_4	140.33	93.53	3.32
	5:5	No salt	25.00	96.42	6.83
		NaCl	99.02	98.64	6.55
		Na_2SO_4	99.00	99.61	9.95
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	38.39	79.21	3.46
		NaCl	82.99	88.13	1.06
		Na_2SO_4	144.57	90.90	4.87
	5:5	No salt	6.04	84.45	4.88
		NaCl	7.32	87.96	3.47
		Na_2SO_4	11.50	92.83	3.23
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	27.32	72.82	5.71
		NaCl	91.63	89.51	4.57
		Na_2SO_4	117.64	92.16	2.85
	5:5	No salt	9.58	90.53	1.81
		NaCl	24.00	93.25	4.57
		Na_2SO_4	9.77	99.11	5.98
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.29 The effect of salting out on % recovery of 2,4,6-trichlorophenol in standard mixture aqueous solution with the various organic solvents.

(A) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	81.80	85.58	5.25
		NaCl	63.10	87.21	2.39
		Na_2SO_4	109.39	92.38	7.60
	5:5	No salt	18.94	94.01	3.87
		NaCl	24.64	96.12	3.42
		Na_2SO_4	61.50	98.41	1.39
	2:8	No salt	7.68	96.44	3.12
		NaCl	2.24	98.53	6.53
		Na_2SO_4	*	102.94	4.86
CS_2	9:1	No salt	52.90	84.03	2.30
		NaCl	153.34	93.86	1.88
		Na_2SO_4	548.92	96.36	2.47
	5:5	No salt	51.51	95.13	5.02
		NaCl	*	101.07	4.39
		Na_2SO_4	*	102.71	3.36
	2:8	No salt	*	101.11	4.38
		NaCl	*	104.10	5.67
		Na_2SO_4	*	106.68	5.93
HEXANE	9:1	No salt	54.01	75.11	3.73
		NaCl	43.12	83.04	3.03
		Na_2SO_4	291.97	87.35	2.91
	5:5	No salt	31.41	86.23	2.87
		NaCl	98.58	98.45	2.44
		Na_2SO_4	*	102.54	1.55
	2:8	No salt	1.41	95.92	6.65
		NaCl	1.51	97.96	3.28
		Na_2SO_4	2.60	101.41	7.85

Note : 1. * can not be calculated due to the experimental concentration of 2,4,6-trichlorophenol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	87.34	87.39	3.28
		NaCl	515.55	97.41	6.66
		Na_2SO_4	162.40	99.62	3.50
	5:5	No salt	13.66	98.28	2.78
		NaCl	*	102.05	2.65
		Na_2SO_4	*	104.51	3.93
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	60.00	85.84	3.86
		NaCl	171.00	95.04	2.20
		Na_2SO_4	125.86	97.86	1.70
	5:5	No salt	7.50	92.95	7.95
		NaCl	*	100.16	5.20
		Na_2SO_4	*	103.99	8.85
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	30.83	75.65	1.99
		NaCl	38.00	79.74	5.89
		Na_2SO_4	42.47	81.77	4.72
	5:5	No salt	5.18	88.75	6.42
		NaCl	25.35	89.96	9.40
		Na_2SO_4	26.99	90.51	7.92
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2,4,6-trichlorophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.30 The effect of salting out on % recovery of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	42.47	77.19	5.85
		NaCl	67.52	88.01	1.96
		Na_2SO_4	117.98	92.86	2.67
	5:5	No salt	4.74	81.20	2.41
		NaCl	49.32	95.16	3.03
		Na_2SO_4	24.83	98.27	3.41
	2:8	No salt	11.32	94.37	8.46
		NaCl	3.09	98.22	4.93
		Na_2SO_4	2.83	99.98	6.48
CS_2	9:1	No salt	17.79	64.25	2.58
		NaCl	51.79	85.17	2.75
		Na_2SO_4	520.24	98.26	1.08
	5:5	No salt	6.04	84.50	6.45
		NaCl	24.72	94.05	3.76
		Na_2SO_4	33.06	95.15	4.66
	2:8	No salt	9.11	97.14	6.33
		NaCl	124.50	99.43	3.08
		Na_2SO_4	*	100.81	3.44
HEXANE	9:1	No salt	2.82	67.83	4.74
		NaCl	58.89	86.68	1.10
		Na_2SO_4	353.00	99.54	3.21
	5:5	No salt	2.28	67.83	7.74
		NaCl	17.16	92.05	5.68
		Na_2SO_4	42.13	96.78	4.41
	2:8	No salt	1.13	79.88	5.65
		NaCl	3.69	91.13	4.77
		Na_2SO_4	1.45	97.22	8.75

Note : 1. * can not be calculate due to the experimental concentration of 4-chloro-3-cresol is higher than its initial concentration of standard solution.

2. Triplicate analyses.

(B) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	SALT	K_d	%E	%RSD
CH_2Cl_2	9:1	No salt	68.99	68.98	2.87
		NaCl	48.58	82.59	3.54
		Na_2SO_4	71.40	87.74	4.39
	5:5	No salt	7.58	87.75	5.46
		NaCl	24.00	96.26	8.90
		Na_2SO_4	10.93	99.46	9.30
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
CS_2	9:1	No salt	11.97	54.59	5.73
		NaCl	71.39	88.03	3.17
		Na_2SO_4	248.83	94.49	3.53
	5:5	No salt	6.31	84.62	4.66
		NaCl	19.14	98.86	2.76
		Na_2SO_4	*	100.40	6.74
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND
HEXANE	9:1	No salt	3.27	25.09	3.02
		NaCl	14.16	60.17	4.47
		Na_2SO_4	20.31	69.23	1.89
	5:5	No salt	1.66	70.05	10.23
		NaCl	7.15	87.18	5.09
		Na_2SO_4	66.97	94.18	10.47
	2:8	No salt	ND	ND	ND
		NaCl	ND	ND	ND
		Na_2SO_4	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 4-chloro-3-cresol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

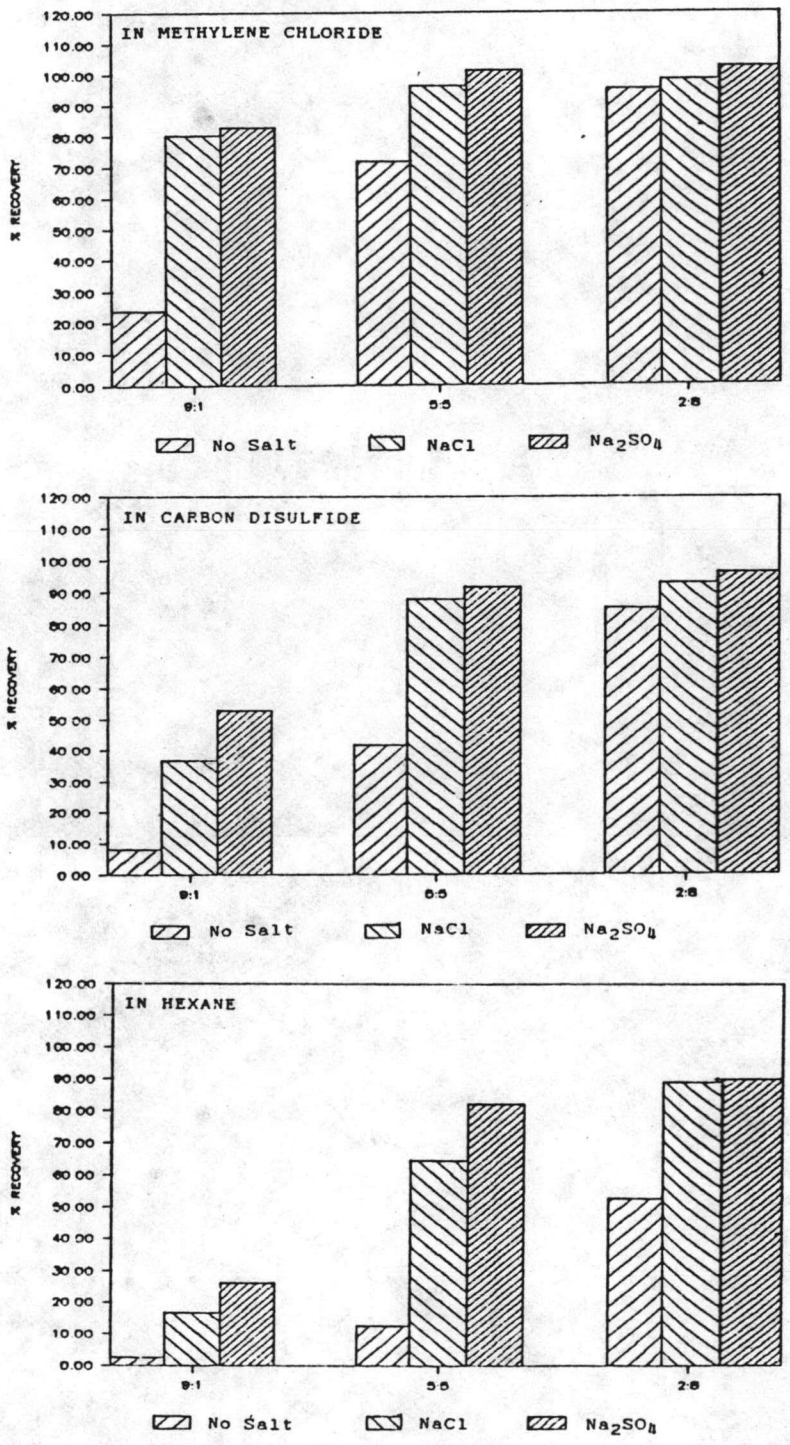


Figure 4.10A The effect of salting out on % recovery of 10.00 ppm of phenol in standard mixture aqueous solution with the various organic solvents.

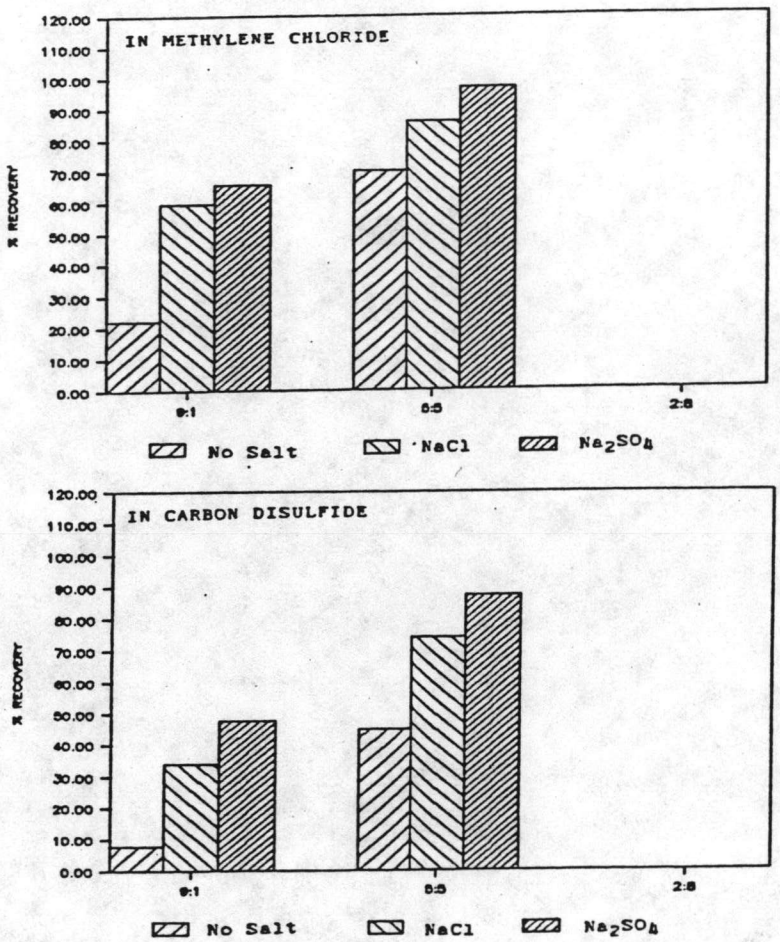


Figure 4.10B The effect of salting out on % recovery of 1.00 ppm of phenol in standard mixture aqueous solution with the various organic solvents.

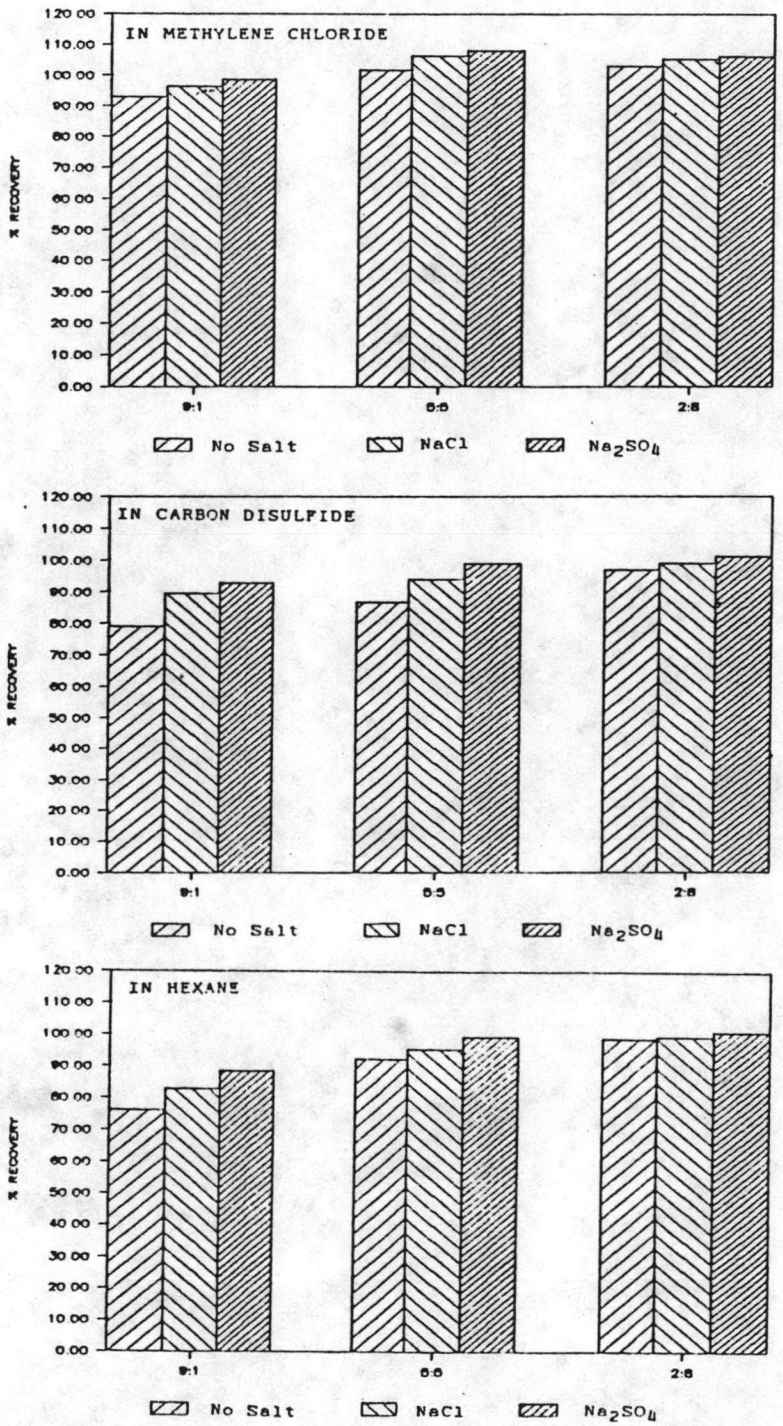


Figure 4.11A The effect of salting out on % recovery of 10.00 ppm of 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.

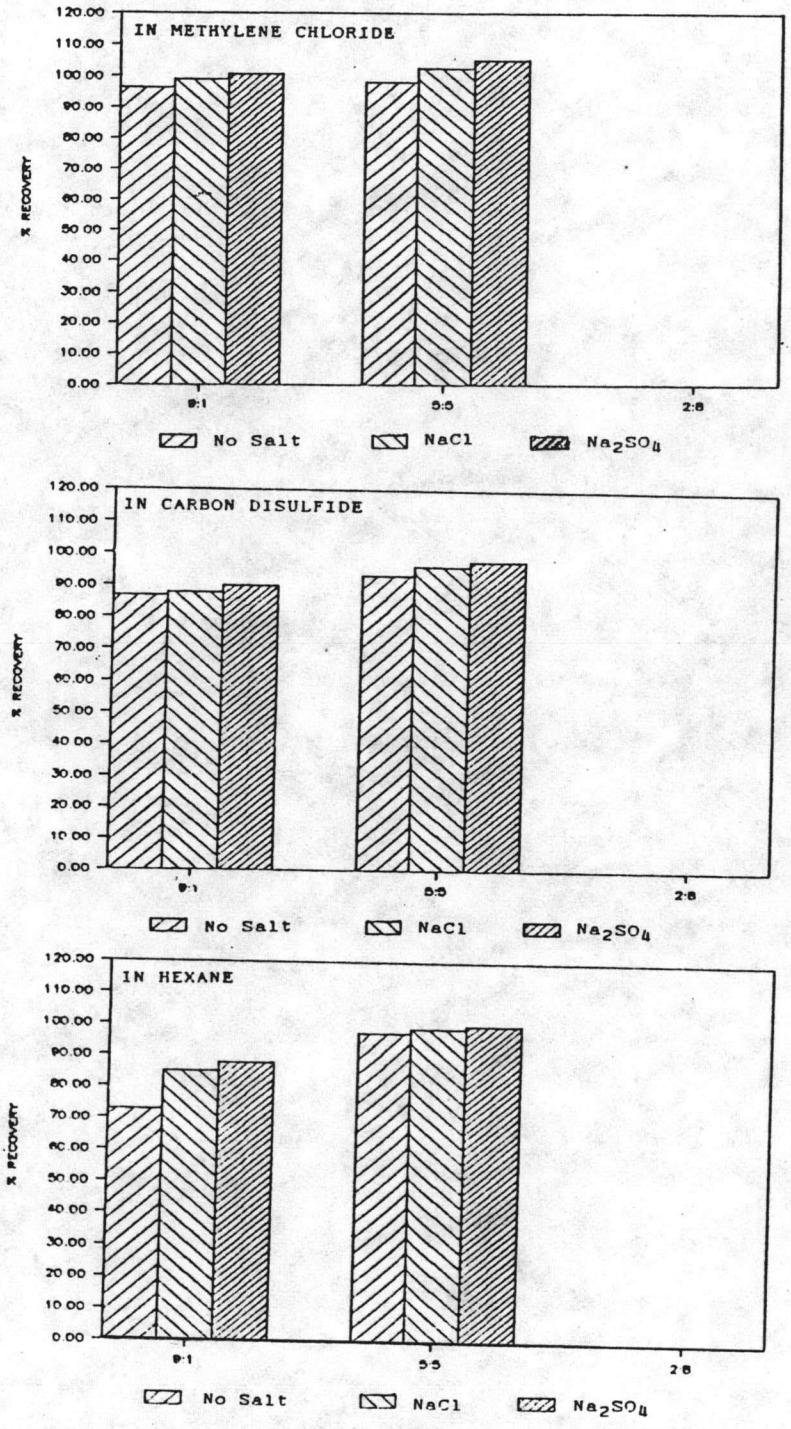


Figure 4.11B The effect of salting out on % recovery of 1.00 ppm of 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.

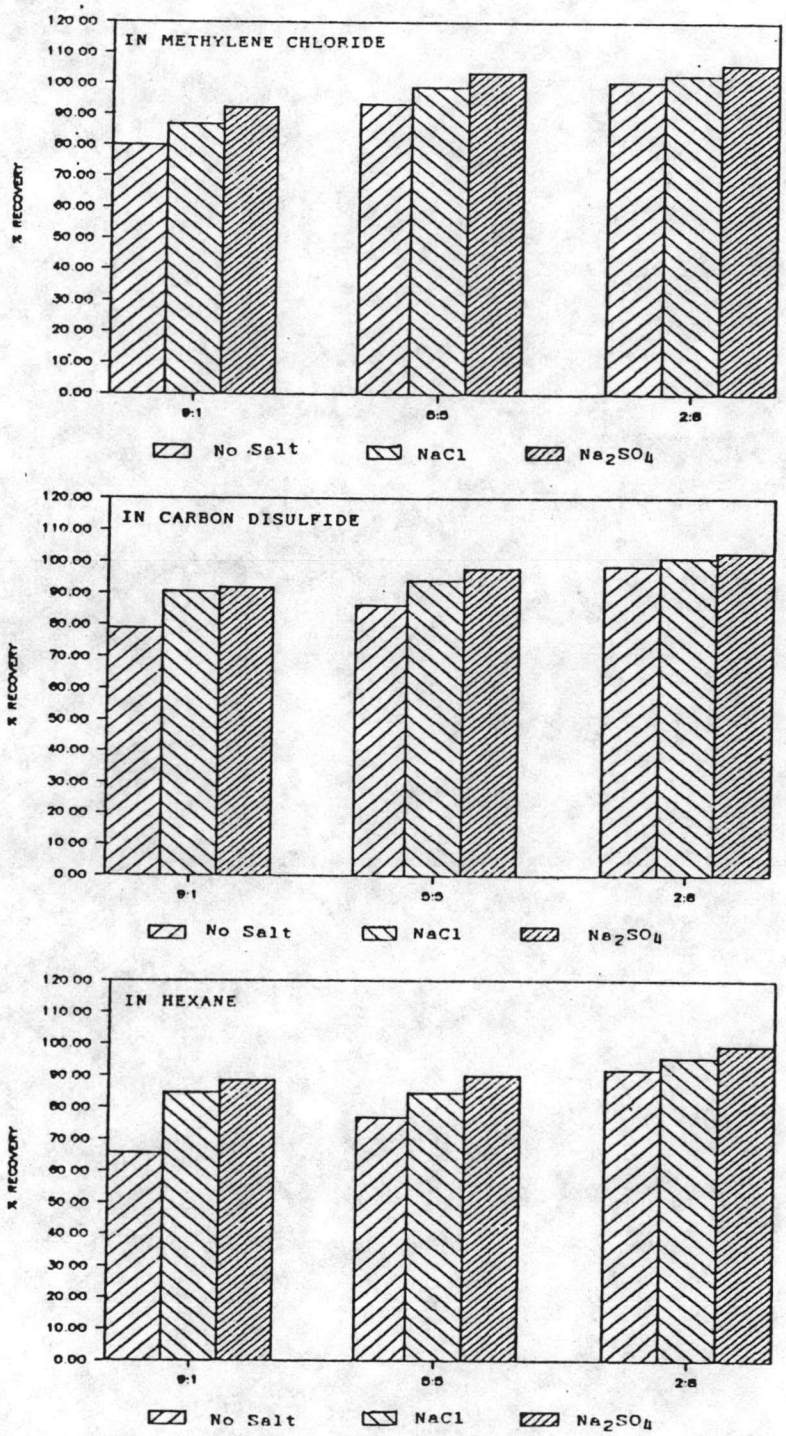


Figure 4.12A The effect of salting out on % recovery of 10.00 ppm of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.

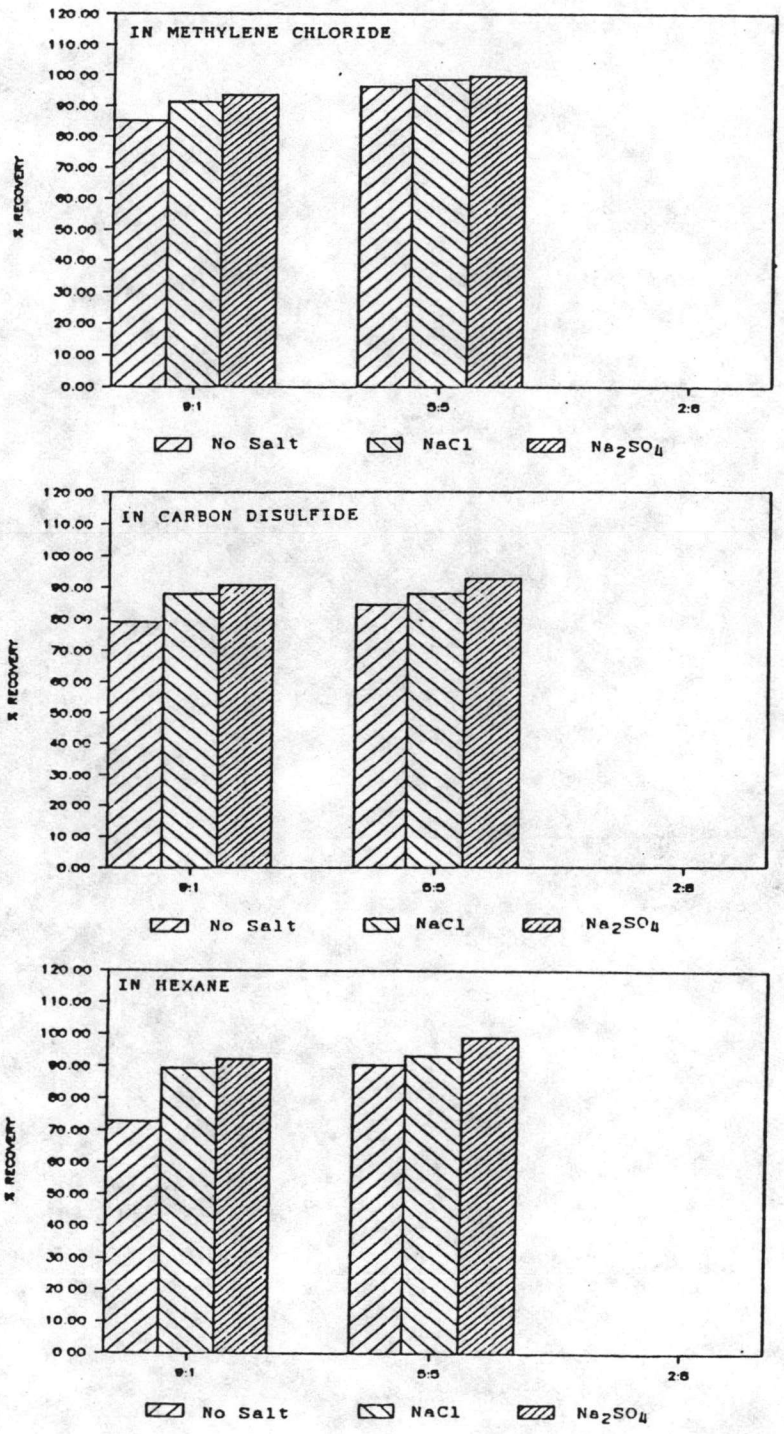


Figure 4.12B The effect of salting out on % recovery of 1.00 ppm of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.

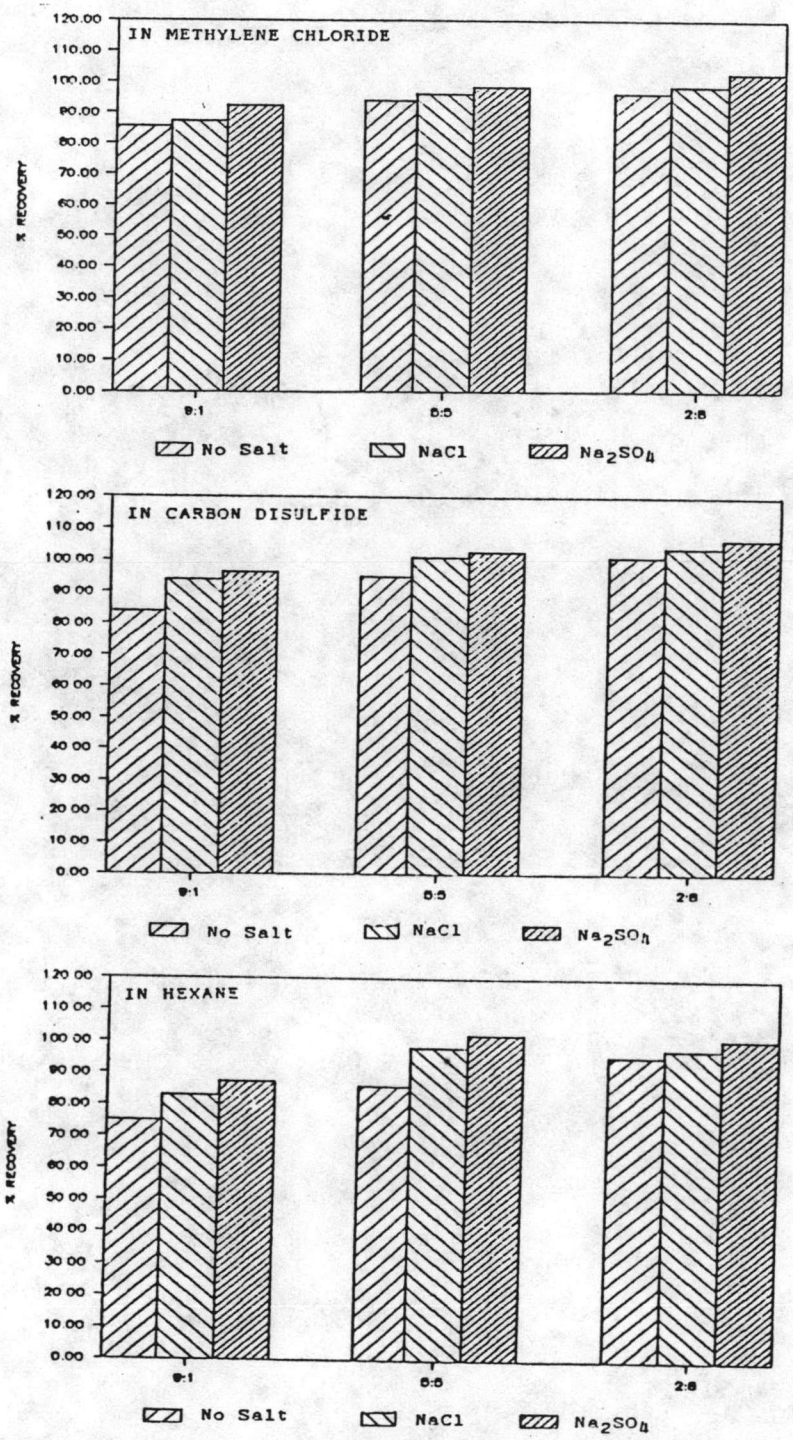


Figure 4.13A The effect of salting out on % recovery of 10.00 ppm of 2,4,6-trichlorophenol in standard mixture aqueous solution with the various organic solvents.

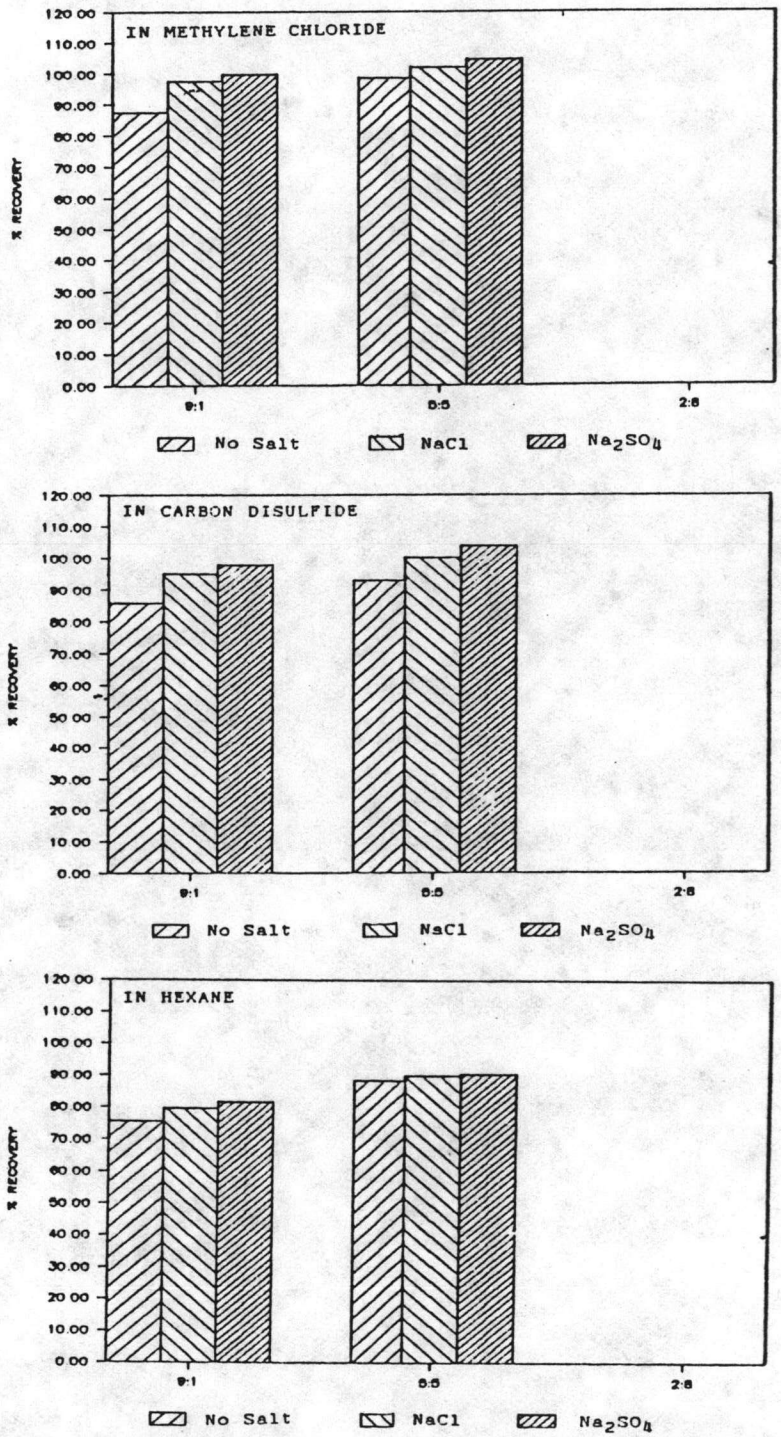


Figure 4.13B The effect of salting out on % recovery of 1.00 ppm of 2,4,6-trichlorophenol in standard mixture aqueous solution with the various organic solvents.

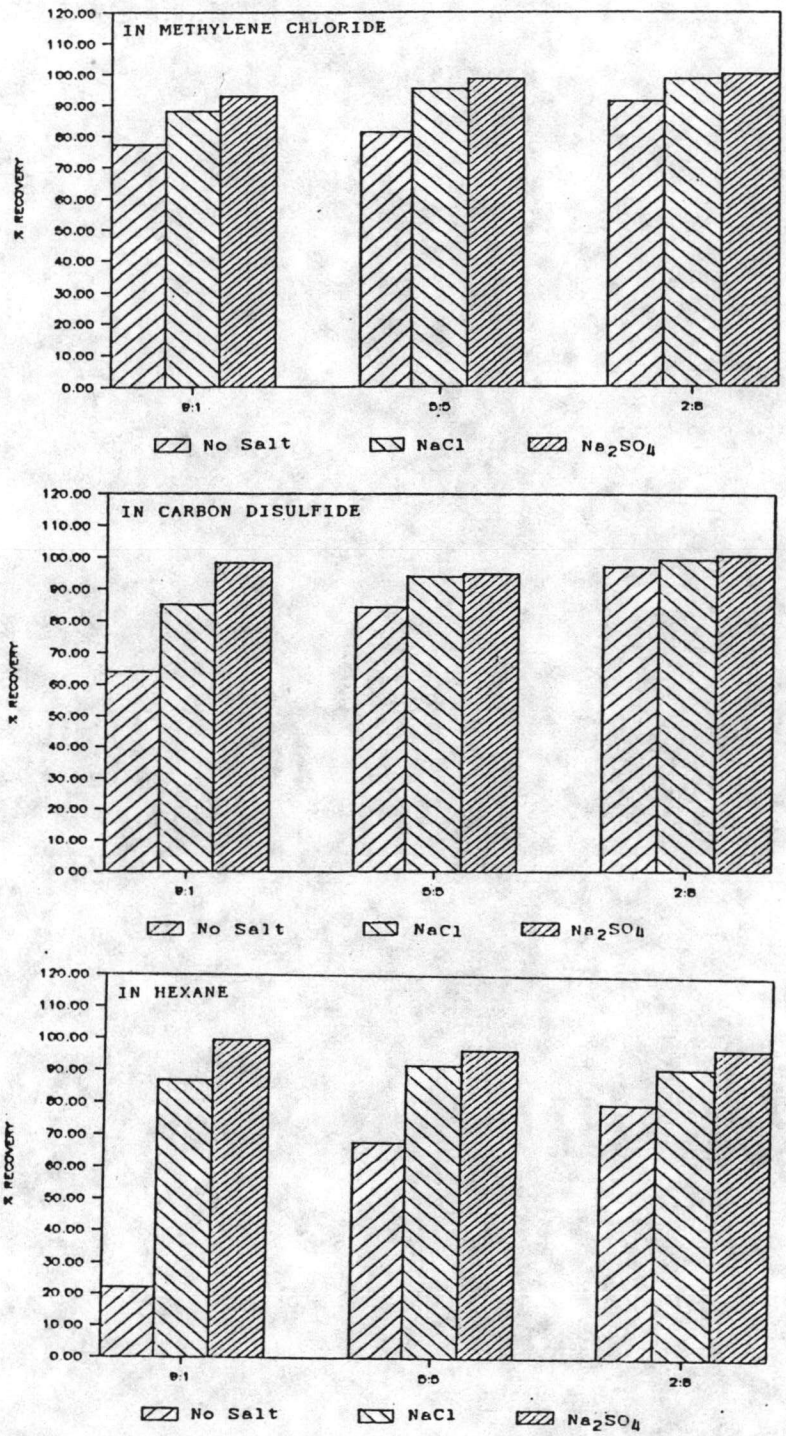


Figure 4.14A The effect of salting out on % recovery of 10.00 ppm of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

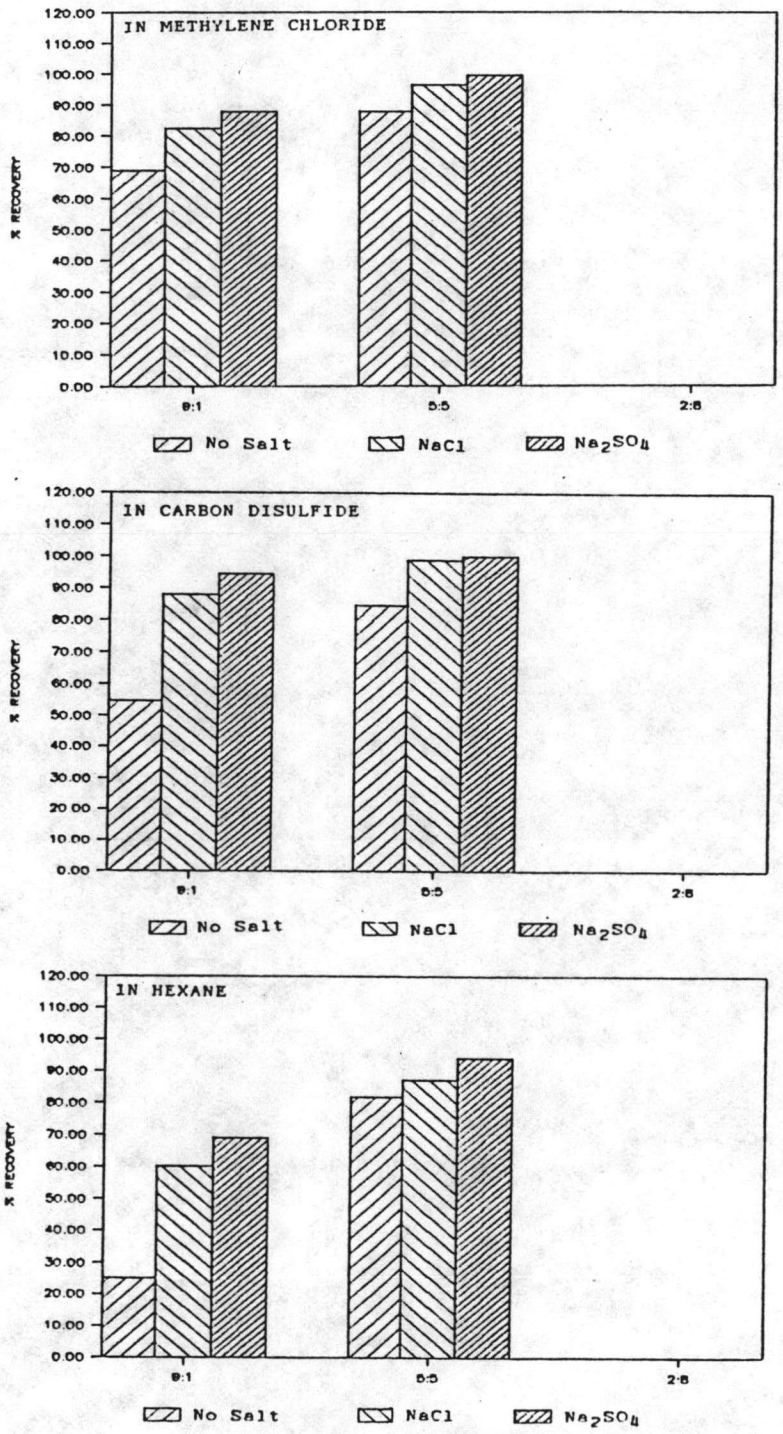


Figure 4.14B The effect of salting out on % recovery of 1.00 ppm of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

4.4 THE EFFECT OF SAMPLE-TO-SOLVENT RATIOS

The effect of sample-to-solvent ratios on percent recovery of each phenolic compound , i.e. , phenol, 2-nitrophenol , 2,4-dichlorophenol , 2,4,6-trichlorophenol , 4-chloro-3-cresol for each extracting organic solvent , i.e. , methylene chloride , carbon disulfide , and hexane is studied. The results of those studies are shown in Table 4.31-4.35 for the single standard in aqueous solutions and Table 4.36-4.40 for the standard mixture in aqueous solutions and the graphs correlated to these results are depicted in Figure 4.15-4.19 and Figure 4.20-4.24 , respectively. The results showing the percent recovery of each phenolic compound at concentration of 10.00 ppm for each sample-to-solvent ratio range from 2.49-94.62 % ,11.88-100.94 % , and 43.14-101.01 % with the percent RSD of 0.04-6.55 % ,0.32-7.58 % , and 1.52-10.92 % for the sample-to-solvent ratio of 9:1 , 5:5 , and 2:8, respectively , and from 4.45-94.60 % and 36.29-98.96 %, with the percent RSD of 0.68-6.12 % and 0.72-10.35 % , for the sample-to-solvent ratio of 9:1 and 5:5 respectively. However , the sample-to-solvent ratio of 2:8 for 1.00 ppm of each phenolic compound in standard solutions can not be detected due to their concentrations are very low in an organic extract.

According to Table 4.31-4.40 , the percent recovery of the ratio of 9:1 is less than the ratios

of 5:5 and 2:8 , respectively. Nevertheless , the concentration of each phenolic compound in the solution decreases as long as the sample-to-solvent ratio has been decreased. This means that the concentration of each phenolic compound in the organic extract for the sample-to-solvent ratio of 9:1 is higher than the sample-to-solvent ratios of 5:5 , 2:8 , respectively, and its percent RSD is lower than that of the other two ratios ,i.e., 5:5, 2:8 as can be seen from Table 4.31-4.40. Therefore , the sample-to-solvent ratio of 9:1 should be considered as the suitable ratio for the microextraction technique.

Table 4.31 The effect of sample-to-solvent ratios of phenol in standard aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	3.79	24.18	0.66
	5:5	2.84	71.38	0.32
	2:8	2.81	90.92	5.80
CS_2	9:1	0.64	6.10	3.20
	5:5	0.61	35.75	2.11
	2:8	0.77	74.38	4.54
HEXANE	9:1	0.15	2.49	5.37
	5:5	0.14	11.88	7.58
	2:8	0.21	43.14	1.87

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	3.72	23.74	2.22
	5:5	2.69	69.42	2.13
	2:8	ND	ND	ND
CS_2	9:1	0.46	4.45	2.43
	5:5	0.75	41.27	5.72
	2:8	ND	ND	ND
HEXANE	9:1	ND	ND	ND
	5:5	ND	ND	ND
	2:8	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.32 The effect of sample-to-solvent ratios of 2-nitrophenol in standard aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	224.18	94.62	1.59
	5:5	119.63	99.53	1.08
	2:8	*	100.51	2.21
CS_2	9:1	44.19	81.73	0.54
	5:5	30.24	95.62	2.31
	2:8	8.87	98.81	3.47
HEXANE	9:1	28.01	74.60	0.04
	5:5	5.04	82.74	2.30
	2:8	10.32	96.12	2.51

(1) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	133.00	92.26	2.22
	5:5	57.86	95.53	2.13
	2:8	ND	ND	ND
CS_2	9:1	81.01	88.70	2.43
	5:5	14.70	93.12	5.72
	2:8	ND	ND	ND
HEXANE	9:1	28.05	73.97	3.28
	5:5	9.42	90.37	1.51
	2:8	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2-nitrophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.33 The effect of sample-to-solvent ratios of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	35.21	74.80	1.73
	5:5	11.87	91.93	3.59
	2:8	14.14	97.75	4.47
CS_2	9:1	27.20	73.20	1.96
	5:5	8.49	87.39	4.60
	2:8	5.83	98.78	4.67
HEXANE	9:1	15.61	60.27	6.55
	5:5	5.43	83.76	2.03
	2:8	2.61	88.88	1.52

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	45.86	79.38	1.70
	5:5	7.92	87.91	1.04
	2:8	ND	ND	ND
CS_2	9:1	34.50	77.72	1.45
	5:5	0.24	88.74	0.72
	2:8	ND	ND	ND
HEXANE	9:1	17.94	64.28	2.53
	5:5	2.80	87.16	4.61
	2:8	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.34 The effect of sample-to-solvent ratios of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	46.48	79.08	0.92
	5:5	18.53	93.46	0.86
	2:8	2.07	96.05	1.38
CS_2	9:1	48.75	80.37	0.69
	5:5	44.99	94.04	1.58
	2:8	46.63	97.77	2.38
HEXANE	9:1	44.55	81.03	2.67
	5:5	58.80	97.18	0.66
	2:8	*	102.99	0.65

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	45.86	79.38	1.70
	5:5	7.92	87.91	1.04
	2:8	ND	ND	ND
CS_2	9:1	34.50	77.72	1.45
	5:5	10.33	90.74	0.72
	2:8	ND	ND	ND
HEXANE	9:1	17.94	64.28	2.53
	5:5	2.80	87.16	4.61
	2:8	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2,4,6-trichlorophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.35 The effect of sample-to-solvent ratios of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

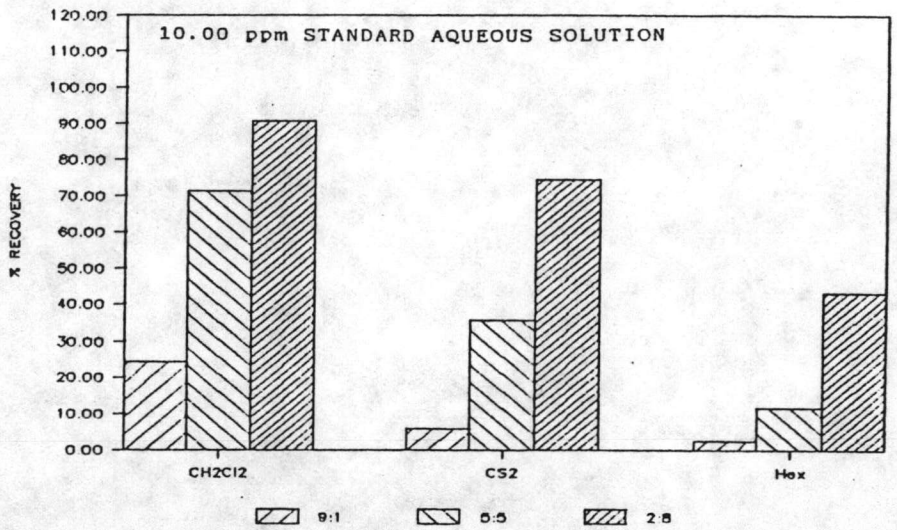
SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	27.13	69.64	1.01
	5:5	6.04	85.24	2.85
	2:8	10.40	96.47	2.33
CS_2	9:1	10.95	52.63	0.82
	5:5	3.04	74.47	4.05
	2:8	7.13	98.43	3.58
HEXANE	9:1	2.25	18.53	1.24
	5:5	1.87	64.20	1.20
	2:8	1.42	83.61	4.95

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	25.40	68.49	2.20
	5:5	15.63	92.72	3.53
	2:8	ND	ND	ND
CS_2	9:1	11.93	54.68	3.45
	5:5	3.39	76.87	2.37
	2:8	ND	ND	ND
HEXANE	9:1	1.86	15.85	6.60
	5:5	1.89	63.72	9.53
	2:8	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.



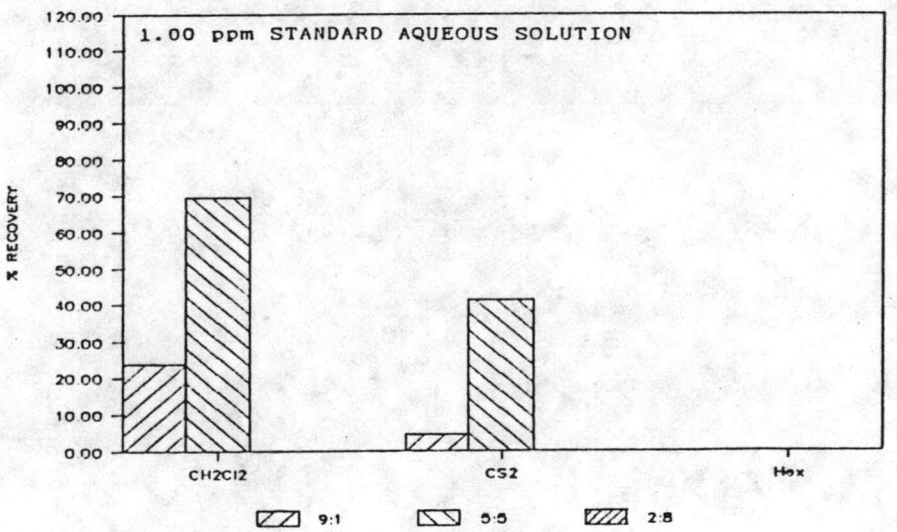


Figure 4.15 The effect of sample-to-solvent ratios on % recovery of phenol in standard aqueous solution with the various organic solvents.

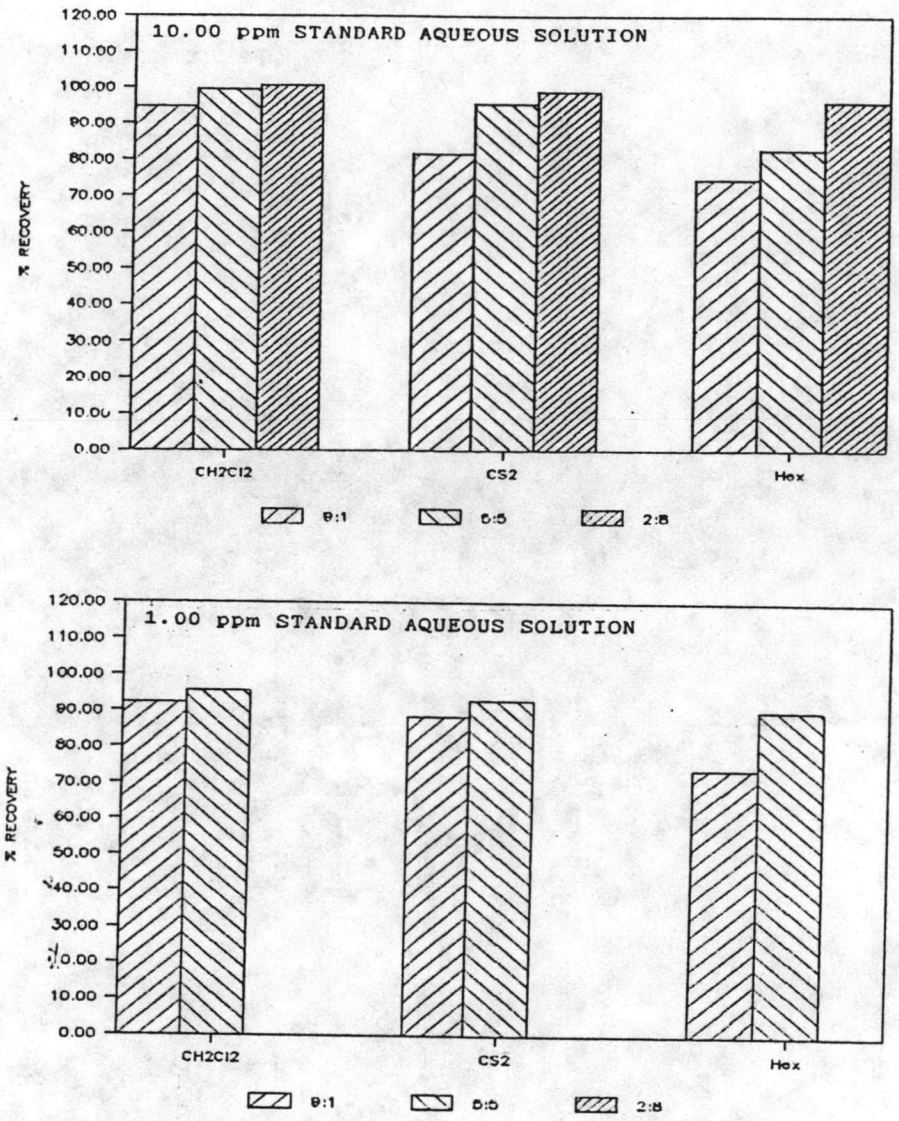


Figure 4.16 The effect of sample-to-solvent ratios on % recovery of 2-nitrophenol in standard aqueous solution with the various organic solvents.

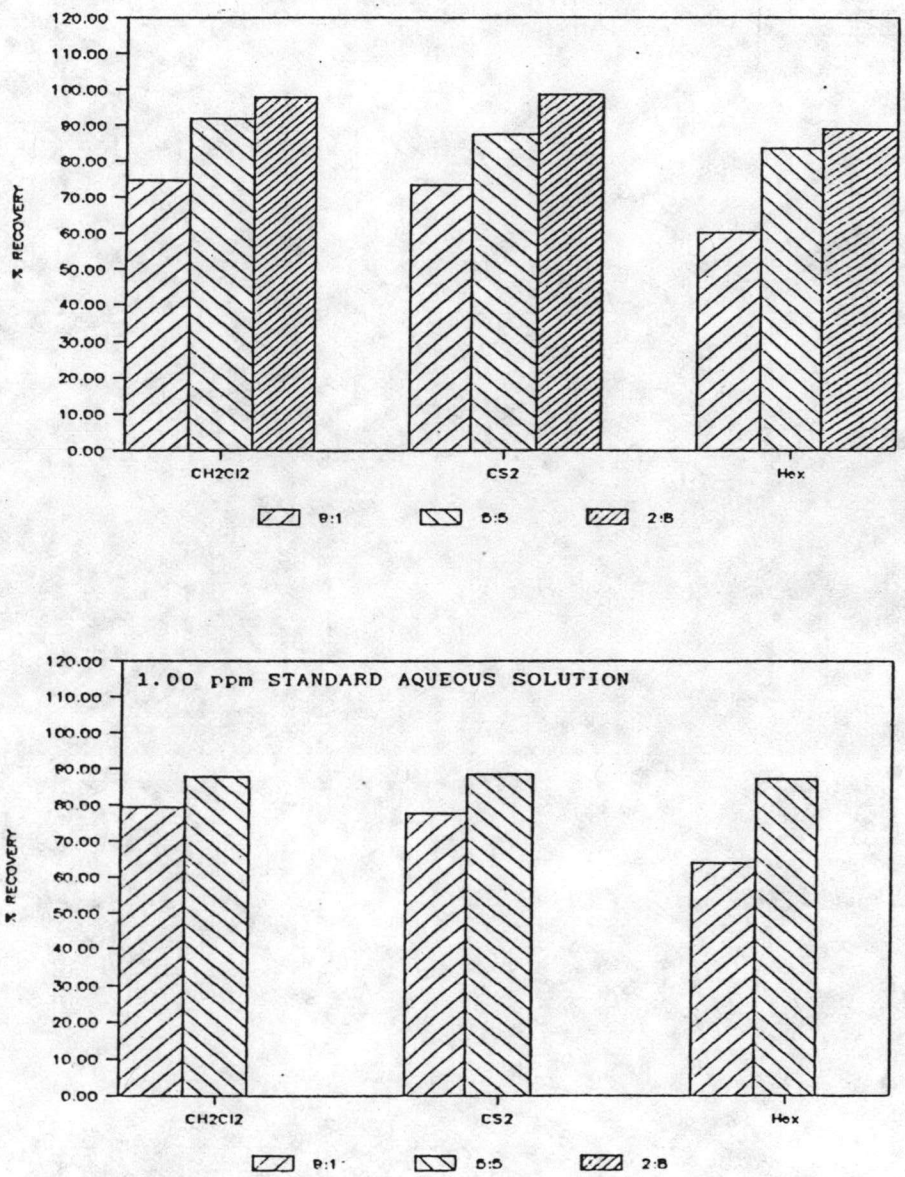
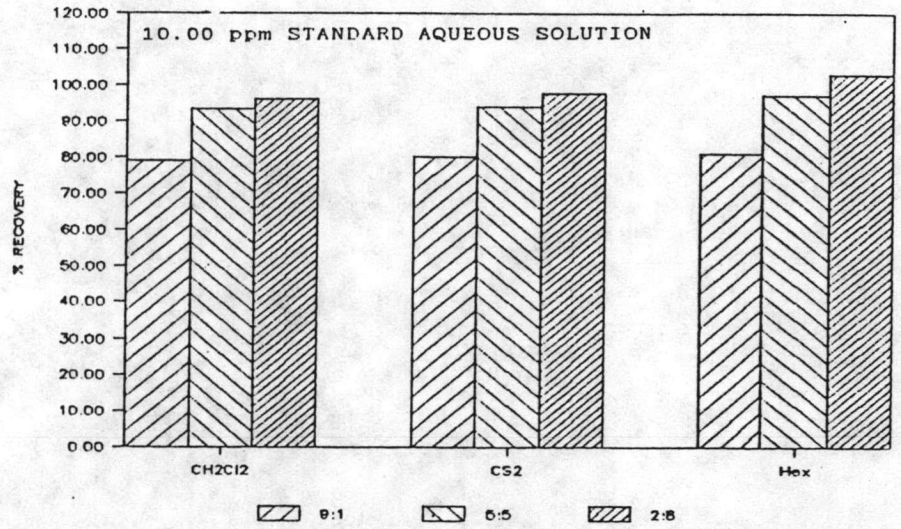


Figure 4.17 The effect of sample-to-solvent ratios on % recovery of 2,4-dichlorophenol in standard aqueous solution with the various organic solvents.



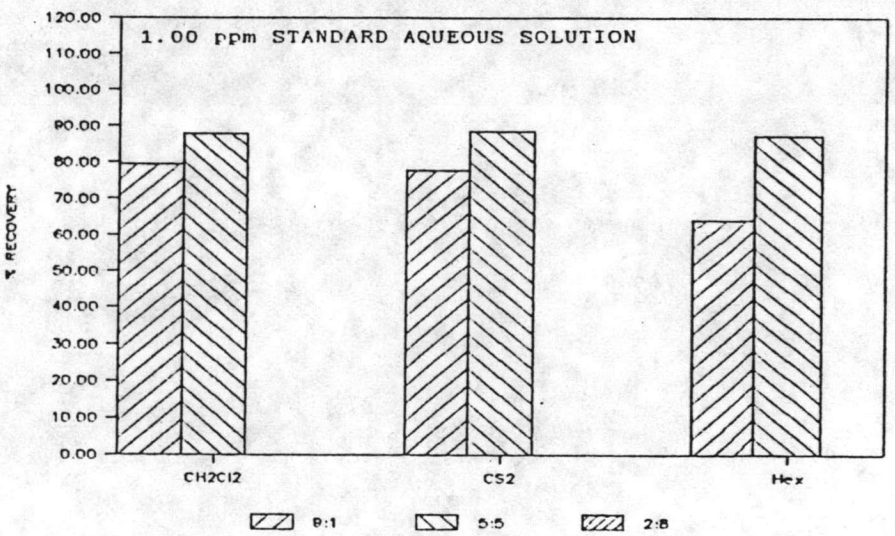


Figure 4.18 The effect of sample-to-solvent ratios on % recovery of 2,4,6-trichlorophenol in standard aqueous solution with the various organic solvents.

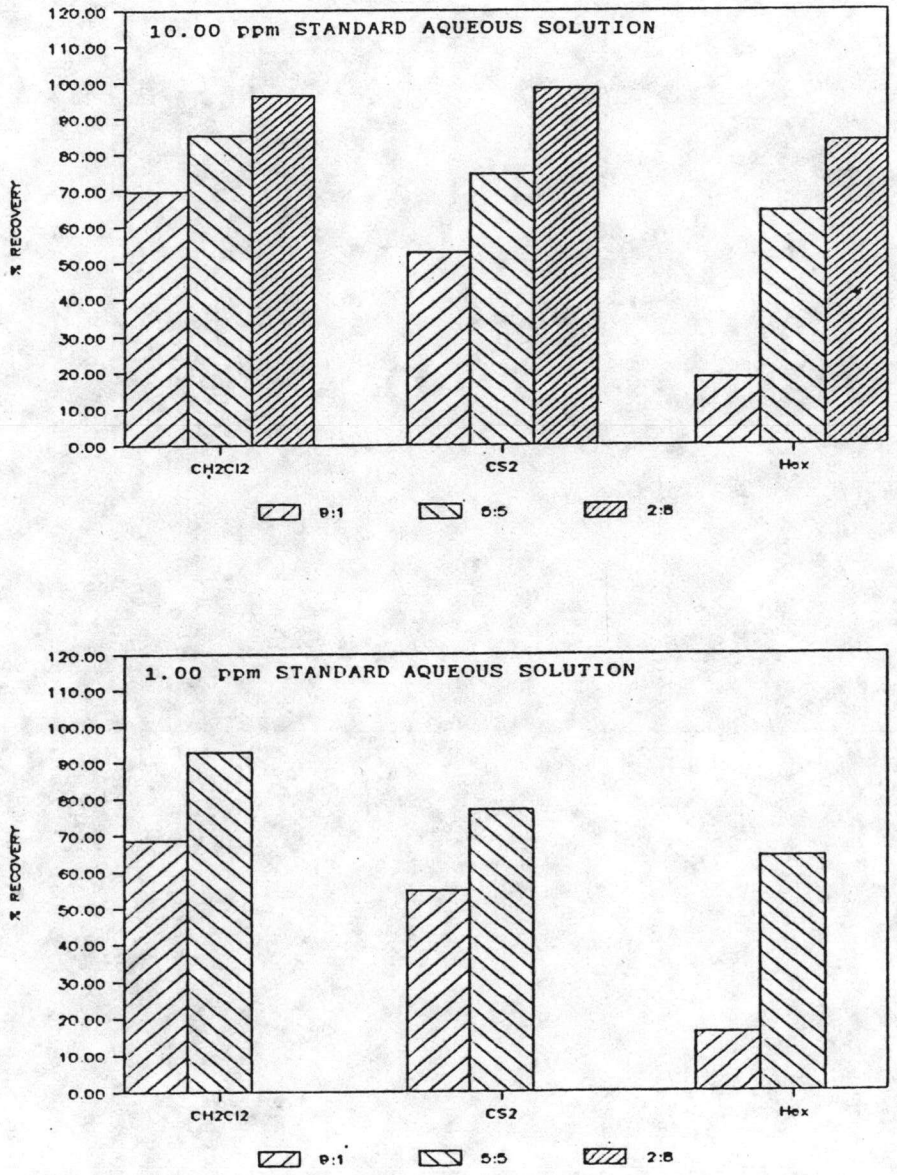


Figure 4.19 The effect of sample-to-solvent ratios on % recovery of 4-chloro-3-cresol in standard aqueous solution with the various organic solvents.

Table 4.36 The effect of sample-to-solvent ratios of phenol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	3.74	24.04	4.38
	5:5	3.64	75.80	6.79
	2:8	5.57	94.70	6.89
CS_2	9:1	0.89	8.26	4.24
	5:5	0.76	41.91	6.41
	2:8	0.99	79.80	8.84
HEXANE	9:1	0.25	2.51	3.20
	5:5	0.13	11.25	5.11
	2:8	0.31	53.18	9.35

(1) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	3.51	22.88	1.56
	5:5	2.54	71.10	8.46
	2:8	ND	ND	ND
CS_2	9:1	1.16	10.50	10.87
	5:5	0.60	36.29	4.20
	2:8	ND	ND	ND
HEXANE	9:1	ND	ND	ND
	5:5	ND	ND	ND
	2:8	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

Table 4.37 The effect of sample-to-solvent ratios of 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	179.71	93.48	1.62
	5:5	*	100.94	2.21
	2:8	*	101.01	3.31
CS_2	9:1	44.14	82.83	1.65
	5:5	12.16	89.44	5.72
	2:8	*	100.23	5.69
HEXANE	9:1	30.30	75.08	0.99
	5:5	4.67	81.03	4.90
	2:8	3.60	98.81	4.23

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	764.75	94.60	0.73
	5:5	45.83	98.96	5.58
	2:8	ND	ND	ND
CS_2	9:1	58.91	85.43	2.17
	5:5	13.97	92.76	1.49
	2:8	ND	ND	ND
HEXANE	9:1	31.41	76.04	1.49
	5:5	37.89	99.76	1.43
	2:8	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2-nitrophenol is higher than its initial concentration of standard soluttion.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.38 The effect of sample-to-solvent ratios of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	59.16	83.19	2.00
	5:5	28.26	98.10	2.53
	2:8	*	100.62	8.48
CS_2	9:1	59.65	83.44	2.72
	5:5	11.56	90.03	4.30
	2:8	*	102.24	2.38
HEXANE	9:1	16.66	62.79	0.72
	5:5	5.22	83.44	4.95
	2:8	2.40	90.17	3.38

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	34.95	82.70	1.27
	5:5	8.24	87.39	7.44
	2:8	ND	ND	ND
CS_2	9:1	28.94	78.35	3.47
	5:5	6.14	85.96	6.83
	2:8	ND	ND	ND
HEXANE	9:1	25.94	72.37	1.91
	5:5	4.81	82.78	5.12
	2:8	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2,4-dichlorophenol is higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.39 The effect of sample-to-solvent ratios of 2,4,6-trichlorophenol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	54.90	82.32	2.05
	5:5	19.66	96.50	4.26
	2:8	11.90	99.27	0.97
CS_2	9:1	83.66	88.96	2.72
	5:5	12.29	95.50	5.81
	2:8	*	98.76	2.99
HEXANE	9:1	38.04	77.45	3.73
	5:5	6.64	86.45	2.72
	2:8	3.65	93.27	4.76

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	107.66	87.10	0.68
	5:5	7.83	90.07	3.59
	2:8	ND	ND	ND
CS_2	9:1	44.56	81.94	4.91
	5:5	16.00	95.91	7.01
	2:8	ND	ND	ND
HEXANE	9:1	25.50	71.94	2.94
	5:5	6.09	85.91	10.35
	2:8	ND	ND	ND

Note : 1. * can not be calculated due to the experimental concentration of 2,4,6-trichlorophenol higher than its initial concentration of standard solution.

2. ND = Not Detectable.

3. Triplicate analyses.

Table 4.40 The effect of sample-to-solvent ratios of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

(1) 10.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	53.79	71.19	2.54
	5:5	4.74	81.20	2.41
	2:8	7.57	97.72	9.08
CS_2	9:1	18.60	65.23	3.21
	5:5	7.63	87.64	2.55
	2:8	16.50	93.80	4.32
HEXANE	9:1	2.50	20.17	8.71
	5:5	2.02	65.75	4.77
	2:8	1.73	80.78	10.92

(2) 1.00 ppm STANDARD SOLUTION

SOLVENT	RATIO	K_d	%E	%RSD
CH_2Cl_2	9:1	24.67	67.61	1.36
	5:5	3.86	76.91	2.42
	2:8	ND	ND	ND
CS_2	9:1	15.18	59.61	10.12
	5:5	8.56	88.56	8.57
	2:8	ND	ND	ND
HEXANE	9:1	3.36	25.46	3.89
	5:5	8.56	88.81	2.46
	2:8	ND	ND	ND

Note : 1. ND = Not Detectable.

2. Triplicate analyses.

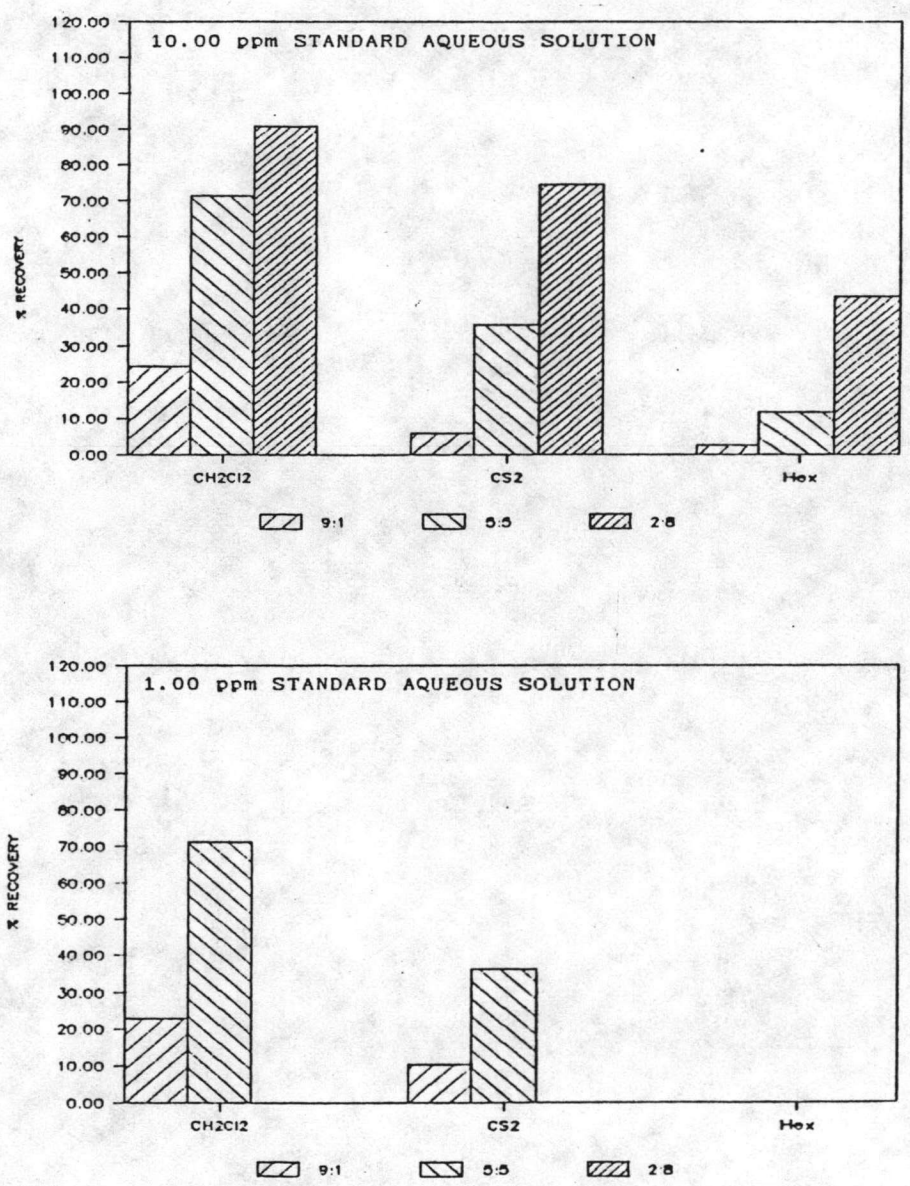


Figure 4.20 The effect of sample-to-solvent ratios on % recovery of phenol in standard mixture aqueous solution with the various organic solvents.

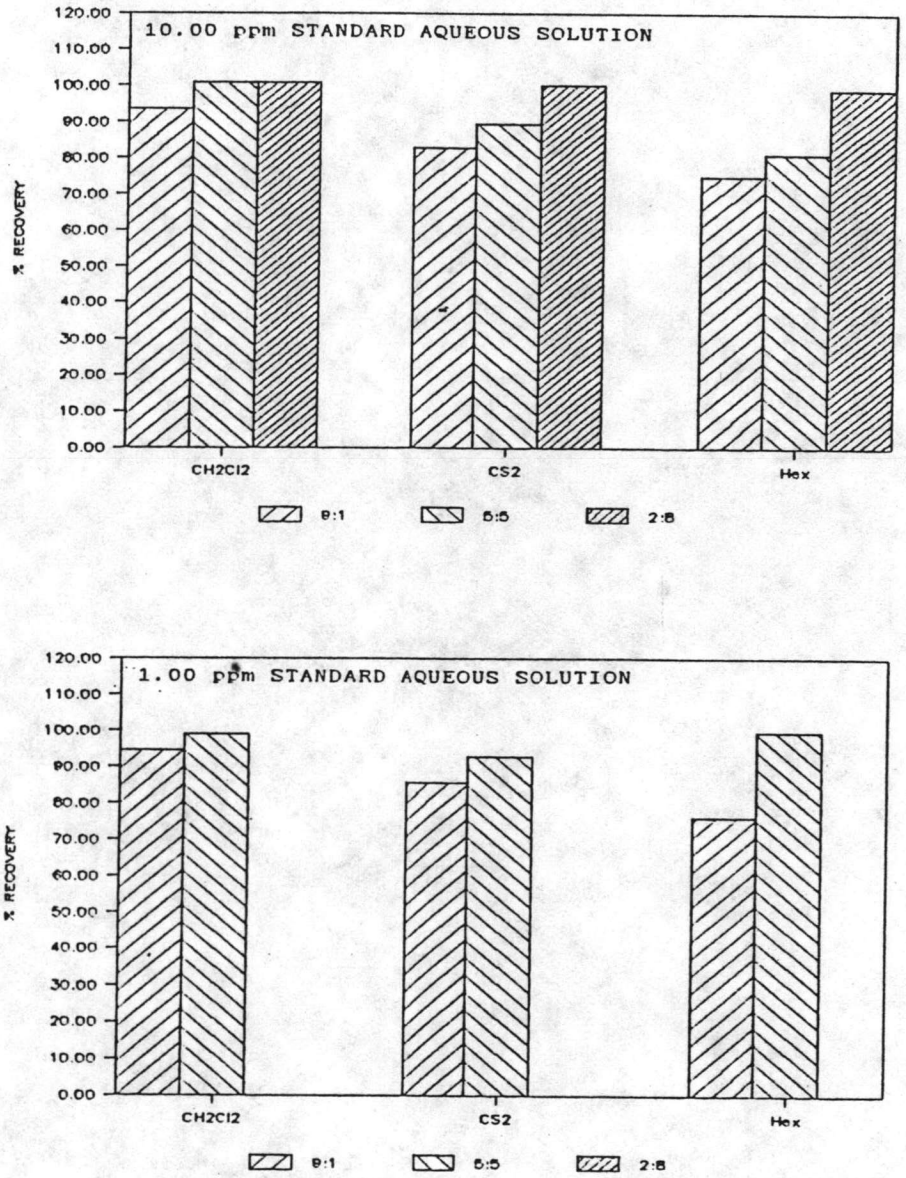
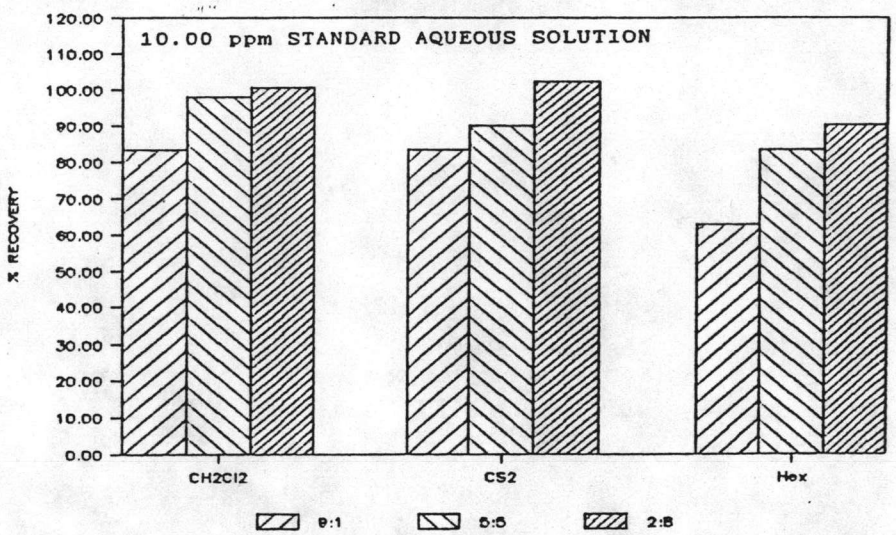


Figure 4.21 The effect of sample-to-solvent ratios on % recovery of 2-nitrophenol in standard mixture aqueous solution with the various organic solvents.



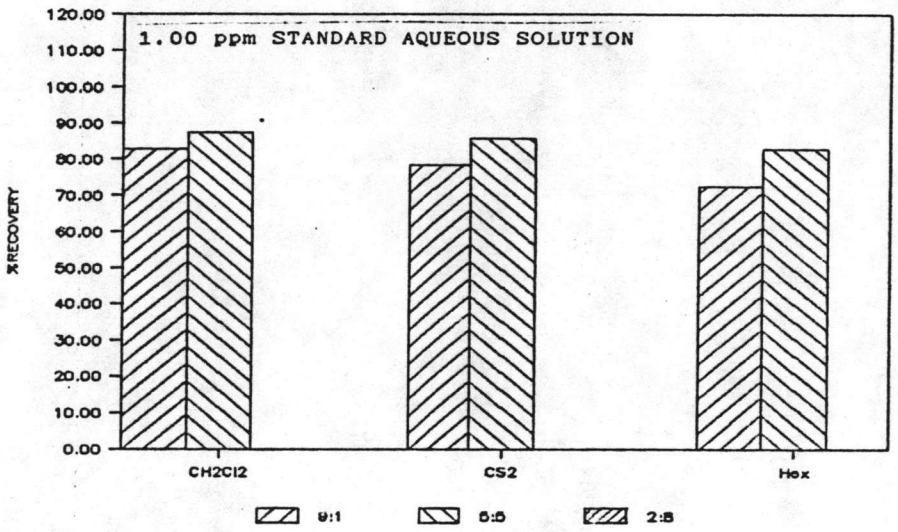
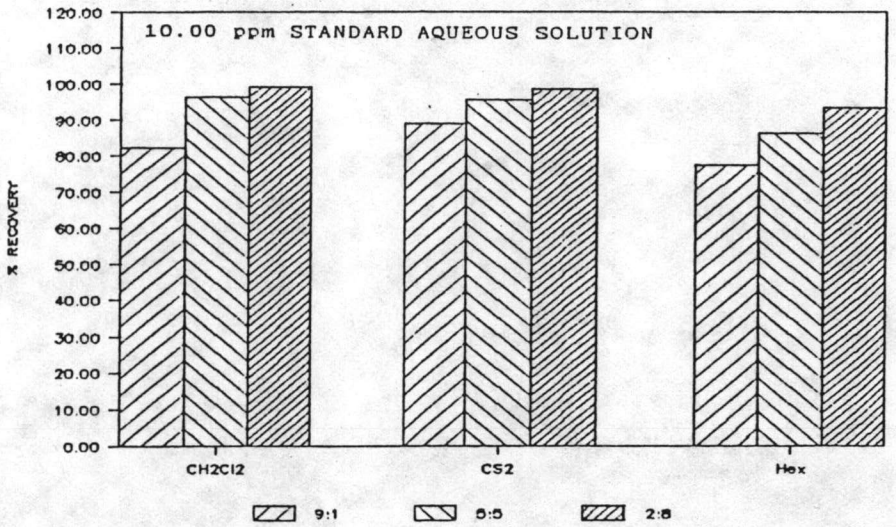


Figure 4.22 The effect of sample-to-solvent ratios on % recovery of 2,4-dichlorophenol in standard mixture aqueous solution with the various organic solvents.



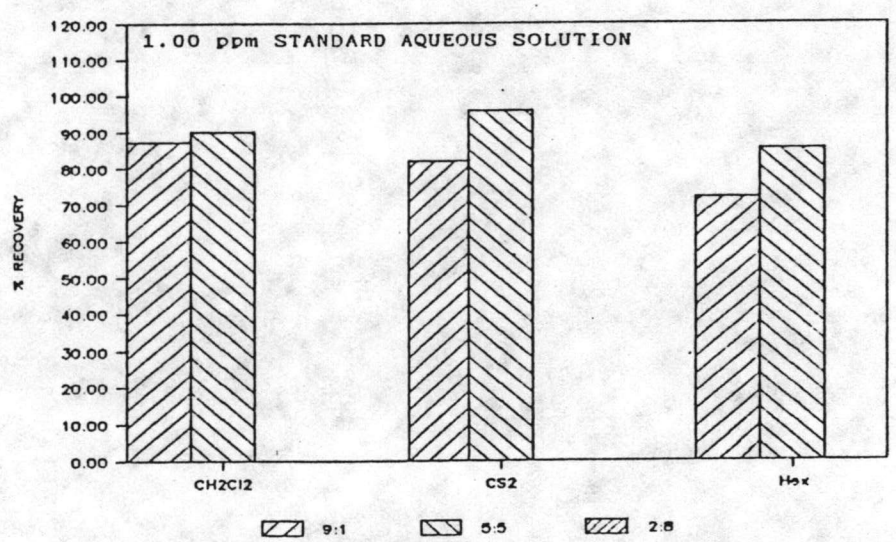


Figure 4.23 The effect of sample-to-solvent ratios on % recovery of 2,4,6-trichlorophenol in standard mixture aqueous solution with the various organic solvents.

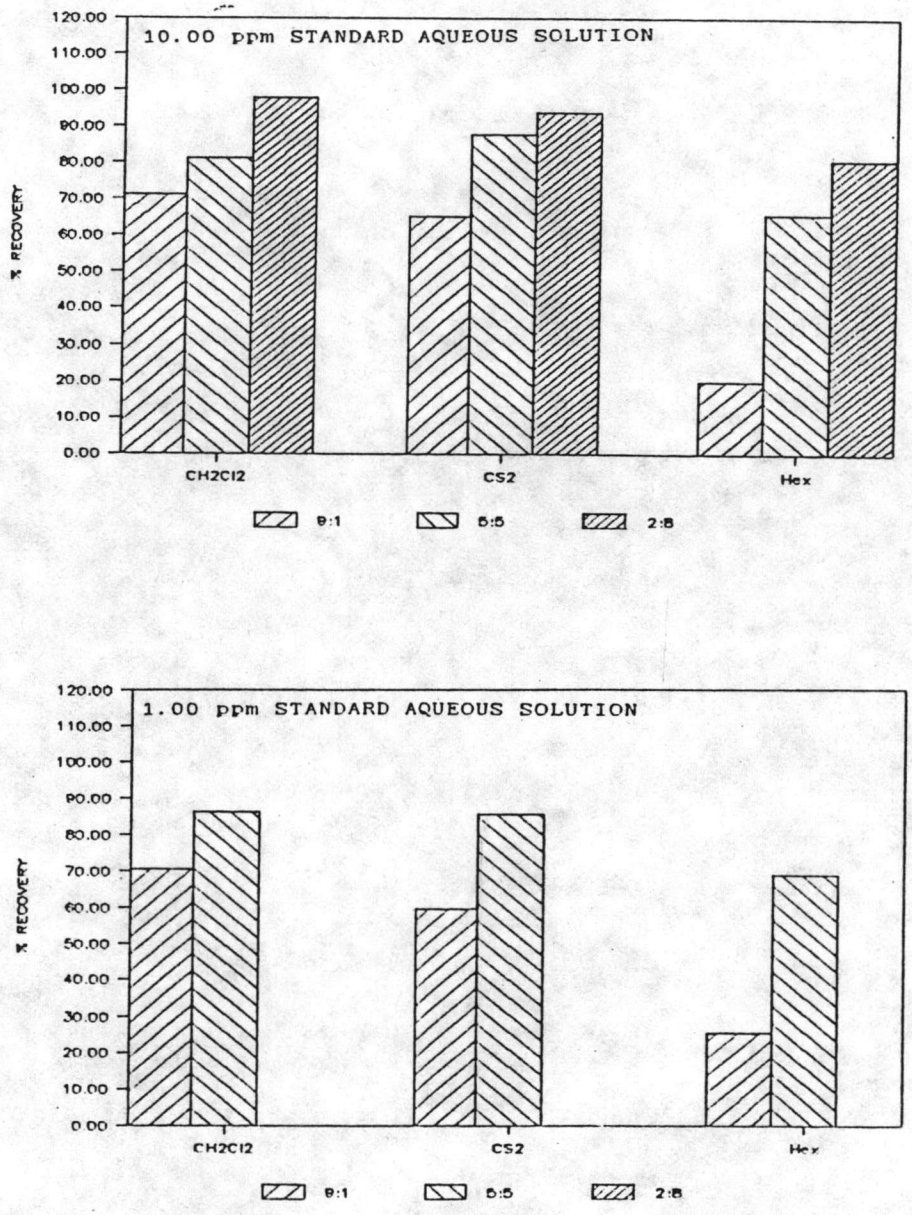


Figure 4.24 The effect of sample-to-solvent ratios on % recovery of 4-chloro-3-cresol in standard mixture aqueous solution with the various organic solvents.

4.5 THE EFFECT OF ORGANIC SOLVENT

The percent recovery of each phenolic compound for each organic solvent ,i.e. ,methylene chloride , carbon disulfide , and hexane and for each sample-to-solvent ratio ,i.e., 9:1 , 5:5 , and 2:8 can be seen from Table 4.21-4.40 for the single standard and standard mixture in aqueous solutions. It is found that the microextraction of the single and mixture components in aqueous solution with methylene chloride as the extracting organic solvent gives the highest percent recovery comparing with carbon disulfide and hexane. The reason is that the polarity of the solvents studied are in the following order ; methylene chloride , carbon disulfide , and hexane and the phenolic compounds are also a polar compounds. Therefore , methylene chloride would be selected as the suitable extracting organic solvent for the microextraction of phenolic compounds in the water samples.

4.6 THE EFFECT OF CONCENTRATIONS

The effect of concentrations of 1.00 and 10.00 ppm of each phenolic compound on the percent recovery of the single standard and standard mixture in aqueous solutions for the sample-to-solvent ratios of 9:1, 5:5, 2:8 , and for the extracting organic solvent ,i.e., methylene chloride , carbon disulfide , and hexane is also investigated. The results are shown in Table 4.21-4.40 and the graphs correlated to these results are depicted in Figure 4.5A-4.24.

It is found that the percent recovery of each phenolic compound in the single standard and standard mixture in aqueous solutions is slightly different for the two different concentrations. In addition , the percent recovery of each phenolic compound in the single standard in aqueous solutions is slightly different from the percent recovery of each phenolic compound in the standard mixture in aqueous solutions. Therefore , the percent recovery of an individual phenolic compound is slightly affected by the presence of the other compound in the standard mixture in aqueous solutions.

4.7 THE MINIMUM DETECTABLE LEVEL (MDL) OF PHENOLIC COMPOUNDS.

The minimum detectable is defined as an amount of the component which gives a detector response equal to twice the average noise level (77). The minimum detectable level of each phenolic compound in each extracting organic solvent is presented in Table 4.41. It is found that the MDL of phenolic compounds are the same for each extracting organic solvent and the MDL is in the range of 0.45-1.40 ppm.

Table 4.41 The minimum detectable level of phenolic compounds in the various organic solvents.

Phenolic Compounds	Minimum Detectable Level (ppm)		
	CH_2Cl_2	CS_2	Hexane
Phenol	0.50	0.50	0.50
2-Nitrophenol	0.45	0.45	0.45
2,4-Dichlorophenol	0.70	0.70	0.70
2,4,6-Trichlorophenol	1.40	1.40	1.40
4-chloro-3-cresol	0.80	0.80	0.80

Triplicate analyses.

4.8 THE ACCURACY OF MICROEXTRACTION TECHNIQUE

The accuracy of microextraction technique is investigated by comparing the concentration of phenolic compounds obtained from the analysis of unknown synthetic mixture solutions with their true concentrations. The suitable combination used in the determination of phenolic compounds in the sample is the pH of 2 , the equilibration time of 20 min , the ratio of 9:1 , salting out with 2.00 g anhydrous sodium sulfate ,and methylene chloride as an extracting organic solvent and the procedure of microextraction would be the same as described in section 3.4.3

The result of the concentration of each phenolic compound found and % error are demonstrated in Table 4.42. It is shown that the % error in the determination of each phenolic compound in the unknown synthetic mixture solution is in the range of 0.53-4.97 % and the reasons of the high percent error is that the baseline is drifted during the analysis by means of temperature program resulting the difference in the integration of the peaks by an integrator for each analysis. Thus , the microextraction technique would give the high accuracy for the analysis of phenolic compounds in water samples. Therefore , the microextraction technique should be considered as the alternative method for the analysis of phenolic compounds in water samples.

Table 4.42 The analysis of phenolic compounds in the unknown synthetic mixture solutions.

Phenolic compounds	Concentration (ppm)		%Error
	True	Experiment	
Phenol	42.66	40.80	4.36
2-Nitrophenol	40.42	42.43	4.97
2,4-Dichlorophenol	41.54	41.77	0.55
2,4,6-Trichlorophenol	40.48	41.65	2.89
4-chloro-3-cresol	39.76	39.55	0.53

Triplicated analyses.

4.9 THE DETERMINATION OF PHENOLIC COMPOUNDS IN REAL WATER SAMPLES.

Three water samples are collected from two pools nearby Chemistry building 2 and one pool near the main gate of Chulalongkorn University and the last two samples are obtained from the laboratory of samsen station at the Metropolitan Water Work Authoritty. Those samples are analysed by microextraction procedure as described in section 4.8 and the gas chromatogram of the unknown samples are shown in Figure 4.25-4.29. It is found that there are no peaks of interested phenolic compounds in the unknown samples. The reason of this is that the sample were collected in the rainy season and the pollutants may be diluted by the rain and the water coming from the north of this country. Therefore , those water samples do not have any interested phenolic compounds.

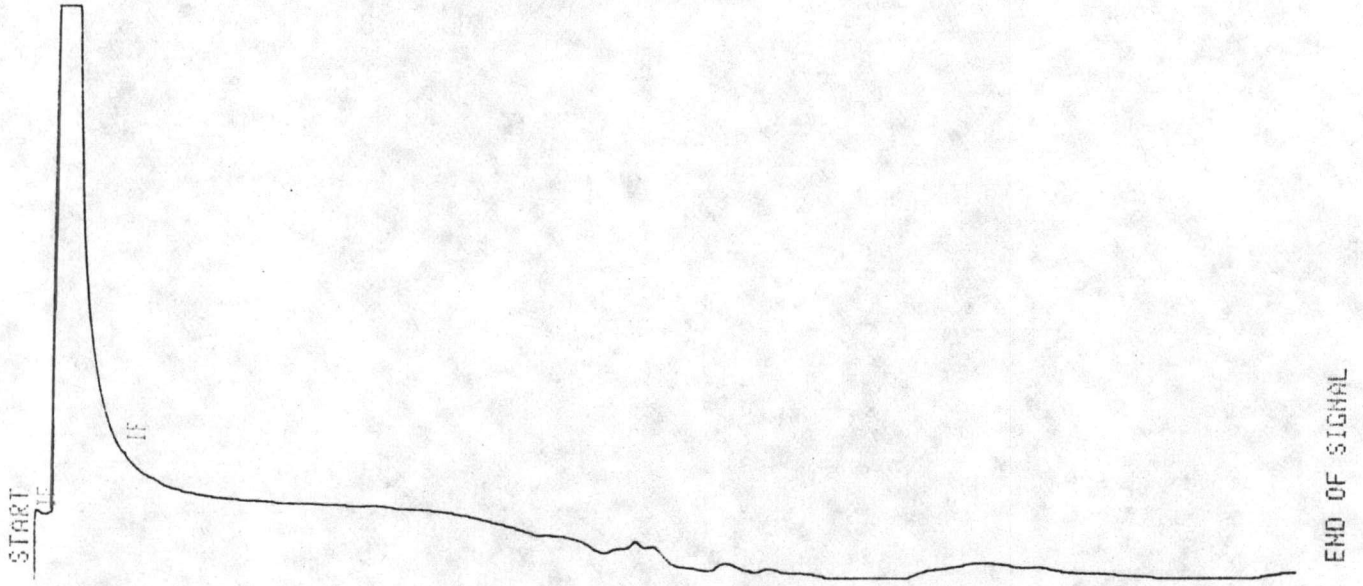


Figure 4.25 Gas chromatogram of the real sample No. 1*

Chromatographic conditions : column , 1% SP - 1240DA on Supelcoport 100/120 , 2 min initial hold at 100 °C , then to 150 °C at rate 12 °C/min and hold until the last peak eluted , injector and FID , 250 °C : N_2 carrier gas , 30 mL/min : sample size 1.00 µL.

* collected from the pond near the main gate of Chulalongkorn University.

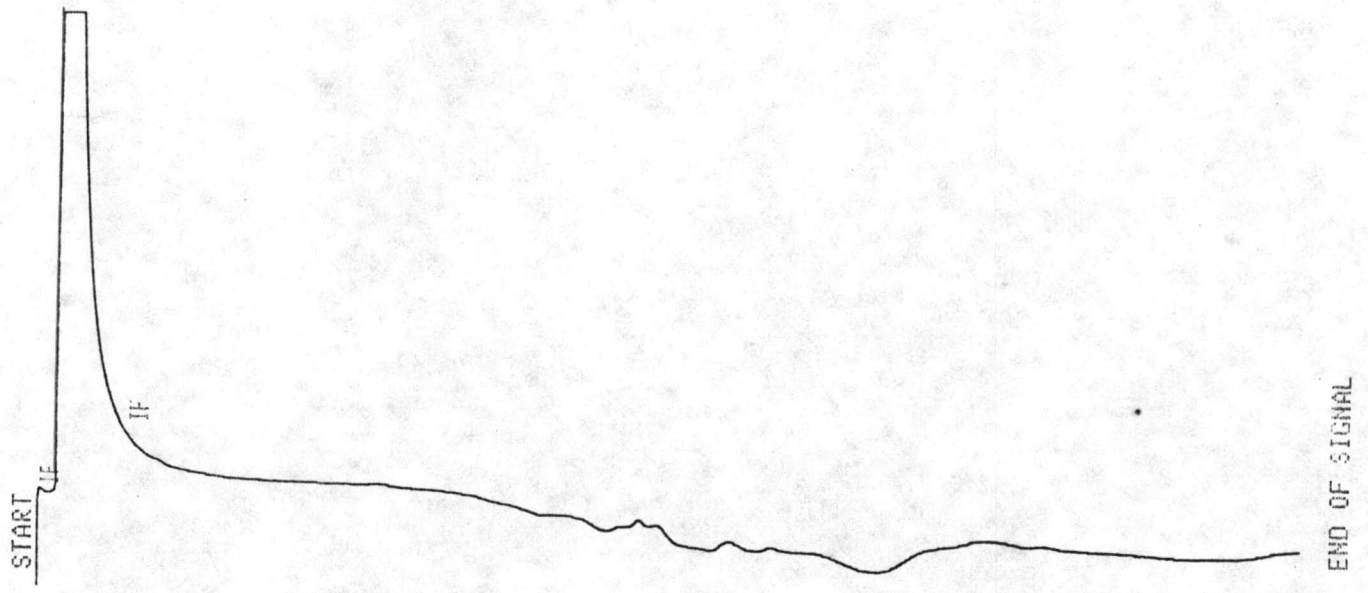


Figure 4.26 Gas chromatogram of the real sample No. 2*

Chromatographic conditions : column , 1% SP - 1240DA on Supelcoport 100/120 , 2 min initial hold at 100 °C , then to 150 °C at rate 12 °C/min and hold until the last peak eluted , injector and FID , 250 °C : N_2 carrier gas , 30 mL/min : sample size 1.00 µL.

* collected from the pond beside the Chem. Building 2 of Chulalongkorn University.

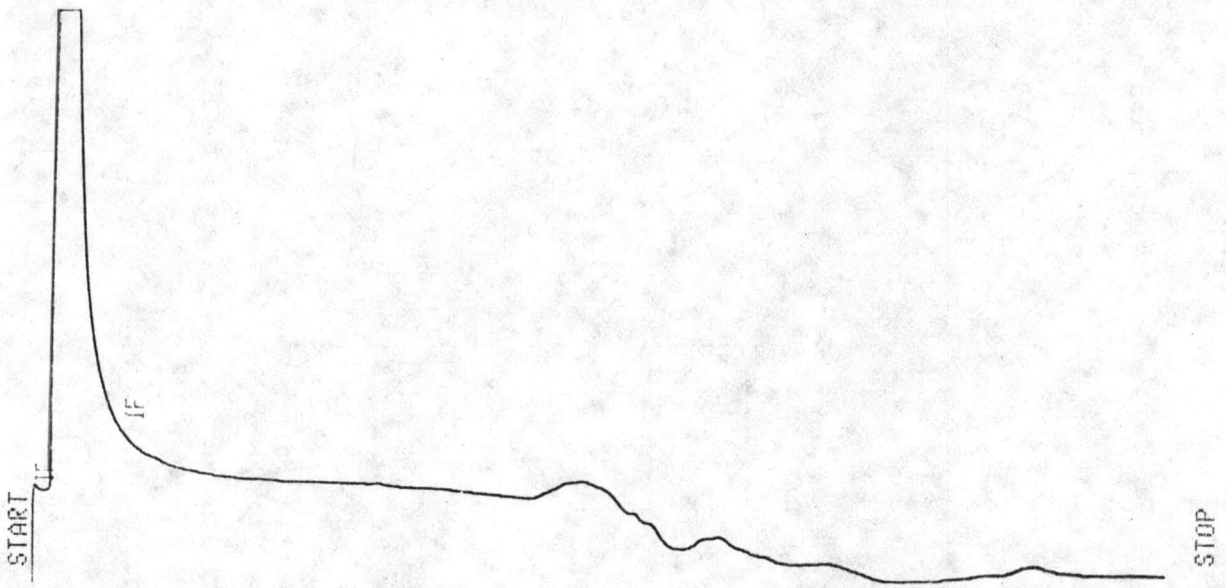


Figure 4.27 Gas chromatogram of the real sample No. 3*

Chromatographic conditions : column , 1% SP - 1240DA on Supelcoport 100/120 , 2 min initial hold at 100 °C , then to 150 °C at rate 12 °C/min and hold until the last peak eluted , injector and FID , 250 °C : N_2 carrier gas , 30 mL/min : sample size 1.00 μL.

* collected from the pond in front of the Chem. Building 2 of Chulalongkorn University.

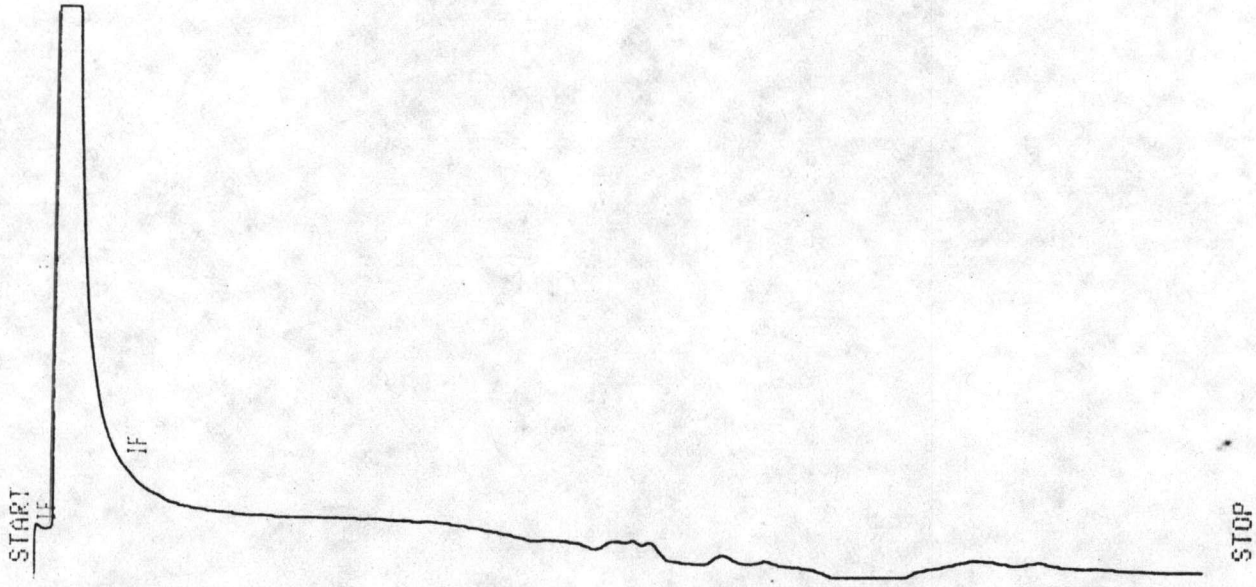


Figure 4.28 Gas chromatogram of the real sample No. 4*

Chromatographic conditions : column , 1% SP - 1240DA on Supelcoport 100/120 , 2 min initial hold at 100 °C , then to 150 °C at rate 12 °C/min and hold until the last peak eluted , injector and FID , 250 °C : N_2 carrier gas , 30 mL/min : sample size 1.00 µL.

* collected from the laboratory of samsen station.

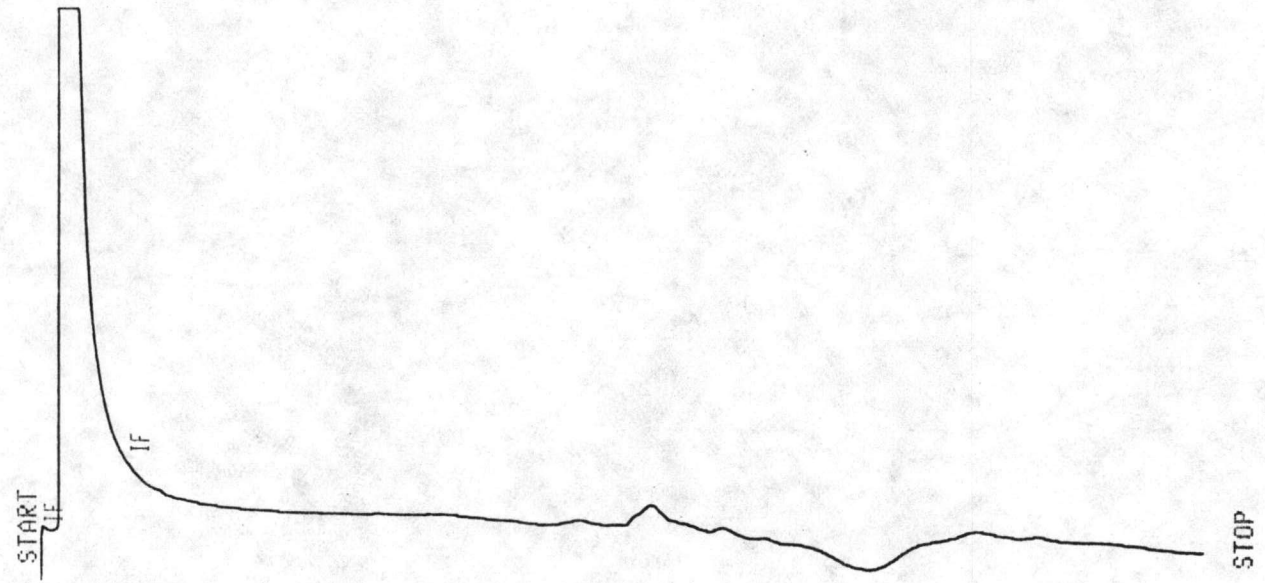


Figure 4.29 Gas chromatogram of the real sample No. 5*

Chromatographic conditions : column , 1% SP - 1240DA on Supelcoport 100/120 , 2 min initial hold at 100 °C , then to 150 °C at rate 12 °C/min and hold until the last peak eluted , injector and FID , 250 °C : N_2 carrier gas , 30 mL/min : sample size 1.00 µL.

* collected from the laboratory of samsen station.