



CHAPTER 4

RESULT AND DISCUSSION

4.1 THE STUDY OF SHAKING TIME

The various shaking times of each PAH, e.g., acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene are studied in various extracting solvents, i.e., carbon disulfide, cyclohexane and methylene chloride and in each sample to solvent ratio, i.e., 9:1, 5:5 and 2:8. The results of shaking time having the effect on % recovery of each PAH are shown in Table 4.1-4.5. The graph plotted the % recovery of each PAH against the shaking time for the extraction which carbon disulfide as solvent is shown in Figure 4.1. It shows that each PAH reaches the equilibrium in 20 min for the ratio of 9:1, 10 min for the ratio of 5:5 and 6 min for the ratio of 2:8. When cyclohexane is used as extracting solvent, the results are shown in Figure 4.2. The equilibration time for each PAH is 10 min, 6 min and 4 min for the sample to solvent ratios of 9:1, 5:5 and 2:8, respectively. The results with methylene chloride as extracting solvent are shown in Figure 4.3. The equilibration time for each PAH is 20 min for the ratio of 9:1, 2 min for ratio of 5:5 and 4 min for ratio of 2:8.

Table 4.1 The results of the effect of shaking time on
% recovery of acenaphthene in various solvents

(A) SOLVENT: CARBON DISULFIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	45.35	4.37	88.63	0.33	96.29	1.18
4	60.28	1.16	89.08	0.57	95.19	2.08
6	70.27	2.32	90.74	0.33	94.65	1.93
10	78.55	1.07	90.57	0.35	ND	ND
15	80.45	0.60	90.57	0.29	94.92	1.91
20	81.59	1.08	90.36	0.76	ND	ND
25	ND	ND	ND	ND	96.27	2.37
30	81.02	0.44	90.74	0.29	ND	ND

(B) SOLVENT: CYCLOHEXANE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	78.74	6.55	93.31	0.59	97.53	0.41
4	84.07	0.98	93.07	0.90	96.96	0.46
6	84.53	4.40	92.71	0.56	96.36	1.32
10	90.59	1.82	ND	ND	ND	ND
15	89.25	2.87	91.42	0.70	97.56	0.69
20	89.25	3.77	ND	ND	ND	ND
25	ND	ND	93.03	1.01	97.21	0.31
30	91.40	0.88	ND	ND	ND	ND

(C) SOLVENT: METHYLENE CHLORIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	51.94	1.62	89.13	1.05	91.74	1.65
4	67.71	0.17	93.50	2.96	96.87	0.53
6	71.82	0.70	90.79	1.26	95.39	2.25
10	74.73	0.26	ND	ND	ND	ND
15	78.96	0.96	91.28	0.68	94.51	2.25
20	80.90	0.15	ND	ND	ND	ND
25	ND	ND	91.04	1.68	93.83	1.90
30	80.75	0.14	ND	ND	ND	ND

Triplicate analyses
ND = Not Determine

Table 4.2 The results of the effect of shaking time on
% recovery of fluorene in various solvents

(A) SOLVENT: CARBON DISULFIDE						
SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	56.18	3.47	86.53	0.46	87.74	1.30
4	62.54	4.66	88.79	0.34	98.56	1.35
6	70.51	1.15	89.65	0.17	99.10	1.86
10	81.85	1.45	89.76	0.08	ND	-
15	83.73	0.73	90.73	0.59	98.34	0.83
20	83.73	1.12	91.43	0.08	ND	-
25	ND	-	ND	-	97.63	1.44
30	83.73	0.96	91.64	0.14	ND	-

(B) SOLVENT: CYCLOHEXANE						
SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	75.04	5.15	86.53	4.72	77.28	1.46
4	80.05	5.04	91.72	0.65	86.95	5.84
6	82.72	4.94	90.87	3.08	95.00	6.09
10	84.95	1.95	ND	-	ND	-
15	88.17	3.52	91.27	1.94	96.27	5.18
20	88.49	4.26	ND	-	ND	-
25	ND	-	90.94	0.75	98.58	2.13
30	88.29	1.95	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE						
SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	30.89	11.00	84.97	1.62	91.71	0.65
4	46.51	9.09	88.04	1.86	92.03	1.70
6	57.13	7.31	89.36	4.22	93.83	1.88
10	76.94	1.00	ND	-	ND	-
15	77.21	1.24	90.78	2.82	92.19	2.80
20	77.03	0.77	ND	-	N	-
25	ND	-	89.71	2.88	92.64	2.52
30	76.98	0.95	ND	-	ND	-

Triplicate analyses
ND = Not Determine



Table 4.3 The results of the effect of shaking time on % recovery of phenanthrene in various solvents

(A) SOLVENT: CARBON DISULFIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	43.04	6.16	93.77	1.91	96.46	3.02
4	65.02	2.81	92.99	2.22	97.67	4.70
6	71.81	3.70	92.80	2.07	95.58	3.37
10	79.07	3.83	94.42	1.12	ND	-
15	84.42	2.84	94.06	2.50	96.74	2.19
20	84.65	0.61	93.75	0.57	ND	-
25	ND	-	ND	-	96.28	6.25
30	84.77	0.64	95.12	4.63	ND	-

(B) SOLVENT: CYCLOHEXANE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	86.36	3.58	79.38	4.98	87.22	5.13
4	88.18	5.49	86.73	6.03	90.22	3.57
6	89.20	4.28	88.44	2.00	92.69	3.12
10	91.06	3.88	ND	-	ND	-
15	91.95	1.26	90.76	3.77	92.47	2.42
20	92.04	1.03	ND	-	ND	-
25	ND	-	91.08	3.88	92.26	4.37
30	91.37	2.96	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	38.78	14.67	82.98	9.67	90.82	1.38
4	60.40	7.84	84.21	1.91	90.20	2.55
6	75.84	2.49	85.10	3.95	90.33	3.31
10	75.56	5.77	ND	-	ND	-
15	77.73	1.71	86.95	0.20	89.89	4.90
20	77.36	1.93	ND	-	ND	-
25	ND	-	87.87	6.28	91.39	5.52
30	77.51	1.71	ND	-	ND	-

Triplicate analyses
 ND = Not Determine

Table 4.4 The results of the effect of shaking time on
% recovery of fluoranthene in various solvents

(A) SOLVENT: CARBON DISULFIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	30.40	2.37	90.15	0.75	59.82	2.58
4	36.75	1.90	91.10	0.39	96.45	1.26
6	42.14	1.10	91.14	0.48	97.41	3.07
10	46.59	5.20	91.85	1.02	ND	-
15	59.26	1.12	91.90	1.28	97.88	4.18
20	73.22	2.23	92.14	0.58	ND	-
25	ND	-	ND	-	98.83	2.97
30	73.18	0.87	92.32	0.88	ND	-

(B) SOLVENT: CYCLOHEXANE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	52.27	3.67	79.63	5.46	86.96	3.48
4	59.21	6.97	87.62	1.46	90.79	4.23
6	66.83	5.11	91.78	2.98	91.43	3.29
10	81.34	3.79	ND	-	ND	-
15	85.09	4.09	92.61	2.48	93.54	3.93
20	88.02	2.11	ND	-	ND	-
25	ND	-	91.15	1.83	92.99	3.86
30	88.06	5.50	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	22.22	5.02	80.44	5.17	89.05	1.70
4	33.98	2.59	84.00	1.45	90.41	6.51
6	41.65	0.65	88.11	4.04	92.30	3.38
10	56.88	1.81	ND	-	ND	-
15	76.23	2.27	90.28	4.73	90.41	1.78
20	79.84	0.82	ND	-	ND	-
25	ND	-	88.42	1.73	91.98	2.11
30	79.84	5.58	ND	-	ND	-

Triplicate analyses
ND = Not Determine

Table 4.5 The results of the effect of shaking time on
% recovery of pyrene in various solvents

(A) SOLVENT: CARBON DISULFIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	20.04	8.19	81.57	0.81	59.62	8.36
4	22.76	3.28	83.82	0.96	71.09	2.32
6	28.30	2.42	86.42	1.78	87.24	0.63
10	36.19	3.15	87.37	1.41	ND	-
15	44.34	0.79	88.00	0.82	90.30	0.56
20	45.68	0.23	88.49	0.56	ND	-
25	ND	-	ND	-	91.08	2.52
30	46.57	0.60	87.55	1.05	ND	-

(B) SOLVENT: CYCLOHEXANE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	50.53	7.77	64.67	8.98	82.51	11.87
4	77.19	7.08	79.49	12.77	95.20	8.76
6	88.60	3.08	92.85	0.96	98.65	4.40
10	91.41	1.93	ND	-	ND	-
15	92.75	1.05	94.45	0.43	95.99	7.64
20	93.10	1.86	ND	-	ND	-
25	ND	-	99.35	4.83	96.76	6.49
30	93.27	1.06	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SHAKING TIME (min)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
2	9.73	5.08	81.14	4.83	61.53	6.77
4	28.81	6.27	84.80	1.11	88.22	7.13
6	35.89	3.26	86.72	1.91	91.44	5.32
10	43.36	4.14	ND	-	ND	-
15	52.68	4.70	87.68	1.07	93.16	1.58
20	76.24	0.09	ND	-	ND	-
25	ND	-	87.06	0.43	90.94	3.74
30	76.07	1.78	ND	-	ND	-

Triplicate analyses
ND = Not Determine

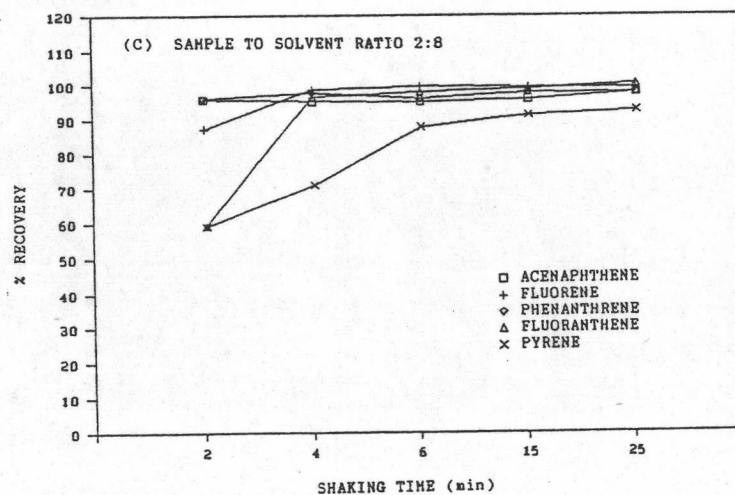
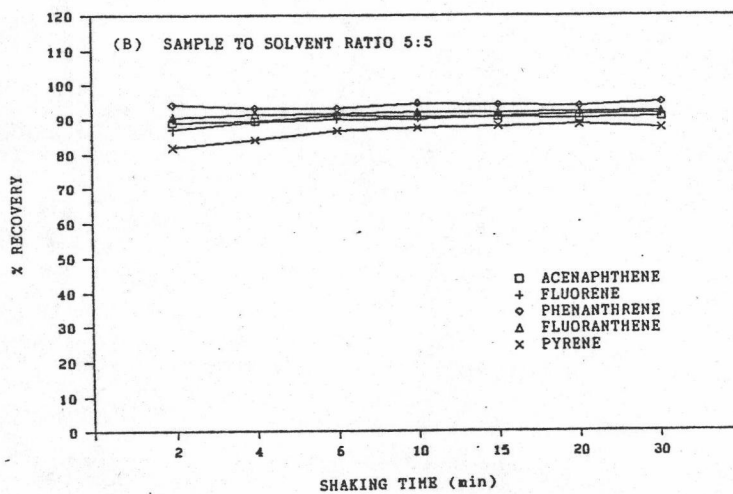
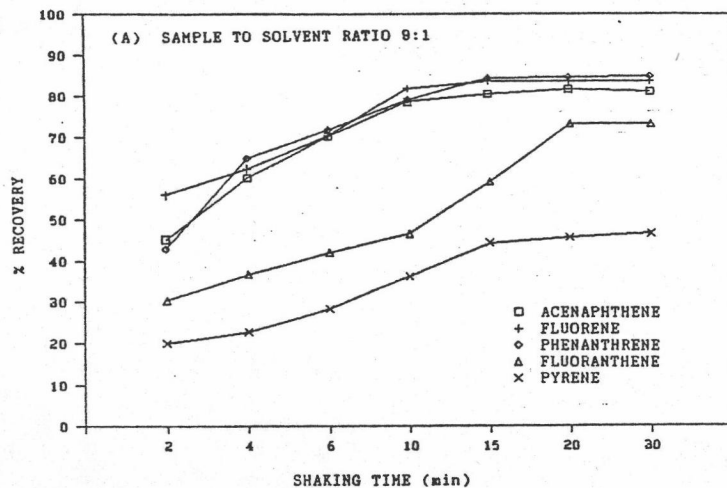


Figure 4.1 The effect of shaking time on % recovery of each PAH with carbon disulfide as solvent

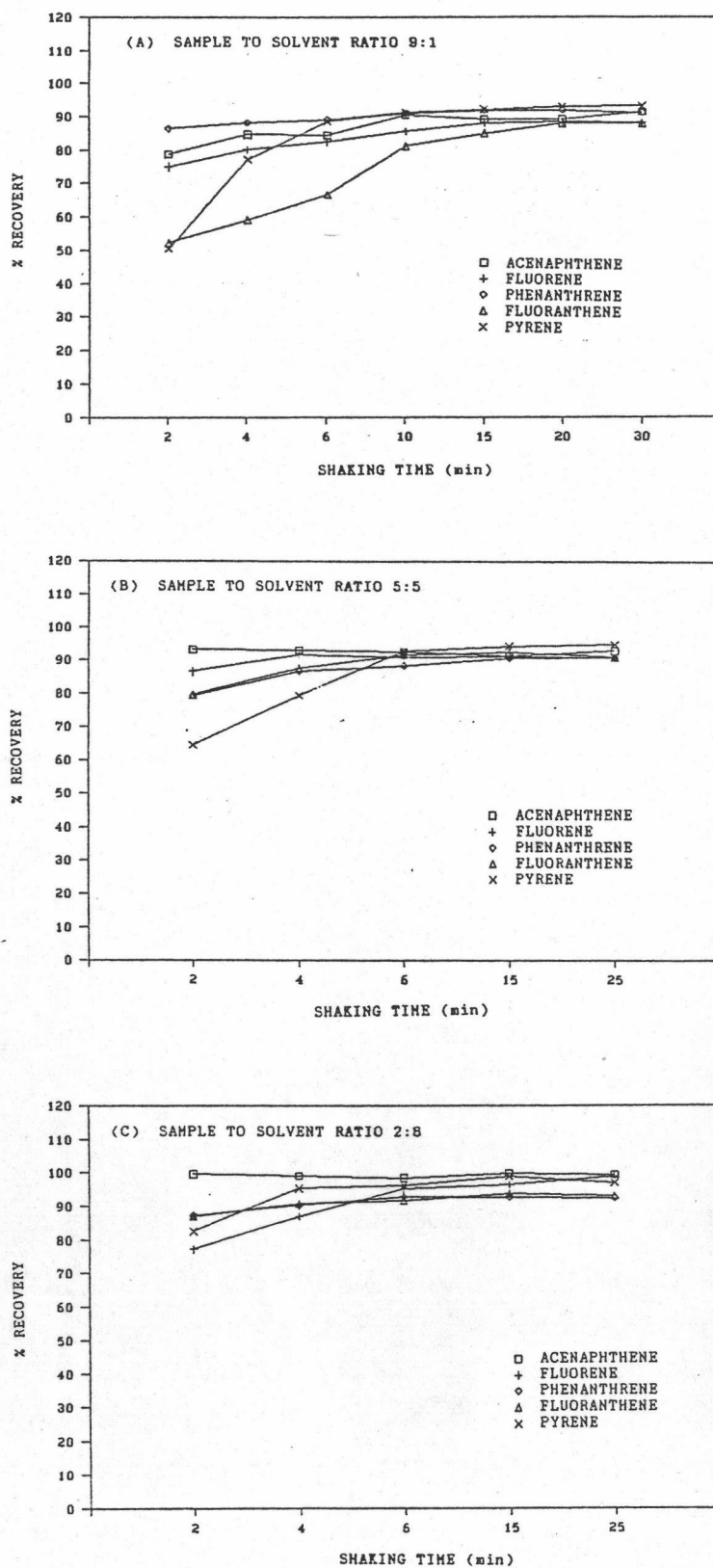


Figure 4.2 The effect of shaking time on % recovery of each PAH with cyclohexane as solvent

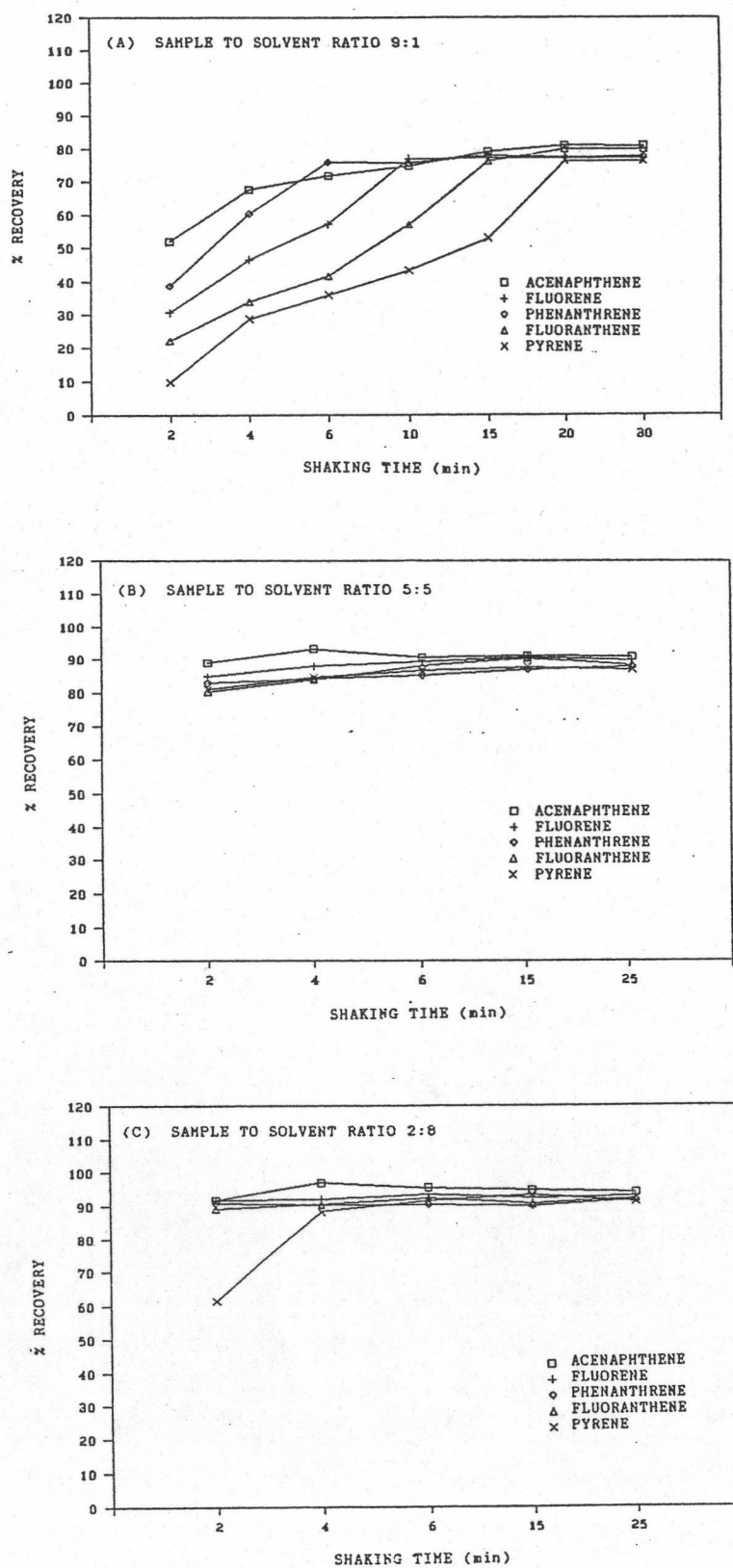


Figure 4.3 The effect of shaking time on % recovery of each PAH with methylene chloride as solvent

4.2 DETERMINATION OF THE OPTIMUM AMOUNT OF SODIUM CHLORIDE USED IN THE EXTRACTION.

Since the equilibration time of each PAH is evaluated in each extracting solvent and in each sample to solvent ratio, then the optimum amount of sodium chloride used in the extraction is studied. The results of the variation of amounts of sodium chloride having the effect on % recovery of each PAH with carbon disulfide, cyclohexane and methylene chloride are shown in Table 4.6-4.10. The graphs plotted in Figure 4.4-4.6 show the relationship between the amounts of sodium chloride used and % recovery of each PAH with carbon disulfide, cyclohexane and methylene chloride, respectively. It is found that % recovery of each PAH increases when the sodium chloride is added into the solution and the optimum amount of sodium chloride used depends on the sample to solvent ratios, however, it does not depend on solvents used. The 2.0 g is the optimum amount of sodium chloride used in the extraction of sample to solvent ratio of 9:1, 1.0 g is for the ratio of 5:5 and 0.5 g is the ratio of 2:8.

4.3 DETERMINATION OF THE OPTIMUM AMOUNT OF SODIUM SULFATE USED IN THE EXTRACTION.

The amounts of sodium sulfate used in the extraction having the effect on % recovery of each PAH in each solvent and each sample to solvent ratio are studied. The results are shown in Table 4.11-4.15. The graphs plotted in Figure 4.7-4.9 show that the optimum amount of sodium sulfate used in the extraction

for the sample to solvent ratios of 9:1, 5:5 and 2:8 are 2.0, 1.0 and 0.5 g, respectively.

Table 4.6 The results of the effect of sodium chloride added on % recovery of acenaphthene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	81.02	0.44	90.74	0.33	98.02	0.00
0.5	91.08	0.85	94.79	0.09	100.60	1.24
1.0	93.41	0.58	95.73	0.14	99.33	0.19
1.5	93.41	0.70	95.90	0.05	97.98	2.36
2.0	93.41	1.05	96.44	0.14	105.00	8.42
3.0	93.62	1.92	96.55	1.00	ND	-

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	88.03	5.46	93.04	1.01	99.18	0.31
0.5	91.82	0.22	97.39	0.10	101.80	2.29
1.0	92.81	0.37	100.51	0.58	102.80	0.10
1.5	90.82	4.84	99.74	0.50	99.13	0.88
2.0	92.81	2.62	97.76	1.97	97.92	0.42
3.0	92.67	0.22	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	80.85	0.10	91.28	0.68	93.83	1.90
0.5	98.05	0.29	94.17	0.67	95.11	0.27
1.0	99.14	0.09	95.01	0.48	98.19	1.57
1.5	99.37	0.03	93.18	0.60	93.27	1.93
2.0	99.65	0.03	93.33	0.82	93.94	1.94
3.0	100.30	0.27	ND	-	ND	-

Triplicate analyses
ND = Not Determine

Table 4.7 The results of the effect of sodium chloride added
on % recovery of fluorene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	83.73	0.96	91.60	0.22	98.44	0.94
0.5	98.95	0.22	93.97	0.05	99.46	2.96
1.0	99.54	0.13	94.26	0.24	99.17	0.95
1.5	99.58	0.26	94.59	0.06	101.62	1.55
2.0	99.45	0.34	91.93	0.66	97.74	3.00
3.0	99.76	0.11	91.95	0.54	ND	-

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	88.29	1.95	90.95	0.75	99.20	2.13
0.5	89.54	2.94	99.82	0.26	100.00	3.20
1.0	96.22	2.25	90.95	1.09	99.38	0.46
1.5	97.97	1.34	91.76	0.93	96.14	2.52
2.0	101.10	0.49	92.05	3.97	93.87	1.46
3.0	94.11	2.94	94.11	2.94	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	76.98	0.95	90.50	2.02	93.05	2.55
0.5	99.71	0.04	98.63	0.25	97.69	2.69
1.0	99.82	0.04	98.26	0.72	99.46	1.05
1.5	99.86	0.05	96.52	1.25	93.18	5.13
2.0	99.87	0.06	95.51	0.96	86.89	3.18
3.0	99.96	0.09	ND	-	ND	-

Triplicate analyses
ND = Not Determine

Table 4.8 The results of the effect of sodium chloride added on % recovery of phenanthrene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	84.77	0.64	93.96	1.53	99.24	0.75
0.5	94.68	0.15	98.58	1.13	99.15	1.60
1.0	95.21	0.04	98.45	0.51	99.40	1.66
1.5	95.68	0.27	98.00	0.24	96.58	2.34
2.0	96.26	0.07	94.19	1.48	90.58	1.56
3.0	96.34	0.20	89.44	1.04	ND	-

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	89.55	1.89	91.08	3.88	91.44	3.18
0.5	94.47	3.03	101.30	0.81	100.70	0.91
1.0	94.21	3.16	97.01	2.61	96.67	0.59
1.5	93.54	6.02	95.51	0.95	88.31	1.14
2.0	97.12	3.36	92.42	5.30	85.35	1.05
3.0	95.61	1.31	84.11	2.94	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	77.51	2.02	87.87	6.28	90.20	2.55
0.5	99.97	0.19	98.45	1.64	96.60	0.32
1.0	100.40	0.10	96.85	3.12	96.09	2.49
1.5	100.30	0.04	93.13	5.15	86.12	1.46
2.0	100.30	0.09	93.13	1.16	89.83	2.34
3.0	100.30	0.27	ND	-	ND	-

Triplicate analyses
 ND = Not Determine

Table 4.9 The results of the effect of sodium chloride added on % recovery of fluoranthene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	73.18	0.87	92.15	0.51	95.03	1.54
0.5	83.19	0.62	96.32	0.08	99.81	3.92
1.0	84.47	0.07	99.87	0.78	90.73	5.56
1.5	84.47	1.20	91.72	4.90	91.22	4.62
2.0	84.03	1.60	83.50	8.88	90.24	7.13
3.0	84.95	4.35	81.68	6.08	ND	-

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	88.02	2.11	91.15	1.83	92.35	3.13
0.5	96.79	1.73	96.54	3.04	101.00	1.37
1.0	96.95	1.03	96.09	1.48	102.20	3.03
1.5	95.38	2.71	93.13	2.23	91.00	0.66
2.0	99.99	0.54	94.57	2.37	90.16	3.41
3.0	94.94	1.38	94.11	2.94	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	79.84	0.82	88.42	1.73	89.05	1.70
0.5	99.96	0.46	95.74	0.83	90.41	6.51
1.0	100.50	0.52	94.85	4.29	92.30	3.38
1.5	100.80	0.45	93.72	1.27	90.41	1.78
2.0	100.80	0.48	92.51	0.21	91.98	2.11
3.0	100.90	0.17	ND	-	ND	-

Triplicate analyses
ND = Not Determine

Table 4.10 The results of the effect of sodium chloride added
on % recovery of pyrene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	46.57	0.60	87.73	0.45	91.01	1.83
0.5	91.89	1.62	93.20	0.16	99.78	3.28
1.0	93.75	0.22	100.00	0.60	95.40	1.42
1.5	95.24	0.11	97.89	0.60	91.87	1.31
2.0	99.00	0.06	94.48	8.68	85.66	7.28
3.0	100.70	0.41	89.32	7.24	ND	-

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	93.62	2.66	95.95	1.01	96.24	2.74
0.5	97.30	0.25	100.20	0.05	94.57	7.40
1.0	99.40	0.72	99.88	0.49	98.33	1.52
1.5	103.10	1.01	93.93	1.86	57.58	3.32
2.0	100.20	1.20	94.07	2.31	58.86	4.91
3.0	99.40	1.90	94.11	2.94	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	76.07	1.78	89.98	4.15	90.94	3.74
0.5	100.50	0.96	96.76	1.65	99.09	0.58
1.0	100.70	1.61	96.92	1.30	95.79	1.33
1.5	100.50	0.22	94.68	1.65	86.07	3.18
2.0	100.40	0.15	93.02	0.96	94.16	1.90
3.0	100.30	0.15	ND	-	ND	-

Triplicate analyses
ND = Not Determine

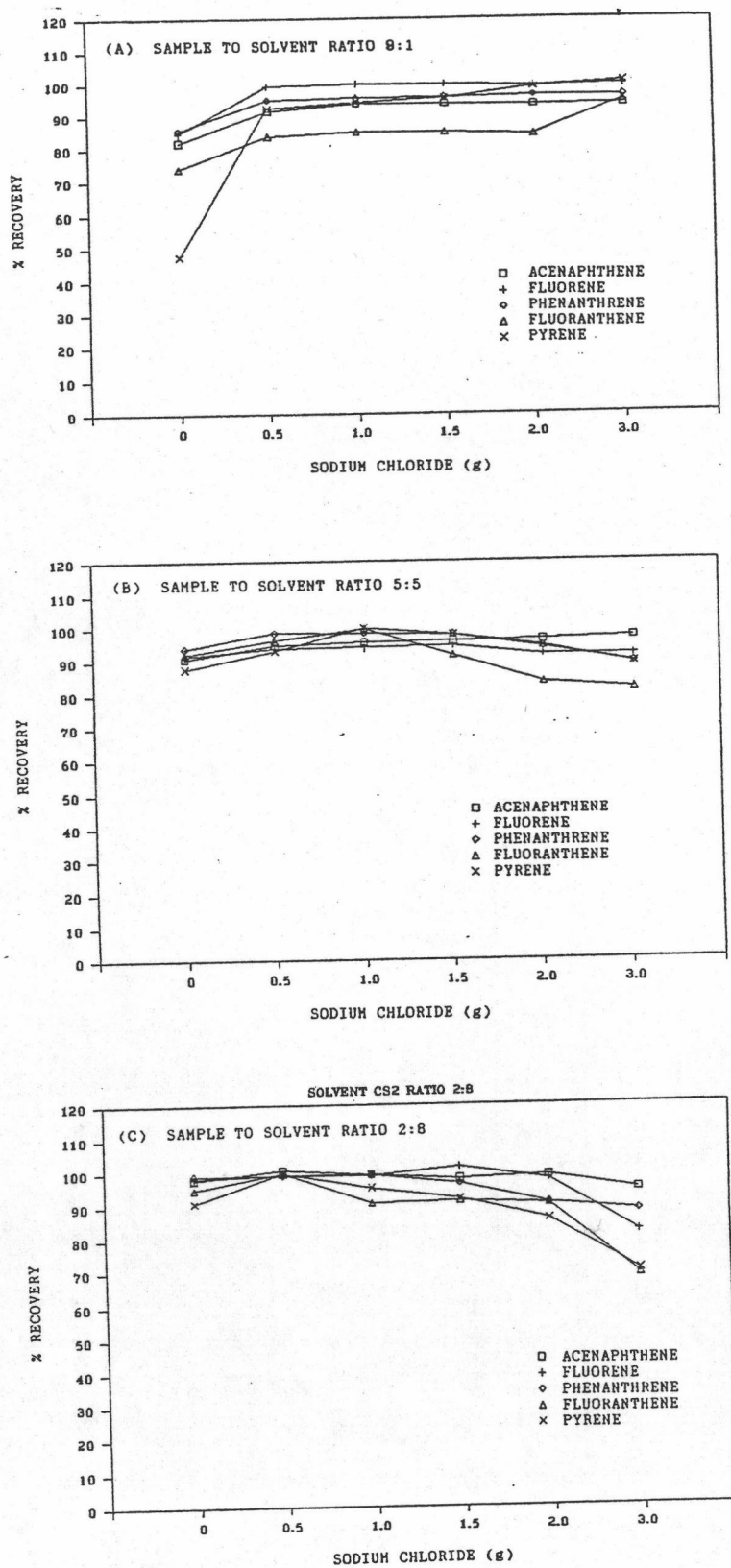


Figure 4.4 The effect of sodium chloride added on % recovery of each PAH with carbon disulfide as solvent.

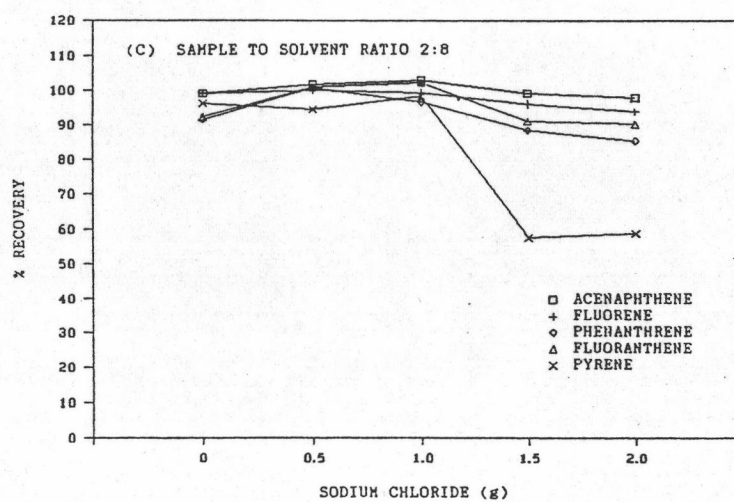
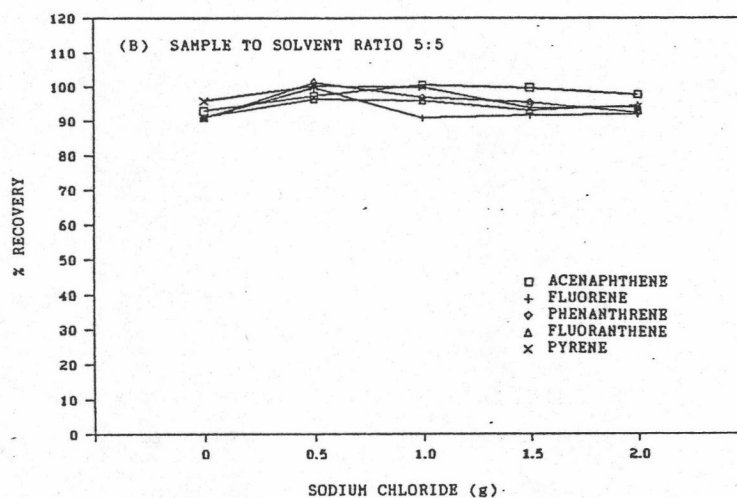
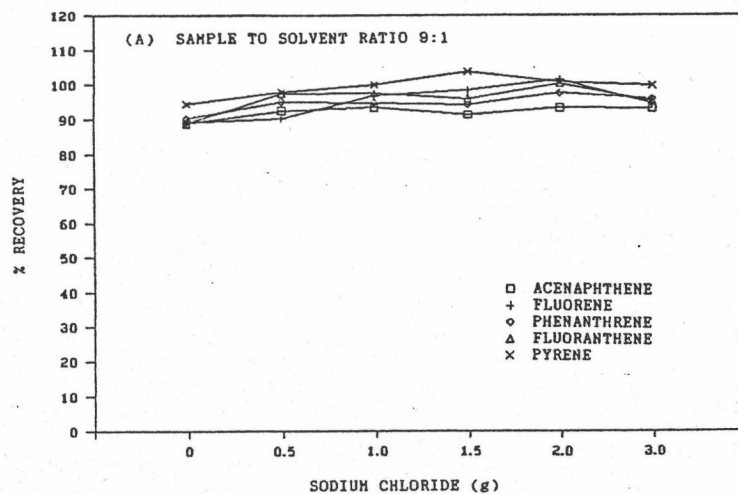


Figure 4.5 The effect of sodium chloride added on % recovery of each PAH with cyclohexane as solvent.

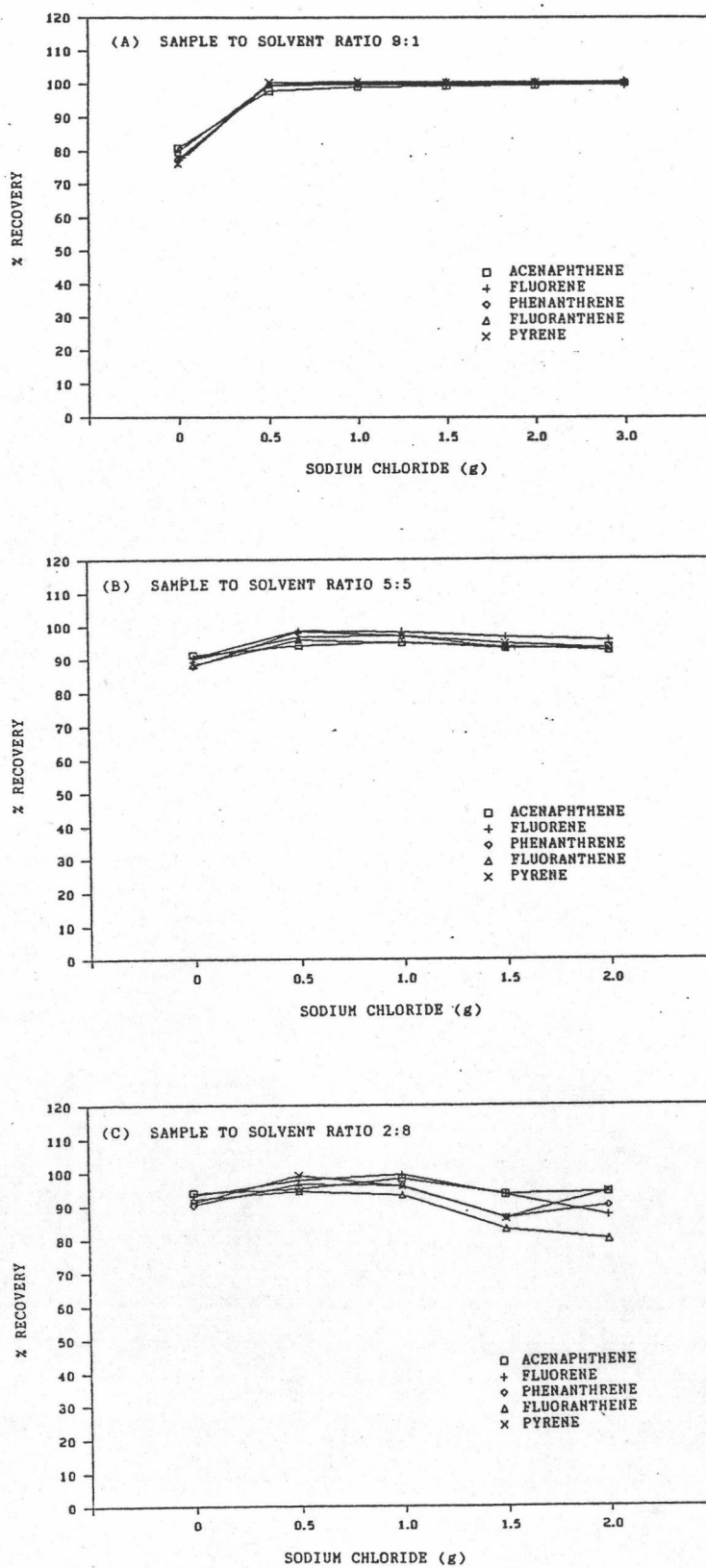


Figure 4.6 The effect of sodium chloride added on % recovery of each PAH with methylene chloride as solvent.

Table 4.11 The results of the effect of sodium sulfate added on % recovery of acenaphthene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	81.02	0.04	90.74	0.33	98.02	0.00
0.5	96.85	0.19	96.41	0.16	101.60	0.56
1.0	98.88	0.04	97.27	0.41	100.40	1.19
1.5	98.94	0.20	94.61	0.05	97.04	0.86
2.0	98.83	0.34	94.40	2.48	97.71	1.09
3.0	98.91	0.38	92.86	1.62	85.99	2.24

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	91.40	0.88	93.03	1.01	99.18	0.31
0.5	92.38	0.38	96.04	2.05	99.09	0.34
1.0	93.94	0.21	97.52	0.34	98.32	4.21
1.5	90.54	0.22	97.11	2.60	95.87	0.96
2.0	90.26	0.80	97.52	1.02	82.63	2.08
3.0	86.71	0.61	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	80.85	0.10	91.28	0.68	93.83	1.90
0.5	98.49	0.15	95.01	0.22	99.04	4.70
1.0	99.05	0.10	95.49	0.59	102.30	6.05
1.5	99.49	0.07	96.59	0.57	96.43	2.93
2.0	99.88	0.06	90.46	1.63	97.02	1.44
3.0	100.40	0.10	ND	-	ND	-

Triplicate analyses
 ND = Not Determine

Table 4.12 The results of the effect of sodium sulfate added on % recovery of fluorene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	83.73	0.96	91.59	0.22	98.43	0.94
0.5	99.31	0.23	94.08	0.28	102.50	3.92
1.0	99.58	0.45	100.30	0.43	103.20	0.14
1.5	99.63	0.29	95.50	0.12	100.30	2.02
2.0	99.63	0.55	94.81	0.22	96.84	7.05
3.0	99.72	0.46	96.49	0.36	100.80	1.71

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	88.29	1.95	90.95	0.75	99.20	2.13
0.5	99.83	2.35	95.03	1.32	100.30	0.47
1.0	97.92	1.91	96.36	1.18	96.31	5.19
1.5	97.16	2.42	92.78	0.59	87.28	3.90
2.0	99.45	0.54	93.79	0.68	82.60	0.99
3.0	97.54	1.11	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	76.98	0.95	90.50	2.02	91.81	2.52
0.5	97.38	0.30	96.48	0.62	101.00	9.73
1.0	98.24	0.22	98.71	0.58	102.20	6.45
1.5	98.87	0.38	97.35	0.50	92.48	2.59
2.0	98.82	0.59	95.22	2.70	82.57	6.27
3.0	99.22	1.13	ND	-	ND	-

Triplicate analyses
ND = Not Determine

Table 4.13 The results of the effect of sodium sulfate added
on % recovery of phenanthrene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	84.77	0.64	96.25	1.40	99.24	0.75
0.5	97.32	0.16	94.57	1.09	101.40	3.64
1.0	98.47	0.16	95.77	4.61	98.43	2.39
1.5	98.57	0.13	93.93	0.57	95.61	1.83
2.0	98.52	0.10	92.79	1.48	95.12	3.47
3.0	98.60	0.93	86.64	3.91	85.47	3.57

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	89.55	1.89	91.08	3.88	91.44	3.18
0.5	98.78	3.19	97.83	7.41	101.40	0.85
1.0	95.61	4.75	102.20	2.59	93.01	5.27
1.5	94.37	2.09	96.22	3.05	84.82	3.62
2.0	94.62	3.68	95.53	2.96	83.85	1.31
3.0	90.79	3.06	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	77.51	2.02	87.87	6.28	90.20	2.55
0.5	104.10	0.40	96.17	3.79	100.70	2.20
1.0	103.80	0.69	97.10	0.65	92.71	1.09
1.5	104.10	1.03	94.86	3.22	87.21	1.36
2.0	103.90	0.37	91.05	2.60	80.11	6.35
3.0	99.27	1.14	ND	-	ND	-

Triplicate analyses
ND = Not Determine



Table 4.14 The results of the effect of sodium sulfate added on % recovery of fluoranthene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	73.18	0.87	91.98	0.38	95.03	1.54
0.5	83.79	3.44	100.20	0.47	101.70	3.03
1.0	89.57	1.57	90.04	1.71	102.70	5.31
1.5	93.00	1.37	86.99	3.49	92.20	5.88
2.0	95.63	1.96	87.97	6.44	90.48	3.99
3.0	95.71	0.77	88.76	3.28	76.24	7.07

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	88.02	2.11	91.15	1.83	92.35	3.13
0.5	93.62	1.10	91.57	1.28	100.20	0.92
1.0	92.87	1.35	95.38	0.86	89.01	3.12
1.5	93.49	1.08	93.27	2.85	88.18	3.92
2.0	99.97	0.89	90.34	6.97	84.94	4.43
3.0	86.54	0.78	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	79.84	0.82	88.42	1.73	91.97	2.11
0.5	97.01	1.45	95.26	1.51	98.16	1.78
1.0	98.70	0.37	91.73	2.24	96.61	1.50
1.5	100.00	0.09	92.74	1.73	92.44	3.11
2.0	101.50	2.46	89.80	1.53	89.83	2.67
3.0	101.60	0.09	ND	-	ND	-

Triplicate analyses
ND = Not Determine

Table 4.15 The results of the effect of sodium sulfate added on % recovery of pyrene in various solvents.

(A) SOLVENT: CARBON DISULFIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	49.16	0.49	87.73	0.45	91.01	1.83
0.5	62.45	5.29	93.96	0.44	98.92	2.37
1.0	74.69	0.34	98.71	0.33	90.29	0.72
1.5	96.48	0.36	89.46	0.43	86.91	1.79
2.0	99.08	0.10	89.79	2.31	81.05	2.70
3.0	95.32	2.74	83.15	0.73	71.52	2.74

(B) SOLVENT: CYCLOHEXANE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	93.62	2.66	95.95	1.01	95.96	2.75
0.5	98.48	1.34	103.40	2.17	101.40	3.13
1.0	99.11	1.28	104.30	4.27	83.56	5.45
1.5	99.62	1.62	101.80	1.88	68.05	3.63
2.0	99.99	3.58	95.80	5.79	52.48	7.21
3.0	102.30	1.31	ND	-	ND	-

(C) SOLVENT: METHYLENE CHLORIDE

SALT CONTENT (g)	RATIO 9:1		RATIO 5:5		RATIO 2:8	
	% E	% RSD	% E	% RSD	% E	% RSD
0	76.22	2.41	89.98	4.15	90.94	3.74
0.5	100.50	2.75	99.80	0.56	100.20	0.97
1.0	102.70	0.36	95.35	1.01	98.57	1.24
1.5	101.80	0.26	95.46	1.11	97.23	2.54
2.0	101.80	3.13	92.27	0.72	93.83	1.26
3.0	102.20	0.05	ND	-	ND	-

Triplicate analyses
 ND = Not Determine

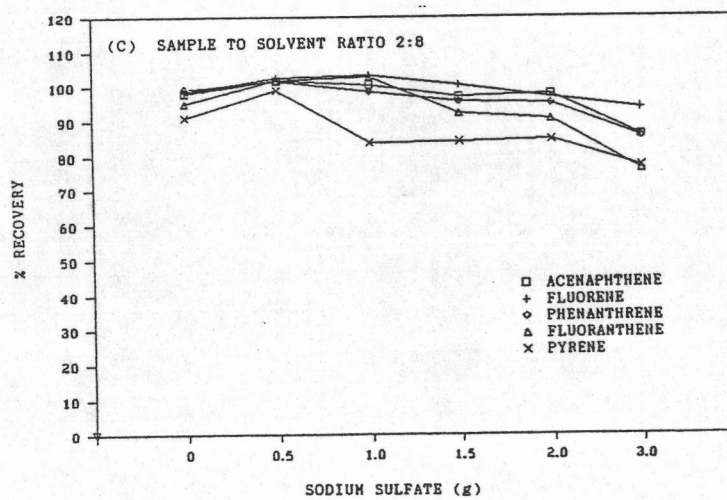
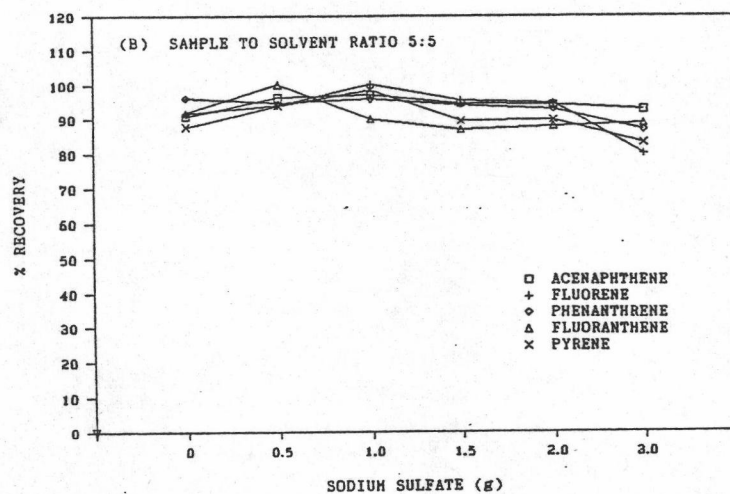
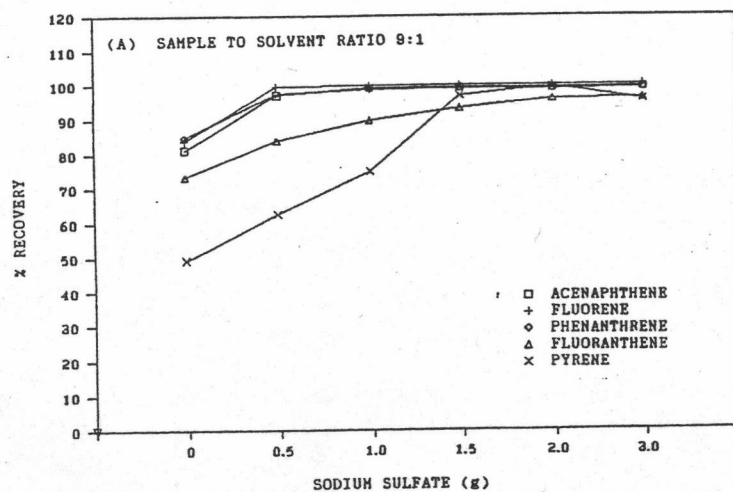


Figure 4.7 The effect of sodium sulfate added on % recovery of each PAH with carbon disulfide as solvent.

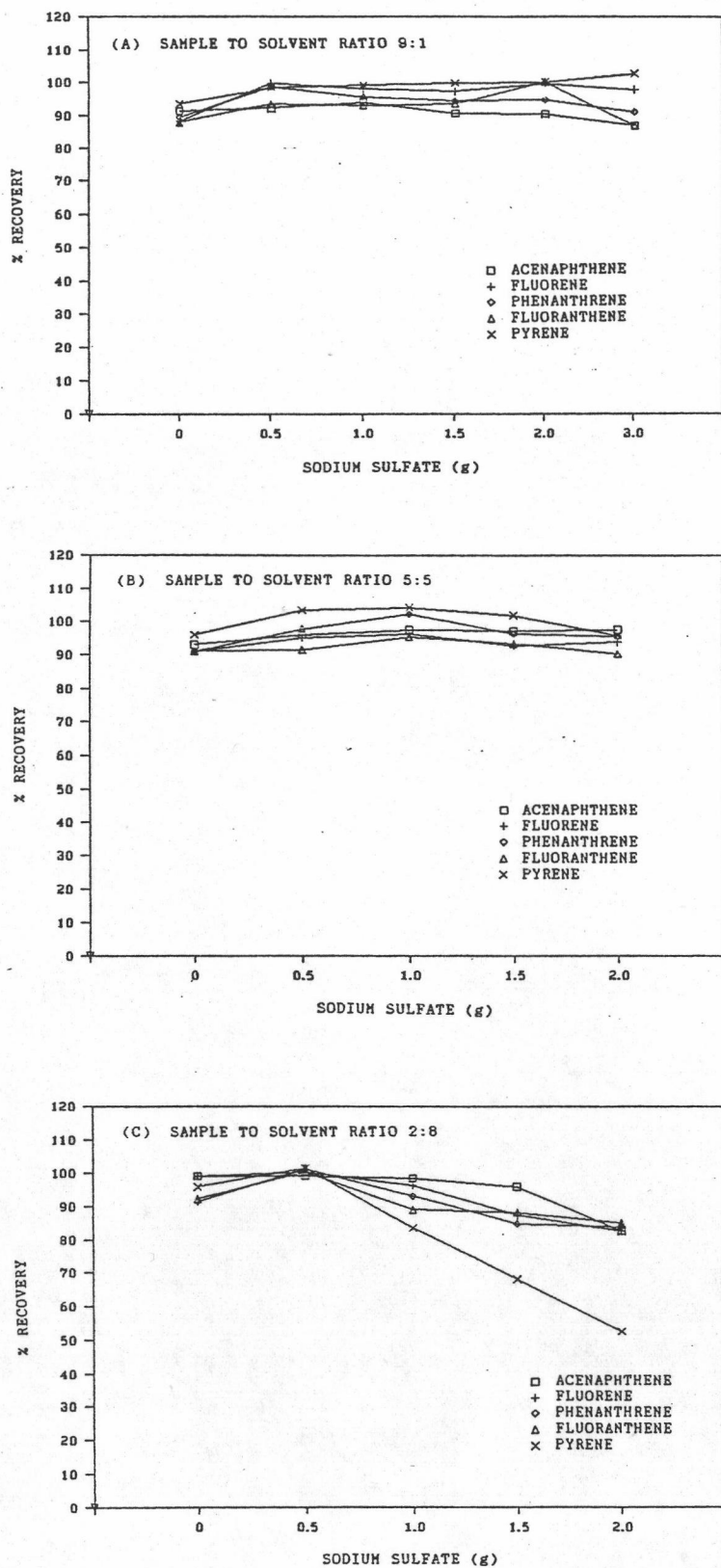


Figure 4.8 The effect of sodium sulfate added on % recovery of each PAH with cyclohexane as solvent.

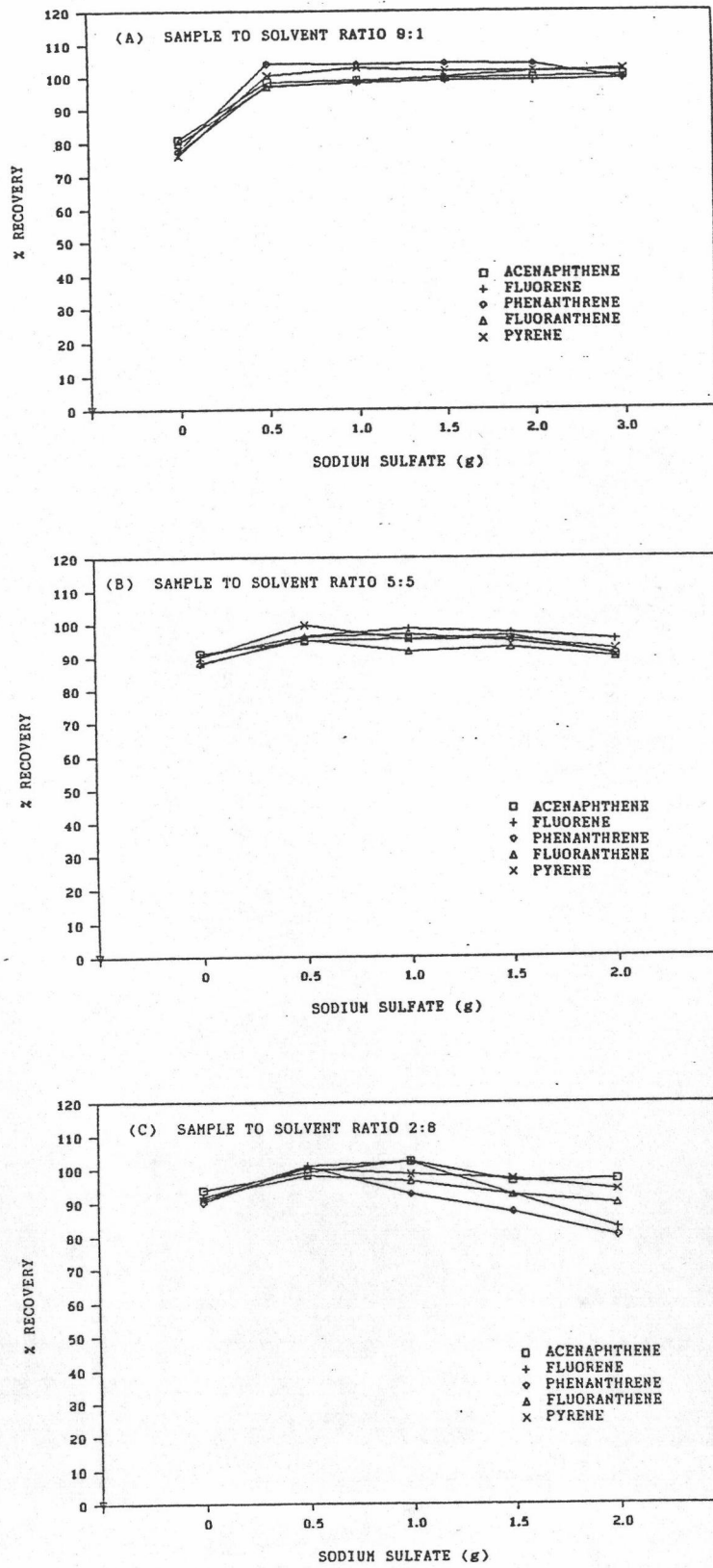


Figure 4.9 The effect of sodium sulfate added on % recovery of each PAH with methylene chloride as solvent.

4.4 MICROEXTRACTION OF PAHs IN SINGLE COMPONENT SOLUTIONS

The various effects on % recovery of each PAH in the single component solutions are studied in various solvents, i.e., carbon disulfide, cyclohexane, and methylene chloride, and in the various sample to solvent ratios, i.e., 9:1, 5:5, and 2:8. The results are shown in Table 4.16-4.20 and the graphs correlated to these results are shown in Figure 4.10-4.14. It is found that the % recovery of each PAH in each sample to solvent ratio ranges from 46.56-93.28 % with % RSD 0.14-5.46 % for the 1 ppm of each PAH solution and 47.13-93.28 % with % RSD 0.00-3.91 % for 5 ppm solution for the ratio of 9:1, from 86.89-96.11 % with % RSD 0.22-9.13 % for 1 ppm solution and 87.55-95.96 % with % RSD 0.14-6.28 % for 5 ppm solution for the ratio of 5:5 and from 91.01-97.59 % with % RSD 0-5.05 % for 1 ppm solution and 90.21-97.81 % with % RSD 0.31-9.80 % for 5 ppm solution for the ratio of 2:8. They are shown that the % recovery of the ratio of 9:1 is less than the ratios of 5:5 and 2:8, respectively. The initial concentration of standard solutions of each PAH do not have any effect on % recovery of each PAH significantly as can be seen from Table 4.16-4.20. The concentrations of each PAH in the extracting solvents for the sample to solvent ratio of 9:1 range from 4.66-9.09 ppm for the initial concentration of 1 ppm of standard solution of each PAH and from 23.57-45.14 ppm for the initial concentration of 5 ppm of standard solution of each PAH. For the ratio of 5:5, the concentrations of each PAH range from 0.90-0.97 ppm for 1 ppm standard solution and from 4.47-4.85 ppm for 5 ppm standard solution. For the ratio of 2:8, the

concentrations of PAH range from 0.23-0.25 ppm for 1 ppm standard solution and from 1.16-1.24 ppm for 5 ppm standard solution. It can be seen that the PAH in the solution is concentrated about 4.66 to 9.09 fold for the ratio of 9:1, the PAH in the solution is not concentrated in the ratio of 5:5 and it is diluted about 4 fold in the ratio of 2:8. Thus, the concentration of each PAH in the solution decreases as long as the sample to solvent ratio has been decreased. Therefore, the sensitivity of each PAH for the ratio of 9:1 is higher than the sensitivity for the ratios of 5:5 and 2:8, respectively.

In addition, the ratio of 9:1 gives the lowest % RSD as can be seen from Table 4.16-4.20. Therefore, the sample to solvent ratio of 9:1 would give the good precision for the analysis of these compounds and the ratio of 9:1 should be considered as a suitable ratio for microextraction technique.

The recovery data of each PAH in each solvent range from 46.58-97.81 % with % RSD 0.00-3.91 %, from 85.48-97.59 % with % RSD 0.31-9.80 % and from 75.73-94.14 % with % RSD 0.11-9.12 %, for carbon disulfide, cyclohexane and methylene chloride, respectively. They indicate that the microextraction using cyclohexane as solvent gives the higher % recovery than carbon disulfide and methylene chloride, respectively. It can be explained that the polarity of the solvents studied are in the following order, methylene chloride, carbon disulfide and cyclohexane and the PAHs also are nonpolar compounds. Therefore, cyclohexane would be selected as the appropriate solvent for microextraction of PAHs.

The salting out with sodium chloride and sodium sulfate having the effect on % recovery of the extraction of each PAH are evaluated. The results of % recovery of each PAH in each extracting solvent and each sample to solvent ratio which can be seen in Table 4.16-4.20 show the higher % recovery of each PAH with sodium sulfate than sodium chloride and nonsalting out, respectively. The reason of this is that sodium sulfate added into the solution results in higher ionic strength than the sodium chloride and nonsalting out do. Therefore, sodium sulfate seems to be the most appropriated salt for this application.

Table 4.16 The microextraction of acenaphthene solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	8.103	43.19	81.03	0.44
		NaCl	8.410	136.19	93.42	1.04
		Na ₂ SO ₄	8.895	816.61	98.84	0.34
	5:5	NO SALT	0.926	10.20	90.74	0.33
		NaCl	0.959	25.56	95.91	0.05
		Na ₂ SO ₄	0.973	37.78	97.27	0.41
	2:8	NO SALT	0.243	6.37	96.00	0.00
		NaCl	0.252	-	100.69	1.24
		Na ₂ SO ₄	0.254	-	101.63	0.56
CYCLOHEXANE	9:1	NO SALT	8.341	70.12	88.04	5.46
		NaCl	8.350	124.01	92.81	2.62
		Na ₂ SO ₄	8.455	144.40	93.95	0.21
	5:5	NO SALT	0.922	10.71	91.30	1.52
		NaCl	0.980	52.83	98.01	1.44
		Na ₂ SO ₄	0.970	33.94	96.97	0.00
	2:8	NO SALT	0.245	10.29	97.55	1.13
		NaCl	0.250	-	101.17	1.69
		Na ₂ SO ₄	0.246	15.12	98.25	0.92
CH ₂ Cl ₂	9:1	NO SALT	9.085	48.27	80.76	0.14
		NaCl	8.970	2752.12	99.65	0.03
		Na ₂ SO ₄	8.990	8269.14	99.88	0.06
	5:5	NO SALT	0.937	9.65	89.91	1.82
		NaCl	0.940	17.14	94.17	1.88
		Na ₂ SO ₄	0.957	23.43	95.67	0.54
	2:8	NO SALT	0.241	4.53	94.14	4.49
		NaCl	0.240	9.25	97.18	1.28
		Na ₂ SO ₄	0.248	37.18	99.28	2.82

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of acenaphthene is higher than its initial concentration.

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	40.610	43.46	81.12	0.00
		NaCl	42.000	133.88	93.31	0.28
		Na ₂ SO ₄	44.510	872.81	98.91	1.44
	5:5	NO SALT	4.630	10.16	90.74	0.29
		NaCl	4.750	20.61	94.98	0.59
		Na ₂ SO ₄	4.810	26.80	96.20	0.60
	2:8	NO SALT	1.220	6.85	96.27	2.37
		NaCl	1.270	-	101.36	1.05
		Na ₂ SO ₄	1.260	-	100.69	0.83
CYCLOHEXANE	9:1	NO SALT	40.490	56.08	85.48	1.36
		NaCl	41.960	132.42	93.24	0.65
		Na ₂ SO ₄	42.277	150.58	94.01	0.56
	5:5	NO SALT	4.699	13.63	93.04	1.52
		NaCl	4.990	57.83	99.74	0.50
		Na ₂ SO ₄	4.875	41.72	97.52	0.34
	2:8	NO SALT	1.211	6.62	96.25	0.31
		NaCl	1.273	-	101.80	2.29
		Na ₂ SO ₄	1.229	15.78	98.33	4.21
CH ₂ Cl ₂	9:1	NO SALT	45.140	48.91	80.96	0.11
		NaCl	45.200	-	100.39	0.07
		Na ₂ SO ₄	45.175	-	100.39	0.14
	5:5	NO SALT	4.755	11.35	91.29	0.68
		NaCl	4.660	14.90	93.18	0.60
		Na ₂ SO ₄	4.775	22.47	95.50	0.59
	2:8	NO SALT	1.203	4.29	93.84	1.90
		NaCl	1.189	5.23	95.11	0.27
		Na ₂ SO ₄	1.238	27.94	99.05	4.70

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of acenaphthene is higher than its initial concentration

Table 4.17 The microextraction of fluorene solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	8.373	51.92	83.73	0.96
		NaCl	8.950	1751.48	99.45	0.34
		Na ₂ SO ₄	8.951	1753.29	99.46	0.55
	5:5	NO SALT	0.935	11.34	91.59	0.22
		NaCl	0.950	19.06	94.59	0.05
		Na ₂ SO ₄	1.003	-	100.31	0.43
	2:8	NO SALT	0.244	7.45	96.56	0.94
		NaCl	0.248	31.94	99.17	0.95
		Na ₂ SO ₄	0.258	-	103.26	0.27
CYCLOHEXANE	9:1	NO SALT	8.364	71.80	88.29	1.95
		NaCl	9.100	-	101.14	0.49
		Na ₂ SO ₄	8.951	1753.29	99.46	0.54
	5:5	NO SALT	0.928	11.45	91.88	1.53
		NaCl	1.040	-	103.97	2.20
		Na ₂ SO ₄	0.979	49.21	97.89	0.82
	2:8	NO SALT	0.240	5.17	95.25	4.25
		NaCl	0.250	-	101.27	2.02
		Na ₂ SO ₄	0.249	56.94	99.53	4.28
CH ₂ Cl ₂	9:1	NO SALT	8.660	38.47	76.99	0.95
		NaCl	8.890	766.20	99.87	0.06
		Na ₂ SO ₄	8.894	804.01	98.82	0.59
	5:5	NO SALT	0.934	9.39	89.66	1.16
		NaCl	0.980	45.67	97.73	0.64
		Na ₂ SO ₄	0.979	49.46	97.91	0.61
	2:8	NO SALT	0.237	3.51	92.57	2.65
		NaCl	0.250	-	100.85	1.44
		Na ₂ SO ₄	0.247	22.01	98.79	2.05

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluorene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K _d	% E	% RSD
CS ₂	9:1	NO SALT	41.865	51.92	83.73	0.17
		NaCl	44.800	2099.66	99.54	0.06
		Na ₂ SO ₄	44.590	4161.10	99.77	0.51
	5:5	NO SALT	4.675	11.42	91.65	0.14
		NaCl	4.830	17.18	94.23	1.89
		Na ₂ SO ₄	4.980	283.54	99.61	1.18
	2:8	NO SALT	1.240	11.87	97.81	1.45
		NaCl	1.243	49.72	99.46	3.22
		Na ₂ SO ₄	1.260	-	100.90	1.71
CYCLOHEXANE	9:1	NO SALT	41.750	70.79	88.13	1.95
		NaCl	45.850	-	100.79	1.48
		Na ₂ SO ₄	44.585	1027.20	99.07	1.89
	5:5	NO SALT	4.593	10.25	90.95	0.75
		NaCl	4.990	602.63	99.82	0.26
		Na ₂ SO ₄	4.818	28.09	96.36	1.18
	2:8	NO SALT	1.224	9.34	97.31	1.26
		NaCl	1.251	-	100.03	3.20
		Na ₂ SO ₄	1.254	-	100.32	0.47
CH ₂ Cl ₂	9:1	NO SALT	43.550	39.49	77.45	1.01
		NaCl	44.450	644.72	99.85	0.03
		Na ₂ SO ₄	44.235	556.11	98.30	0.44
	5:5	NO SALT	4.710	10.32	90.50	2.02
		NaCl	4.910	60.08	98.27	0.72
		Na ₂ SO ₄	4.936	81.59	98.71	0.57
	2:8	NO SALT	1.177	3.17	91.82	2.52
		NaCl	1.243	49.72	99.46	1.04
		Na ₂ SO ₄	1.263	-	101.02	9.72

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluorene is higher than its initial concentration

Table 4.18 The microextraction of phenanthrene solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	8.477	56.30	84.77	0.63
		NaCl	8.670	255.01	96.37	0.23
		Na ₂ SO ₄	8.860	619.32	98.47	0.19
	5:5	NO SALT	0.961	16.76	94.15	1.33
		NaCl	0.990	115.35	99.04	0.92
		Na ₂ SO ₄	0.955	22.54	95.51	1.79
	2:8	NO SALT	0.245	8.00	96.78	0.75
		NaCl	0.251	-	100.40	1.41
		Na ₂ SO ₄	0.249	75.45	99.65	1.36
CYCLOHEXANE	9:1	NO SALT	8.591	92.74	90.69	1.67
		NaCl	8.740	328.86	97.12	3.36
		Na ₂ SO ₄	8.890	741.51	98.78	3.19
	5:5	NO SALT	0.914	9.71	90.49	2.81
		NaCl	0.990	205.43	99.49	4.50
		Na ₂ SO ₄	1.073	-	103.81	1.43
	2:8	NO SALT	0.234	3.35	92.86	3.49
		NaCl	0.250	-	100.27	0.65
		Na ₂ SO ₄	0.249	105.44	99.75	0.25
CH ₂ Cl ₂	9:1	NO SALT	8.720	39.65	77.52	2.02
		NaCl	9.340	-	100.37	0.09
		Na ₂ SO ₄	9.352	-	103.91	0.37
	5:5	NO SALT	0.920	8.13	88.25	9.12
		NaCl	1.020	-	101.66	1.92
		Na ₂ SO ₄	1.037	-	103.68	2.41
	2:8	NO SALT	0.232	2.68	90.47	2.92
		NaCl	0.240	6.72	96.15	1.95
		Na ₂ SO ₄	0.246	15.63	98.31	3.18

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of phenanthrene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K _d	% E	% RSD
CS ₂	9:1	NO SALT	42.275	56.20	84.75	0.28
		NaCl	43.300	247.74	96.27	0.07
		Na ₂ SO ₄	44.335	641.19	98.52	0.10
	5:5	NO SALT	4.770	14.87	93.46	3.73
		NaCl	4.930	71.36	98.45	0.51
		Na ₂ SO ₄	4.790	24.06	95.78	4.61
	2:8	NO SALT	1.220	7.26	96.47	3.02
		NaCl	1.250	44.53	99.40	1.67
		Na ₂ SO ₄	1.270	-	101.47	3.64
CYCLOHEXANE	9:1	NO SALT	43.707	113.71	92.27	1.43
		NaCl	44.380	699.55	98.63	0.56
		Na ₂ SO ₄	44.360	632.29	98.57	0.65
	5:5	NO SALT	4.600	10.43	91.09	3.88
		NaCl	5.070	-	101.39	0.81
		Na ₂ SO ₄	5.114	-	102.27	2.59
	2:8	NO SALT	1.160	3.08	92.26	9.80
		NaCl	1.260	-	100.77	0.91
		Na ₂ SO ₄	1.268	-	101.41	0.85
CH ₂ Cl ₂	9:1	NO SALT	41.815	36.64	76.11	1.60
		NaCl	46.850	-	100.39	0.22
		Na ₂ SO ₄	47.155	-	104.79	3.16
	5:5	NO SALT	4.577	7.81	87.87	6.28
		NaCl	4.920	67.36	98.45	1.64
		Na ₂ SO ₄	4.855	35.57	97.11	0.65
	2:8	NO SALT	1.156	2.60	90.21	2.54
		NaCl	1.210	7.65	96.61	0.32
		Na ₂ SO ₄	1.260	-	100.77	2.20

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of phenanthrene is higher than its initial concentration



Table 4.19 The microextraction of fluoranthene solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	7.319	27.60	73.19	0.87
		NaCl	7.550	50.07	83.91	8.68
		Na ₂ SO ₄	8.607	210.49	95.64	1.96
	5:5	NO SALT	0.940	12.20	92.14	0.51
		NaCl	0.990	4165.97	99.87	0.78
		Na ₂ SO ₄	0.985	619.34	98.47	0.19
	2:8	NO SALT	0.241	5.08	95.03	1.54
		NaCl	0.248	148.81	99.82	3.92
		Na ₂ SO ₄	0.254	-	101.78	3.03
CYCLOHEXANE	9:1	NO SALT	8.339	70.04	88.03	2.11
		NaCl	9.000	-	100.00	0.54
		Na ₂ SO ₄	8.998	36028.5	99.97	0.89
	5:5	NO SALT	0.916	9.90	90.65	1.80
		NaCl	0.950	21.45	95.29	5.64
		Na ₂ SO ₄	0.957	23.46	95.68	6.20
	2:8	NO SALT	0.235	3.68	93.45	1.52
		NaCl	0.240	15.02	98.24	1.42
		Na ₂ SO ₄	0.247	19.12	98.61	3.56
CH ₂ Cl ₂	9:1	NO SALT	8.983	45.56	78.85	0.82
		NaCl	9.077	-	100.86	0.49
		Na ₂ SO ₄	9.140	-	101.55	2.46
	5:5	NO SALT	0.933	9.31	87.58	3.82
		NaCl	0.970	38.27	97.30	3.16
		Na ₂ SO ₄	0.962	27.05	96.23	2.05
	2:8	NO SALT	0.237	3.38	92.30	2.10
		NaCl	0.245	56.34	99.52	1.80
		Na ₂ SO ₄	0.251	-	100.29	3.50

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluoranthene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K _d	% E	% RSD
CS ₂	9:1	NO SALT	36.610	27.65	73.22	0.72
		NaCl	37.800	50.52	84.03	1.60
		Na ₂ SO ₄	43.145	223.26	95.88	0.97
	5:5	NO SALT	4.710	12.53	92.33	0.88
		NaCl	5.010	-	100.10	0.36
		Na ₂ SO ₄	4.926	641.20	98.52	0.10
	2:8	NO SALT	1.225	8.01	96.94	2.75
		NaCl	1.220	11.24	97.66	0.98
		Na ₂ SO ₄	1.290	-	103.26	0.89
CYCLOHEXANE	9:1	NO SALT	41.240	64.10	87.06	2.21
		NaCl	47.000	-	104.40	0.18
		Na ₂ SO ₄	46.950	-	104.34	0.31
	5:5	NO SALT	4.604	10.51	91.15	1.83
		NaCl	4.800	26.05	96.09	1.48
		Na ₂ SO ₄	4.769	21.92	95.39	0.86
	2:8	NO SALT	1.162	3.11	92.35	3.13
		NaCl	1.280	-	102.22	3.03
		Na ₂ SO ₄	1.254	-	100.29	0.92
CH ₂ Cl ₂	9:1	NO SALT	44.870	45.34	79.77	2.02
		NaCl	45.345	-	100.77	0.16
		Na ₂ SO ₄	45.650	-	101.46	1.74
	5:5	NO SALT	4.605	8.28	88.42	1.73
		NaCl	4.790	23.83	95.74	0.83
		Na ₂ SO ₄	4.763	21.34	95.27	1.51
	2:8	NO SALT	1.179	3.84	91.98	2.11
		NaCl	1.210	16.74	98.42	4.96
		Na ₂ SO ₄	1.227	14.41	98.17	1.78

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluoranthene is higher than its initial concentration

Table 4.20 The microextraction of pyrene solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	4.658	8.80	46.58	0.60
		NaCl	8.910	954.55	99.00	0.06
		Na ₂ SO ₄	8.918	1041.86	99.09	0.10
	5:5	NO SALT	0.895	7.44	87.73	0.45
		NaCl	1.000	-	100.03	0.60
		Na ₂ SO ₄	0.987	80.25	98.72	0.33
	2:8	NO SALT	0.230	2.69	91.01	1.83
		NaCl	0.249	124.75	99.79	3.28
		Na ₂ SO ₄	0.247	24.71	98.92	2.37
CYCLOHEXANE	9:1	NO SALT	8.837	132.20	93.28	1.06
		NaCl	9.020	-	100.26	1.20
		Na ₂ SO ₄	9.000	-	100.00	3.58
	5:5	NO SALT	0.971	25.18	96.11	3.94
		NaCl	0.990	131.77	99.20	4.71
		Na ₂ SO ₄	1.050	-	105.01	3.89
	2:8	NO SALT	0.246	10.45	97.59	5.05
		NaCl	0.240	10.17	97.43	2.81
		Na ₂ SO ₄	0.252	-	100.61	3.65
CH ₂ Cl ₂	9:1	NO SALT	8.559	36.57	76.08	1.78
		NaCl	9.030	-	100.33	0.67
		Na ₂ SO ₄	9.169	-	101.88	3.13
	5:5	NO SALT	0.906	7.24	86.98	0.81
		NaCl	0.960	25.96	96.08	3.28
		Na ₂ SO ₄	0.975	40.60	97.46	0.54
	2:8	NO SALT	0.239	3.92	93.29	1.03
		NaCl	0.250	17.25	98.47	1.73
		Na ₂ SO ₄	0.247	22.01	98.79	2.05

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of pyrene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	23.565	9.02	47.13	3.91
		NaCl	44.600	1041.86	99.09	0.12
		Na ₂ SO ₄	44.795	2085.33	99.54	2.54
	5:5	NO SALT	4.465	7.32	87.55	1.05
		NaCl	5.050	-	100.90	1.40
		Na ₂ SO ₄	4.910	57.75	98.23	1.21
	2:8	NO SALT	1.155	2.72	91.08	3.66
		NaCl	1.250	-	100.08	2.10
		Na ₂ SO ₄	1.245	124.75	99.79	1.83
CYCLOHEXANE	9:1	NO SALT	44.185	132.20	93.28	0.60
		NaCl	45.200	-	100.48	4.32
		Na ₂ SO ₄	45.880	-	101.96	2.91
	5:5	NO SALT	4.846	24.22	95.96	1.01
		NaCl	4.990	921.44	99.89	0.49
		Na ₂ SO ₄	5.216	-	104.32	4.27
	2:8	NO SALT	1.210	6.41	96.13	2.82
		NaCl	1.230	15.90	98.34	1.52
		Na ₂ SO ₄	1.268	-	101.45	3.13
CH ₂ Cl ₂	9:1	NO SALT	42.600	35.89	75.73	1.26
		NaCl	45.300	-	100.90	2.09
		Na ₂ SO ₄	46.280	-	102.85	4.18
	5:5	NO SALT	4.687	9.74	89.99	4.14
		NaCl	4.840	30.85	96.77	1.65
		Na ₂ SO ₄	4.990	534.00	99.80	0.56
	2:8	NO SALT	1.166	2.83	90.95	3.74
		NaCl	1.240	29.30	99.09	0.58
		Na ₂ SO ₄	1.263	-	101.02	0.72

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of pyrene is higher than its initial concentration

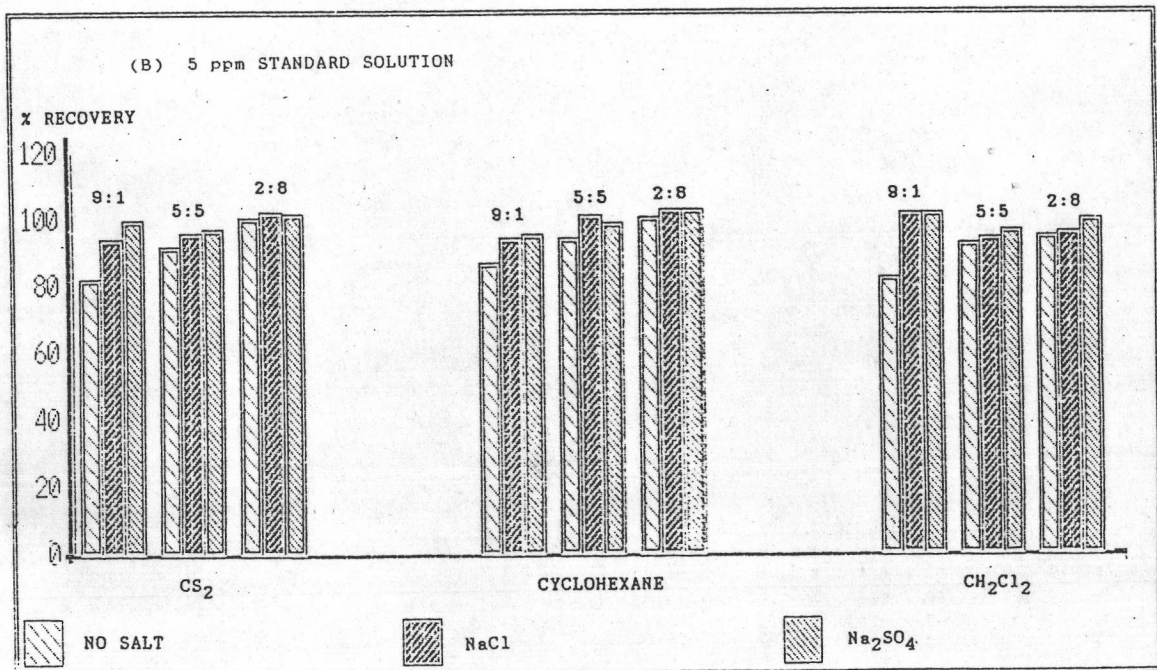
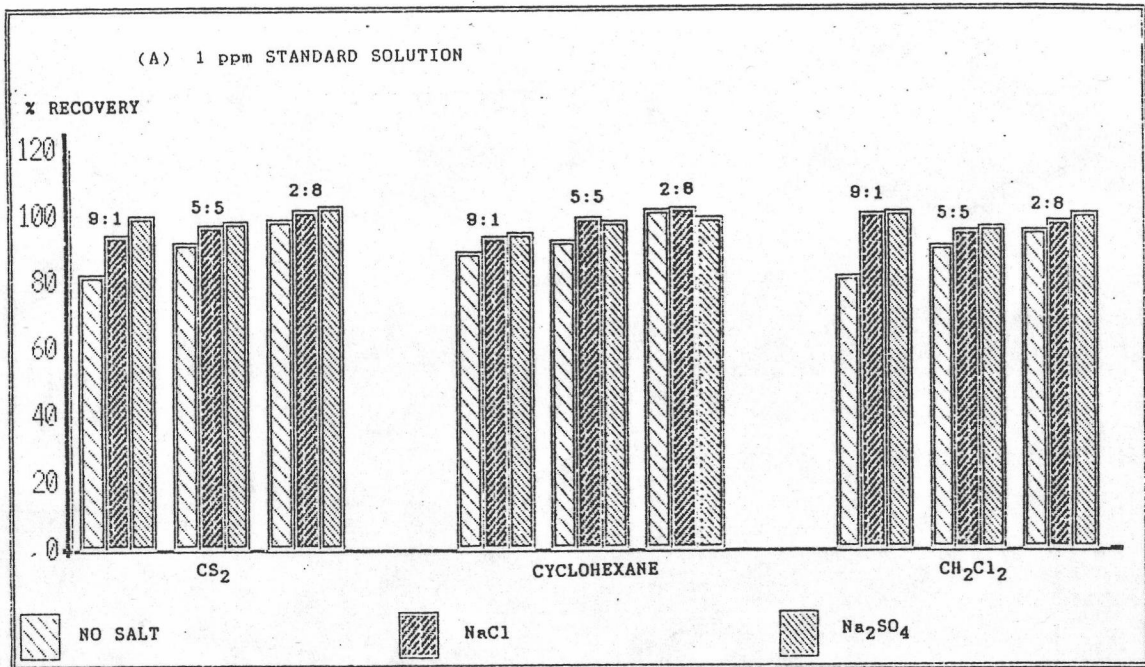


Figure 4.10 The microextraction of acenaphthene solution

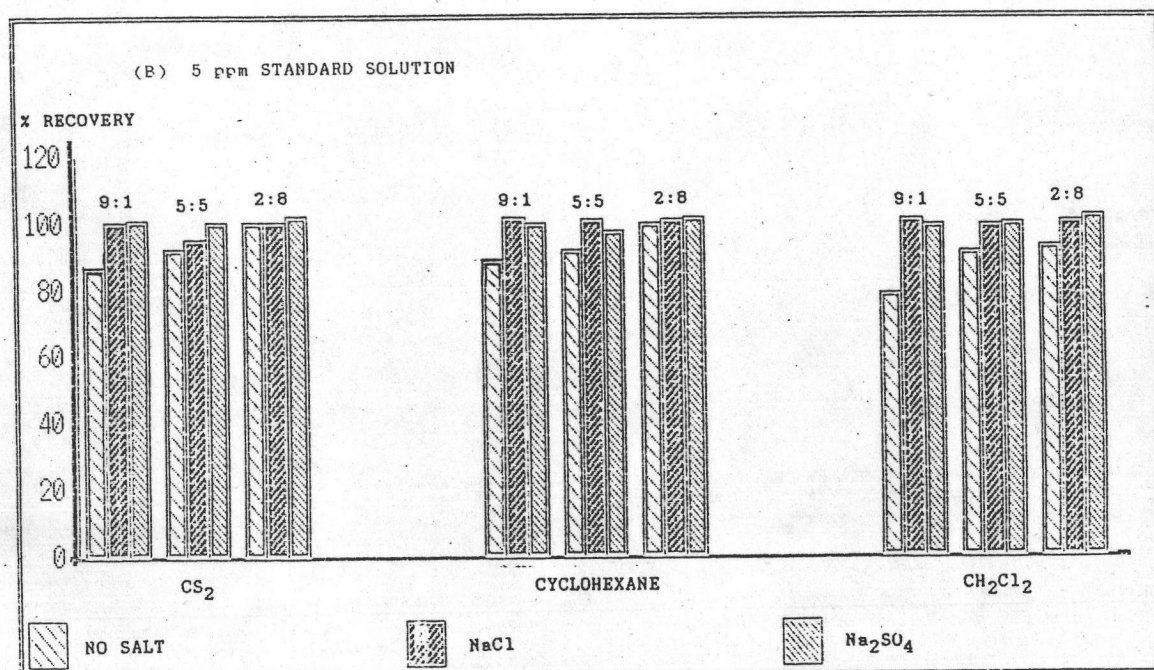
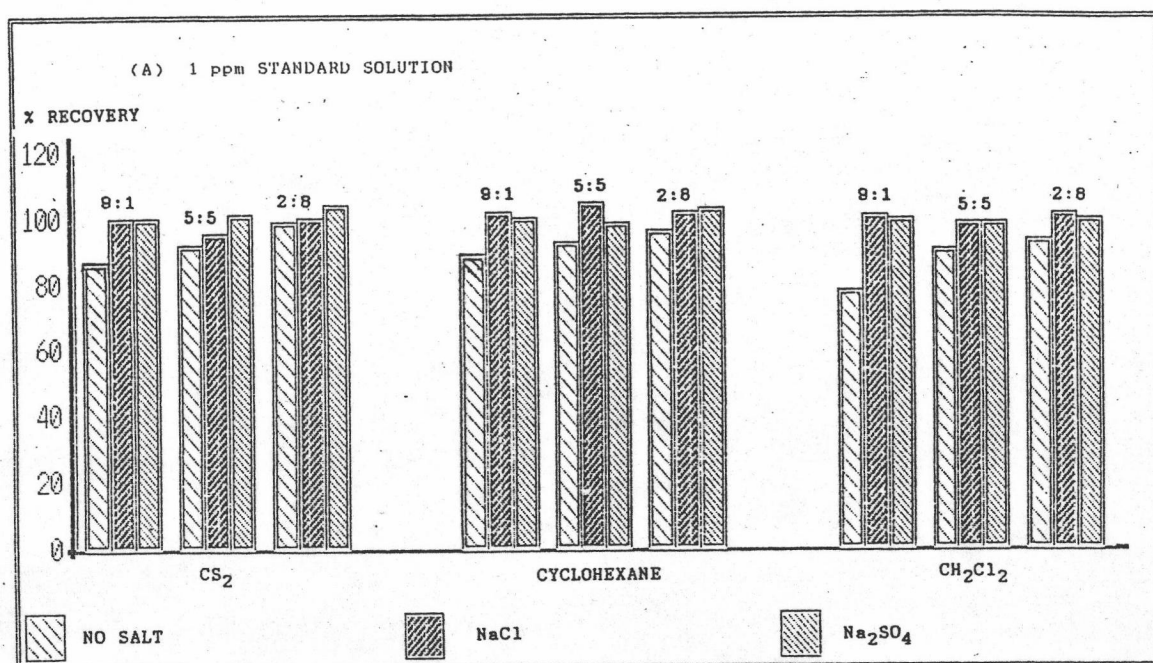


Figure 4.11 The microextraction of fluorene solution

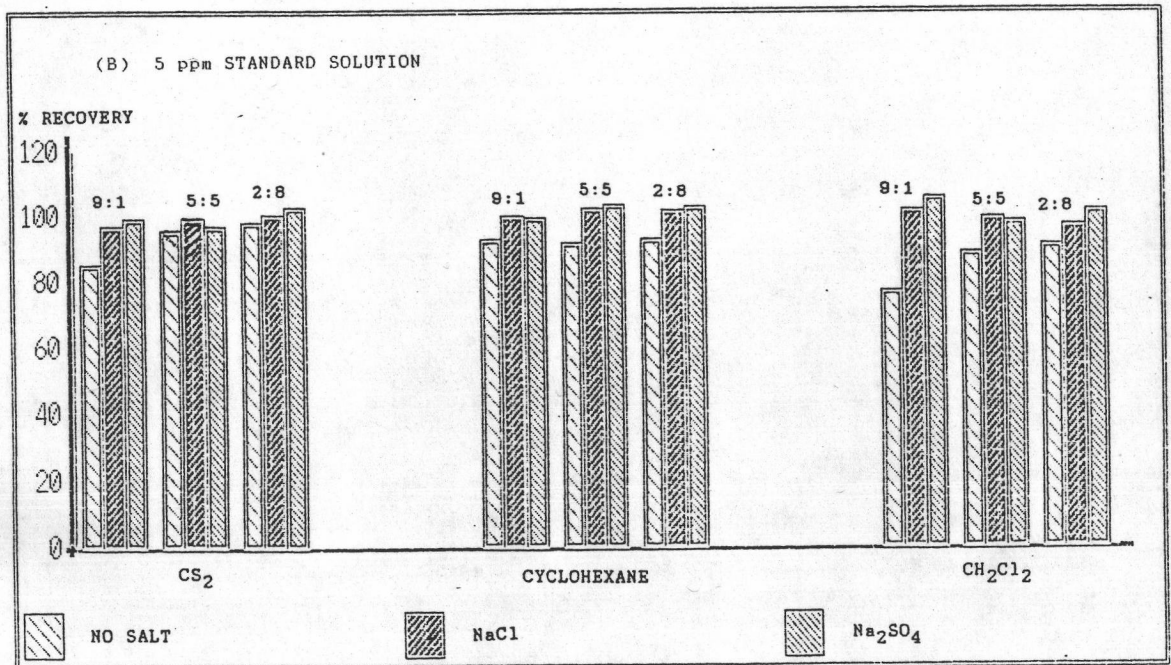
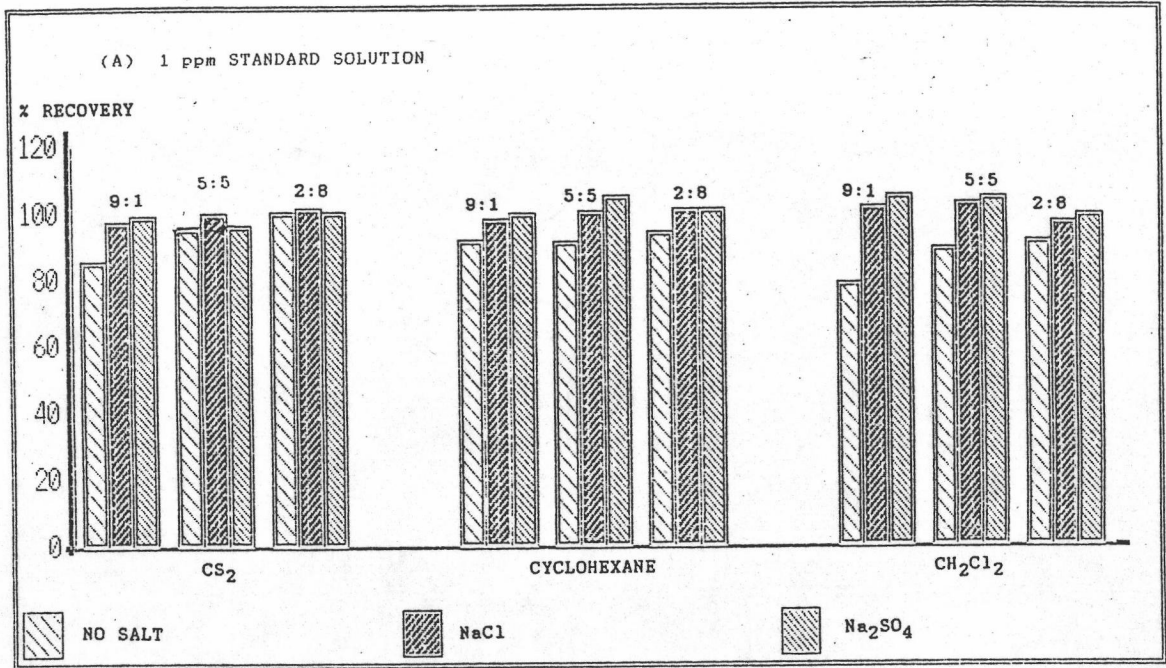


Figure 4.12 The microextraction of phenanthrene solution

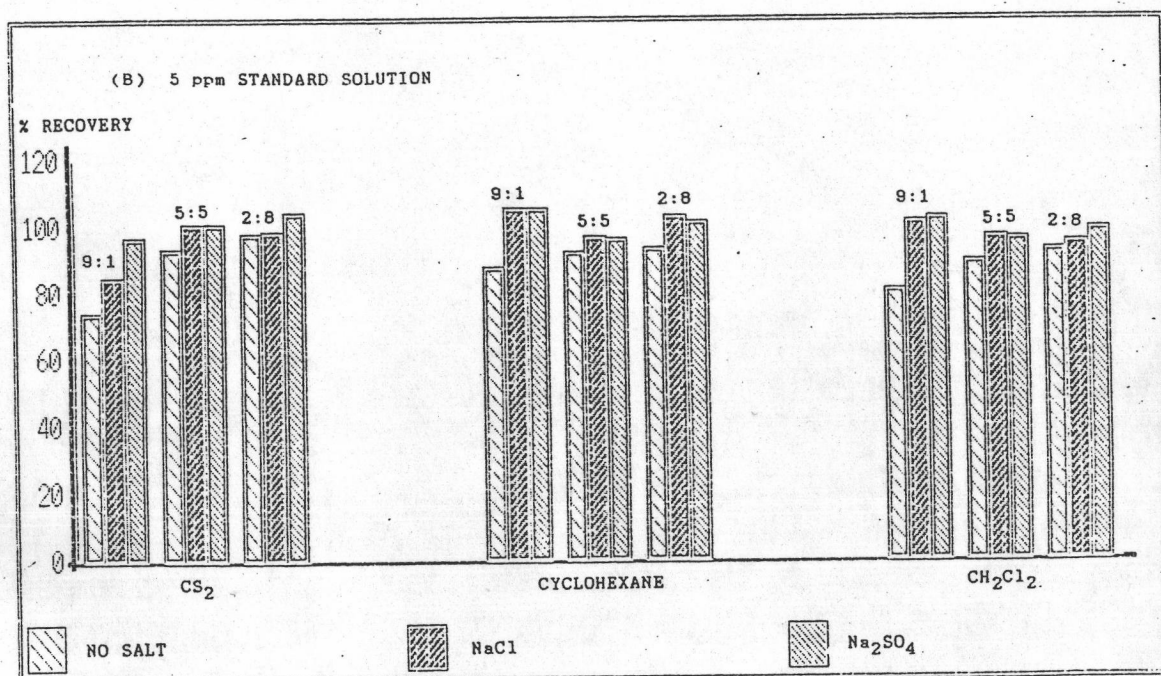
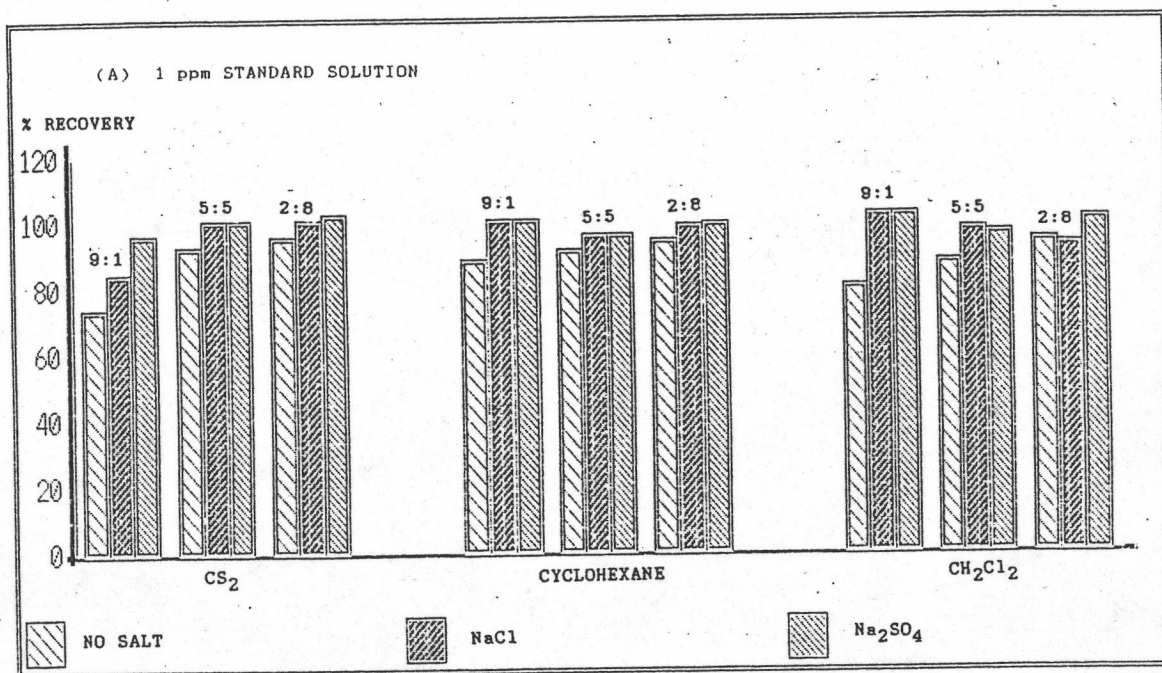


Figure 4.13 The microextraction of fluoranthene solution

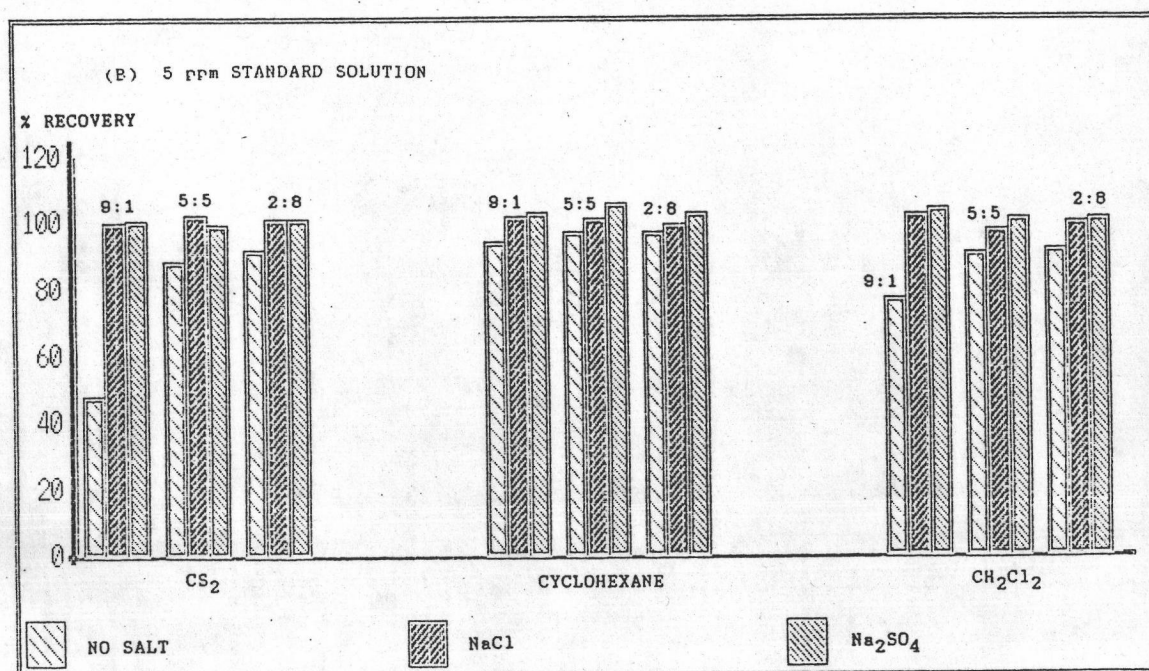
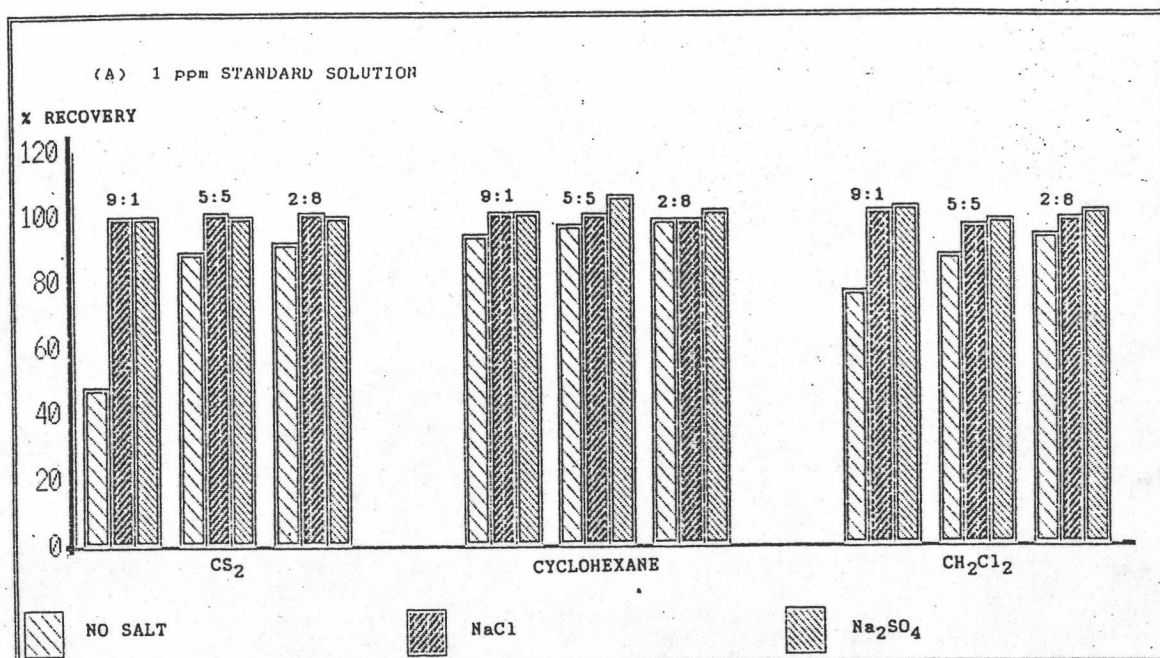


Figure 4.14 The microextraction of pyrene solution

4.5 MICROEXTRACTION OF PAHs IN MIXTURE SOLUTIONS

The various effects on % recovery of each PAH in the mixture solutions are studied in various solvents, i.e., carbon disulfide, cyclohexane, and methylene chloride, and in various sample to solvent ratios, i.e., 9:1, 5:5, and 2:8. The results are shown in Table 4.21-4.25 and the graphs correlated to these results are shown in Figure 4.15-4.19. It is found that the % recovery for the ratio of 9:1 is less than the ratios of 5:5 and 2:8, respectively. The % recovery of each PAH of 1 ppm solution is higher than % recovery of 5 ppm solution. However, the PAH in the solution is concentrated about 2.78 to 8.94 fold for the ratio of 9:1, the PAH solution is not concentrated in the ratio of 5:5 and it is diluted about 4 fold in the ratio 2:8. Thus, the concentration of each PAH decreases as long as the sample to solvent ratio has been decreased. Therefore, the sensitivity of each PAH for the ratio of 9:1 is higher than the sensitivity for ratios of 5:5 and 2:8, respectively.

In addition, the ratio of 9:1 gives the lowest % RSD. Therefore, 9:1 ratio would give the good precision for the analysis of these compounds and 9:1 ratio should be considered as a suitable ratio for microextraction technique.

Table 4.21 The microextraction of acenaphthene in mixture solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K _d	% E	% RSD
CS ₂	9:1	NO SALT	7.518	39.70	80.65	0.57
		NaCl	9.301	-	103.34	0.49
		Na ₂ SO ₄	9.440	-	104.88	0.42
	5:5	NO SALT	0.964	21.51	95.47	1.61
		NaCl	0.965	29.40	96.60	0.54
		Na ₂ SO ₄	0.972	36.73	97.20	0.81
	2:8	NO SALT	0.243	6.37	96.53	1.41
		NaCl	0.253	-	101.08	1.26
		Na ₂ SO ₄	0.249	62.78	99.57	2.98
CYCLOHEXANE	9:1	NO SALT	8.338	69.97	88.01	1.31
		NaCl	8.671	252.86	96.34	0.23
		Na ₂ SO ₄	8.580	196.01	95.33	0.84
	5:5	NO SALT	1.202	-	101.50	0.91
		NaCl	1.017	-	101.70	0.40
		Na ₂ SO ₄	1.030	-	103.01	0.45
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	9.147	50.03	81.31	0.67
		NaCl	9.090	-	101.00	2.62
		Na ₂ SO ₄	9.000	-	100.00	1.00
	5:5	NO SALT	0.926	11.21	91.66	4.18
		NaCl	0.992	128.19	99.78	0.79
		Na ₂ SO ₄	1.005	-	100.50	3.07
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of acenaphthene is higher than its initial concentration



MI1B
(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	38.15	32.57	76.31	1.67
		NaCl	43.65	312.62	97.02	1.41
		Na ₂ SO ₄	45.50	-	101.11	0.27
	5:5	NO SALT	4.83	23.16	95.78	1.16
		NaCl	4.91	63.48	98.36	0.89
		Na ₂ SO ₄	4.90	52.08	98.01	0.29
	2:8	NO SALT	1.21	6.60	96.24	0.67
		NaCl	1.23	22.72	98.83	0.78
		Na ₂ SO ₄	1.23	23.98	98.89	0.81
CYCLOHEXANE	9:1	NO SALT	41.35	65.46	87.30	1.11
		NaCl	41.79	125.26	92.88	1.85
		Na ₂ SO ₄	42.33	152.42	94.07	0.13
	5:5	NO SALT	4.88	30.49	96.76	1.20
		NaCl	4.92	65.17	98.40	1.47
		Na ₂ SO ₄	4.98	304.66	99.65	1.53
	2:8	NO SALT	1.24	10.37	97.57	1.16
		NaCl	1.23	16.94	98.44	1.14
		Na ₂ SO ₄	1.24	174.87	99.85	2.02
CH ₂ Cl ₂	9:1	NO SALT	40.00	48.91	80.96	0.11
		NaCl	45.76	-	101.70	0.99
		Na ₂ SO ₄	45.76	-	101.70	0.51
	5:5	NO SALT	4.53	8.95	89.76	2.80
		NaCl	5.03	-	100.59	0.69
		Na ₂ SO ₄	5.14	-	102.92	1.15
	2:8	NO SALT	1.18	3.58	92.70	1.30
		NaCl	1.19	6.36	95.94	0.48
		Na ₂ SO ₄	1.19	5.85	95.61	0.13

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of acenaphthene is higher than its initial concentration

Table 4.22 The microextraction of fluorene in mixture solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	8.857	78.35	88.57	0.45
		NaCl	8.762	352.17	97.35	0.34
		Na ₂ SO ₄	8.878	700.67	98.65	0.17
	5:5	NO SALT	0.968	23.54	95.85	1.58
		NaCl	0.985	68.48	98.48	1.18
		Na ₂ SO ₄	0.986	73.57	98.58	0.54
	2:8	NO SALT	0.245	9.11	97.25	0.87
		NaCl	0.252	-	100.75	1.95
		Na ₂ SO ₄	0.245	13.42	98.09	1.00
CYCLOHEXANE	9:1	NO SALT	8.017	52.43	84.62	1.31
		NaCl	9.374	-	101.15	0.35
		Na ₂ SO ₄	9.343	-	103.81	0.37
	5:5	NO SALT	0.995	66.52	98.49	0.47
		NaCl	0.995	204.51	99.48	0.23
		Na ₂ SO ₄	1.013	-	101.29	0.79
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	8.812	41.56	78.33	0.48
		NaCl	8.672	254.05	96.36	2.72
		Na ₂ SO ₄	8.707	285.40	96.75	0.24
	5:5	NO SALT	0.891	7.66	88.25	2.68
		NaCl	0.984	63.31	98.35	2.37
		Na ₂ SO ₄	0.983	59.58	98.25	2.17
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluorene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K _d	% E	% RSD
CS ₂	9:1	NO SALT	34.762	22.23	69.52	2.02
		NaCl	42.720	179.82	94.93	1.28
		Na ₂ SO ₄	45.300	-	100.72	0.42
	5:5	NO SALT	4.937	44.57	97.76	0.84
		NaCl	5.029	-	98.07	1.70
		Na ₂ SO ₄	5.002	-	99.32	0.95
	2:8	NO SALT	1.232	12.23	97.93	1.59
		NaCl	1.249	400.46	99.93	0.07
		Na ₂ SO ₄	1.222	11.75	97.76	0.58
CYCLOHEXANE	9:1	NO SALT	37.974	38.51	80.17	1.11
		NaCl	43.822	357.24	97.38	1.43
		Na ₂ SO ₄	44.392	700.45	98.65	0.20
	5:5	NO SALT	4.937	44.57	97.76	0.84
		NaCl	4.904	53.96	98.07	1.70
		Na ₂ SO ₄	4.966	154.64	99.32	0.95
	2:8	NO SALT	1.218	7.80	96.80	0.96
		NaCl	1.222	11.60	97.73	0.76
		Na ₂ SO ₄	1.247	102.73	99.74	1.70
CH ₂ Cl ₂	9:1	NO SALT	35.857	20.22	63.75	0.53
		NaCl	43.086	216.10	95.75	0.91
		Na ₂ SO ₄	43.149	223.81	95.89	1.67
	5:5	NO SALT	4.638	11.47	91.83	1.71
		NaCl	4.902	53.01	98.01	1.34
		Na ₂ SO ₄	4.864	37.97	97.28	1.43
	2:8	NO SALT	1.233	7.14	96.20	1.60
		NaCl	1.268	-	101.45	1.22
		Na ₂ SO ₄	1.254	-	100.35	0.24

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluorene is higher than its initial concentration

Table 4.23 The microextraction of phenanthrene in mixture solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	8.098	56.05	85.47	2.28
		NaCl	8.539	177.78	94.88	0.51
		Na ₂ SO ₄	8.806	434.68	97.84	0.85
	5:5	NO SALT	0.963	21.02	95.37	1.54
		NaCl	1.024	-	102.39	0.47
		Na ₂ SO ₄	0.988	88.06	98.81	1.77
	2:8	NO SALT	0.244	8.70	97.12	1.52
		NaCl	0.253	-	101.00	2.73
		Na ₂ SO ₄	0.253	-	101.18	3.22
CYCLOHEXANE	9:1	NO SALT	8.646	99.55	91.27	0.49
		NaCl	9.039	-	100.43	0.65
		Na ₂ SO ₄	9.084	-	100.93	0.83
	5:5	NO SALT	0.979	31.89	96.90	1.04
		NaCl	0.997	322.53	99.67	1.13
		Na ₂ SO ₄	1.009	-	100.87	1.67
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	9.102	145.63	80.91	0.71
		NaCl	8.891	785.37	98.79	2.36
		Na ₂ SO ₄	9.060	-	100.66	2.05
	5:5	NO SALT	0.876	7.53	88.07	6.41
		NaCl	0.999	708.43	99.85	1.97
		Na ₂ SO ₄	1.003	-	100.25	2.47
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of phenanthrene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	26.074	11.02	52.15	2.47
		NaCl	42.457	160.30	94.35	1.07
		Na ₂ SO ₄	45.504	-	101.11	0.91
	5:5	NO SALT	4.829	22.27	95.62	2.00
		NaCl	4.894	49.00	97.88	0.64
		Na ₂ SO ₄	4.879	42.65	97.75	0.48
	2:8	NO SALT	1.215	7.28	96.58	1.65
		NaCl	1.243	46.48	99.43	1.01
		Na ₂ SO ₄	1.225	13.21	98.01	0.96
CYCLOHEXANE	9:1	NO SALT	41.719	69.94	88.01	1.32
		NaCl	45.719	-	101.60	1.12
		Na ₂ SO ₄	46.239	-	102.75	0.26
	5:5	NO SALT	4.799	19.45	95.01	0.76
		NaCl	4.973	192.85	99.45	1.18
		Na ₂ SO ₄	4.981	282.03	99.63	0.70
	2:8	NO SALT	1.262	-	100.34	0.49
		NaCl	1.278	-	102.23	0.88
		Na ₂ SO ₄	1.296	-	103.65	0.87
CH ₂ Cl ₂	9:1	NO SALT	30.339	13.46	53.93	3.62
		NaCl	43.932	394.71	97.63	0.88
		Na ₂ SO ₄	44.458	787.39	98.80	0.98
	5:5	NO SALT	4.487	8.13	88.84	4.01
		NaCl	5.043	-	100.87	2.68
		Na ₂ SO ₄	4.928	72.57	98.56	1.02
	2:8	NO SALT	1.191	3.71	92.93	1.34
		NaCl	1.243	49.38	99.46	0.81
		Na ₂ SO ₄	1.243	207.71	99.87	0.86

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of phenanthrene is higher than its initial concentration

Table 4.24 The microextraction of fluoranthene in mixture solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K _d	% E	% RSD
CS ₂	9:1	NO SALT	6.444	20.27	68.03	1.24
		NaCl	8.187	96.66	90.67	2.62
		Na ₂ SO ₄	8.696	274.42	96.62	0.38
	5:5	NO SALT	0.931	12.04	92.19	5.25
		NaCl	1.057	-	105.70	3.48
		Na ₂ SO ₄	1.009	-	100.90	4.00
	2:8	NO SALT	0.234	3.37	92.89	2.51
		NaCl	0.252	-	100.87	2.56
		Na ₂ SO ₄	0.252	-	100.87	2.00
CYCLOHEXANE	9:1	NO SALT	8.272	65.57	87.31	2.81
		NaCl	8.884	738.12	98.71	1.53
		Na ₂ SO ₄	8.945	1557.14	99.39	1.37
	5:5	NO SALT	0.986	42.39	97.65	2.04
		NaCl	1.002	-	100.18	3.24
		Na ₂ SO ₄	1.010	-	101.04	1.69
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	8.613	37.55	76.56	0.60
		NaCl	8.867	641.19	98.52	0.41
		Na ₂ SO ₄	9.116	-	101.29	1.39
	5:5	NO SALT	0.869	7.02	87.31	9.24
		NaCl	0.968	32.07	96.82	2.98
		Na ₂ SO ₄	0.973	38.20	97.31	4.19
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluoranthene is higher than its initial concentration



(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	21.620	7.70	43.24	2.73
		NaCl	40.894	95.61	90.87	0.79
		Na ₂ SO ₄	44.016	429.55	97.81	0.61
	5:5	NO SALT	4.676	12.74	92.59	2.55
		NaCl	5.213	-	104.26	0.66
		Na ₂ SO ₄	5.196	-	103.92	1.24
	2:8	NO SALT	1.206	6.03	95.90	5.01
		NaCl	1.279	-	102.29	1.09
		Na ₂ SO ₄	1.266	-	101.27	0.93
CYCLOHEXANE	9:1	NO SALT	38.973	44.22	82.28	0.31
		NaCl	46.054	-	102.34	0.51
		Na ₂ SO ₄	46.363	-	103.02	0.57
	5:5	NO SALT	4.874	28.17	96.51	1.55
		NaCl	4.926	70.74	98.52	0.99
		Na ₂ SO ₄	4.882	48.82	97.64	0.92
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	24.509	8.88	43.57	3.92
		NaCl	45.880	-	101.95	1.18
		Na ₂ SO ₄	44.840	2715.22	99.88	0.58
	5:5	NO SALT	4.477	7.96	88.64	4.19
		NaCl	4.819	28.26	96.39	3.96
		Na ₂ SO ₄	4.785	23.60	95.70	3.04
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of fluoranthene is higher than its initial concentration

Table 4.25 The microextraction of pyrene in mixture solution

(A) 1 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	4.130	7.11	41.30	2.53
		NaCl	8.623	219.33	95.81	0.46
		Na ₂ SO ₄	9.041	-	100.45	0.44
	5:5	NO SALT	0.949	15.98	94.00	5.84
		NaCl	0.996	263.94	99.60	6.43
		Na ₂ SO ₄	0.999	879.93	99.88	2.72
	2:8	NO SALT	0.227	2.35	90.12	5.12
		NaCl	0.259	-	103.79	1.87
		Na ₂ SO ₄	0.255	-	101.81	6.78
CYCLOHEXANE	9:1	NO SALT	8.817	127.80	93.06	1.99
		NaCl	8.951	1758.41	99.45	1.18
		Na ₂ SO ₄	8.892	792.15	98.81	1.17
	5:5	NO SALT	1.028	-	101.75	1.94
		NaCl	0.985	69.92	98.51	4.78
		Na ₂ SO ₄	1.017	-	101.70	3.40
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	7.773	25.71	69.09	4.68
		NaCl	8.740	322.71	97.11	0.57
		Na ₂ SO ₄	9.151	-	101.67	0.47
	5:5	NO SALT	0.857	6.37	86.19	8.06
		NaCl	0.971	35.18	97.08	3.12
		Na ₂ SO ₄	0.995	215.67	99.51	3.05
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of pyrene is higher than its initial concentration

(B) 5 ppm standard solution

SOLVENT	RATIO	SALT	CONC. (ppm)	K_d	% E	% RSD
CS ₂	9:1	NO SALT	13.896	3.89	27.79	2.32
		NaCl	43.330	249.70	96.30	0.98
		Na ₂ SO ₄	46.627	-	103.61	0.94
	5:5	NO SALT	4.768	17.24	94.41	2.31
		NaCl	4.939	85.74	98.78	0.74
		Na ₂ SO ₄	4.928	73.00	98.57	0.30
	2:8	NO SALT	1.117	2.04	88.79	4.60
		NaCl	1.259	-	100.72	0.86
		Na ₂ SO ₄	1.249	391.45	99.93	0.74
CYCLOHEXANE	9:1	NO SALT	44.659	157.02	94.28	1.82
		NaCl	45.780	-	101.72	0.79
		Na ₂ SO ₄	46.039	-	102.31	0.36
	5:5	NO SALT	5.046	1169.41	99.91	4.02
		NaCl	5.057	-	101.13	0.79
		Na ₂ SO ₄	4.998	2751.85	99.96	0.80
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				
CH ₂ Cl ₂	9:1	NO SALT	30.523	13.64	54.26	2.98
		NaCl	46.330	-	102.95	0.59
		Na ₂ SO ₄	44.788	2029.88	99.53	3.66
	5:5	NO SALT	4.511	8.53	89.32	2.53
		NaCl	4.947	98.39	98.93	4.51
		Na ₂ SO ₄	5.099	-	101.98	2.07
	2:8	NO SALT				
		NaCl				
		Na ₂ SO ₄				

Triplicate analyses

- K_d cannot be calculated due to the experimental concentration of pyrene is higher than its initial concentration

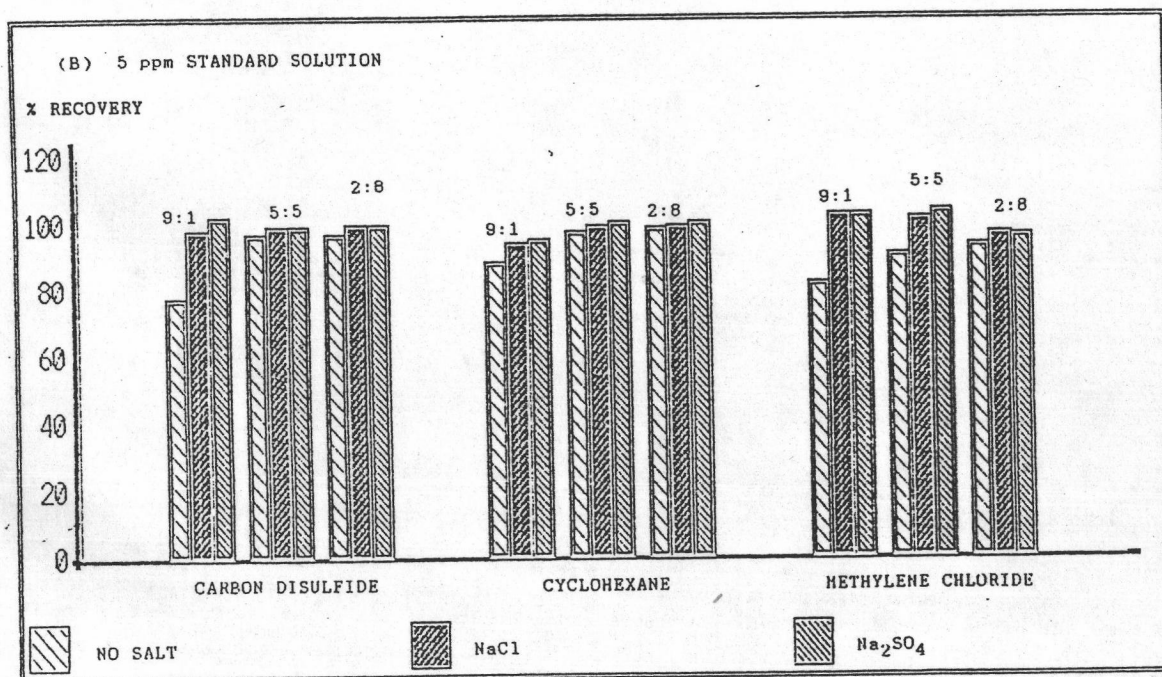
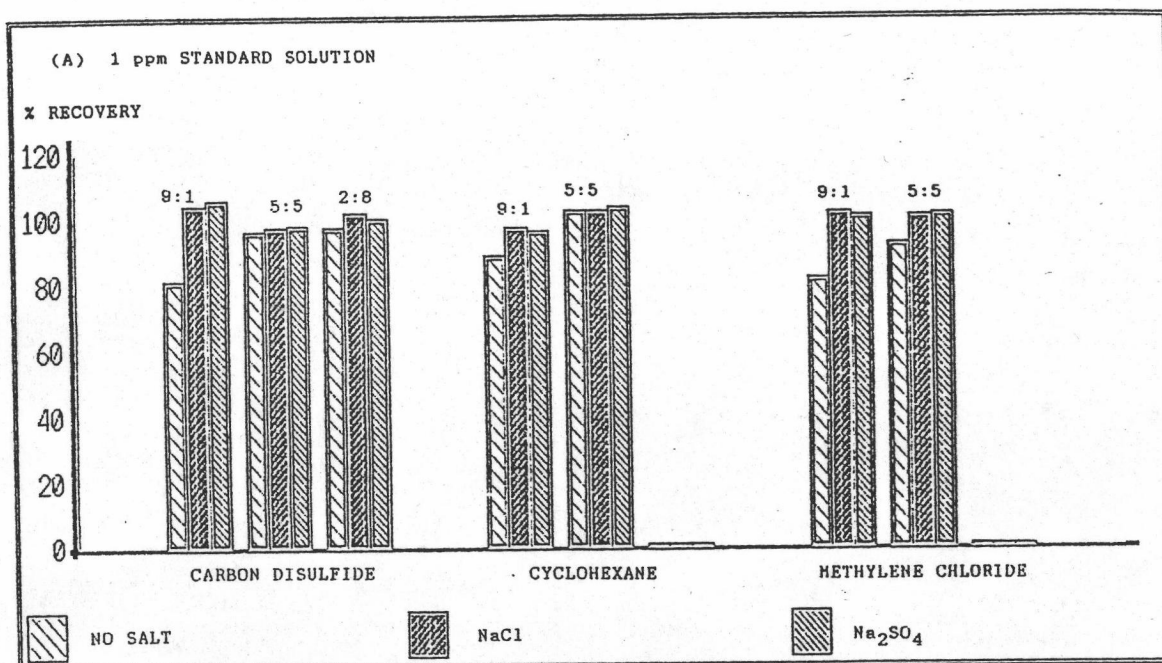


Figure 4.15 The microextraction of acenaphthene in mixture solution

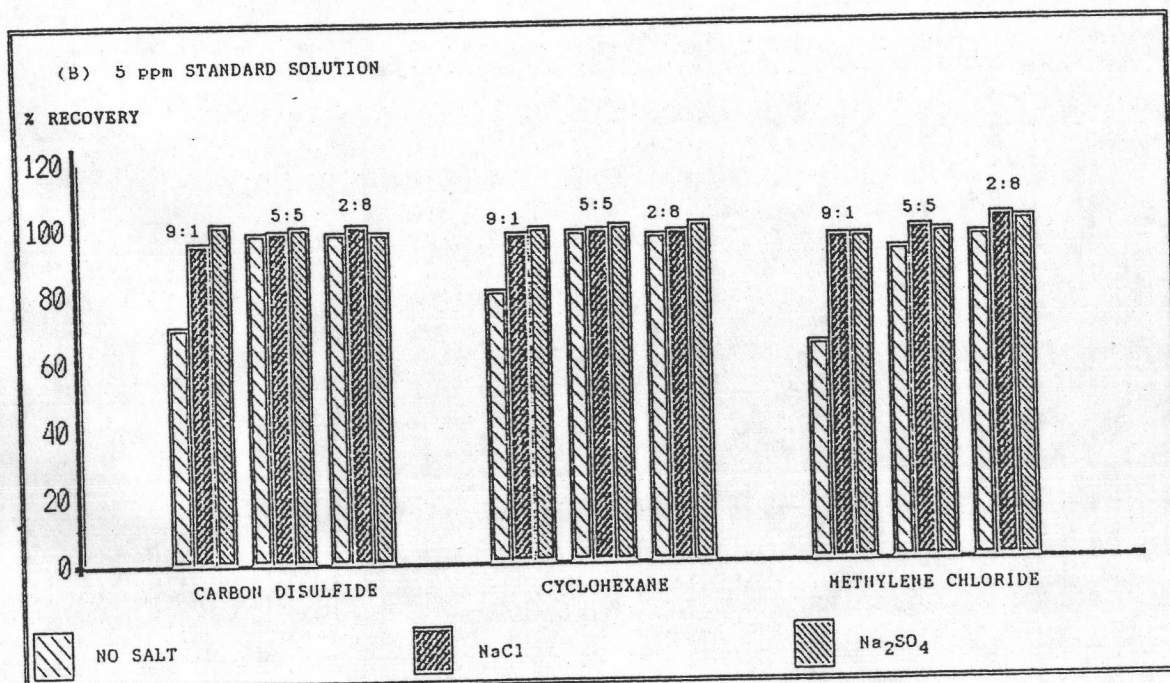
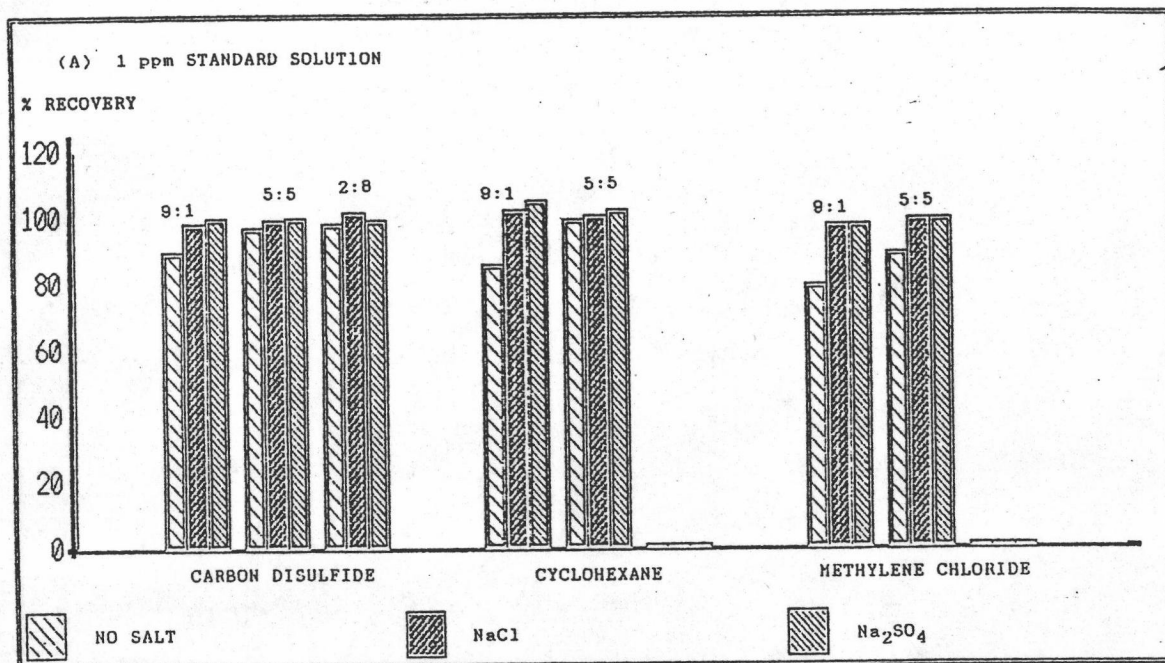


Figure 4.16 The microextraction of fluorene in mixture solution

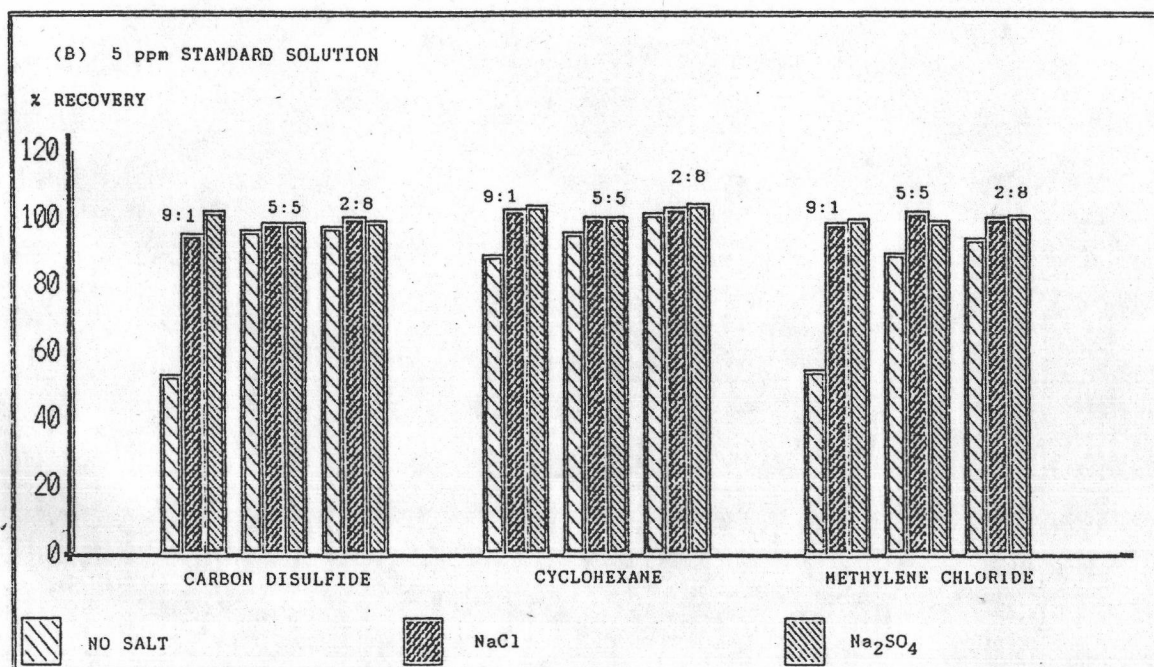
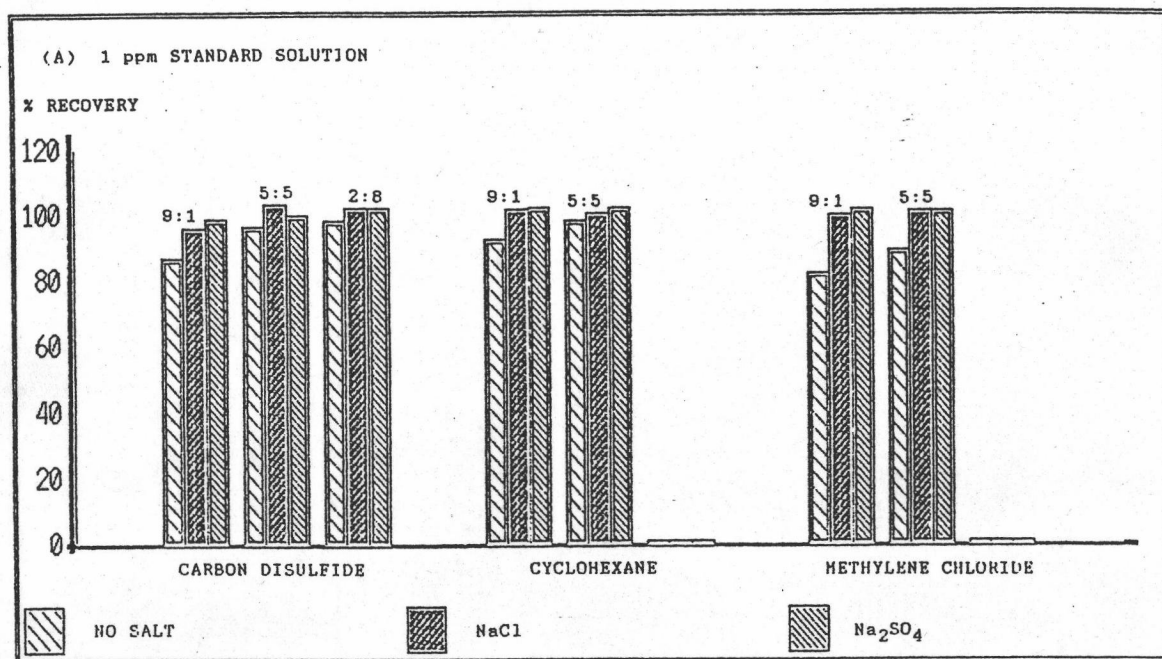


Figure 4.17 The microextraction of phenanthrene in mixture solution

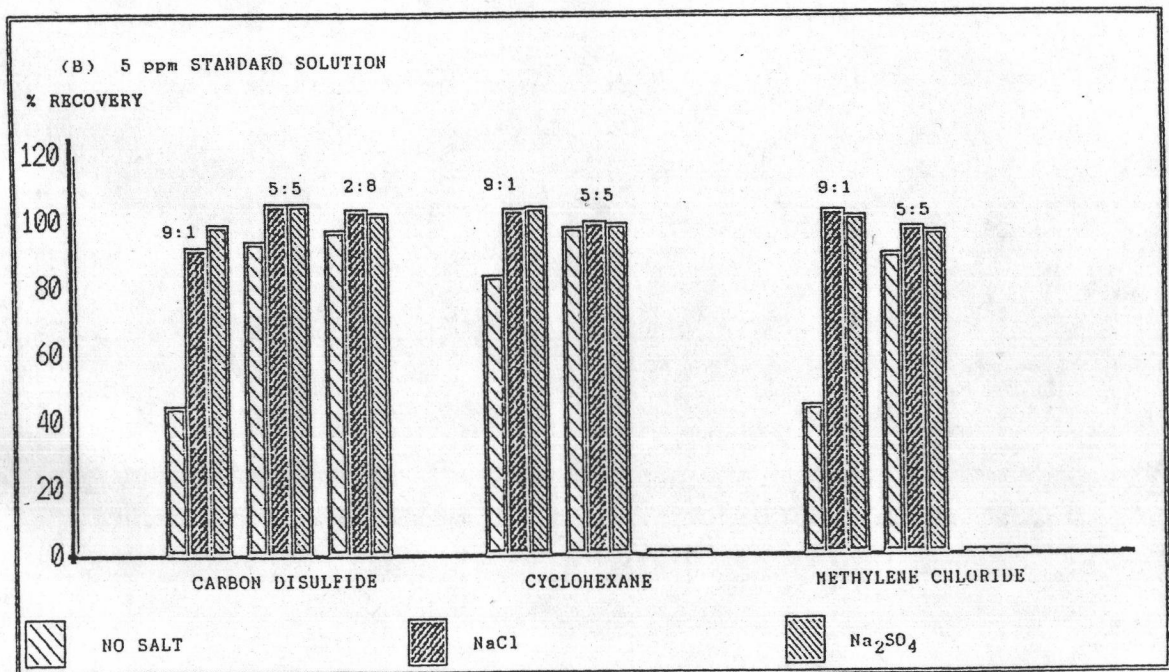
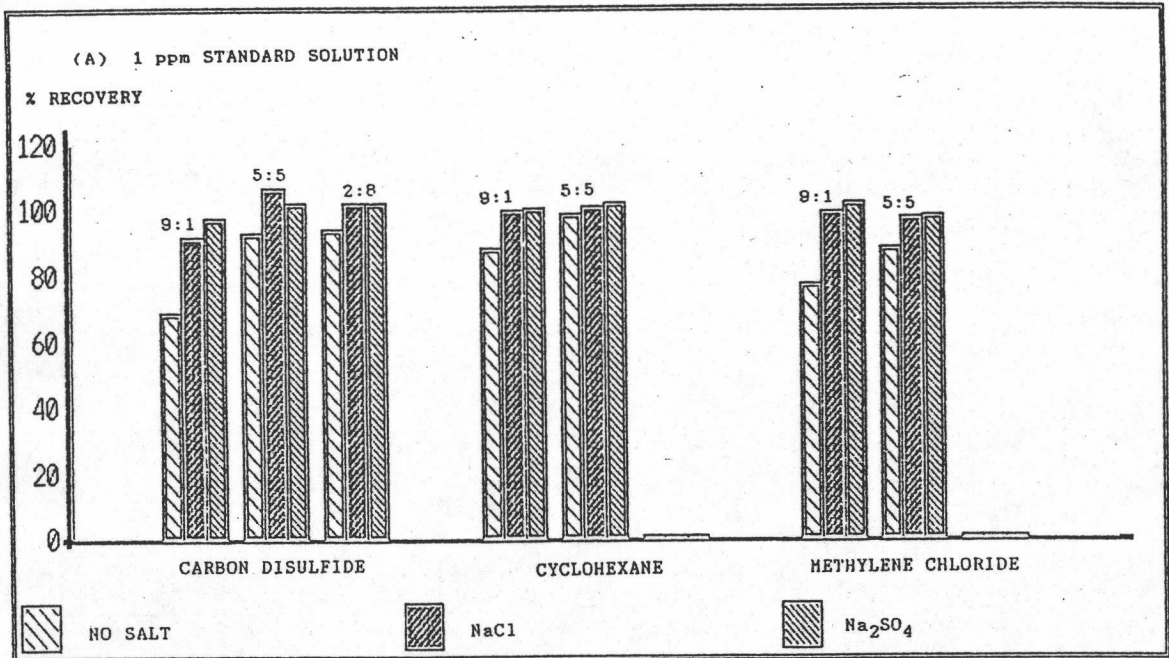


Figure 4.18 The microextraction of fluoranthene in mixture solution

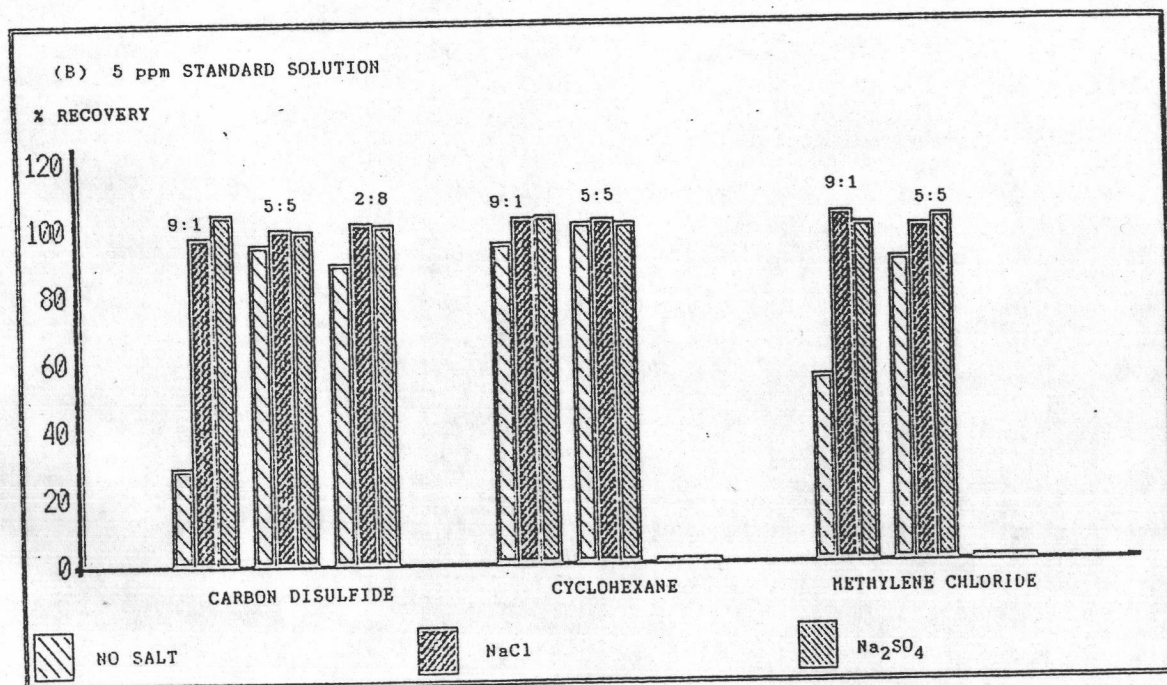
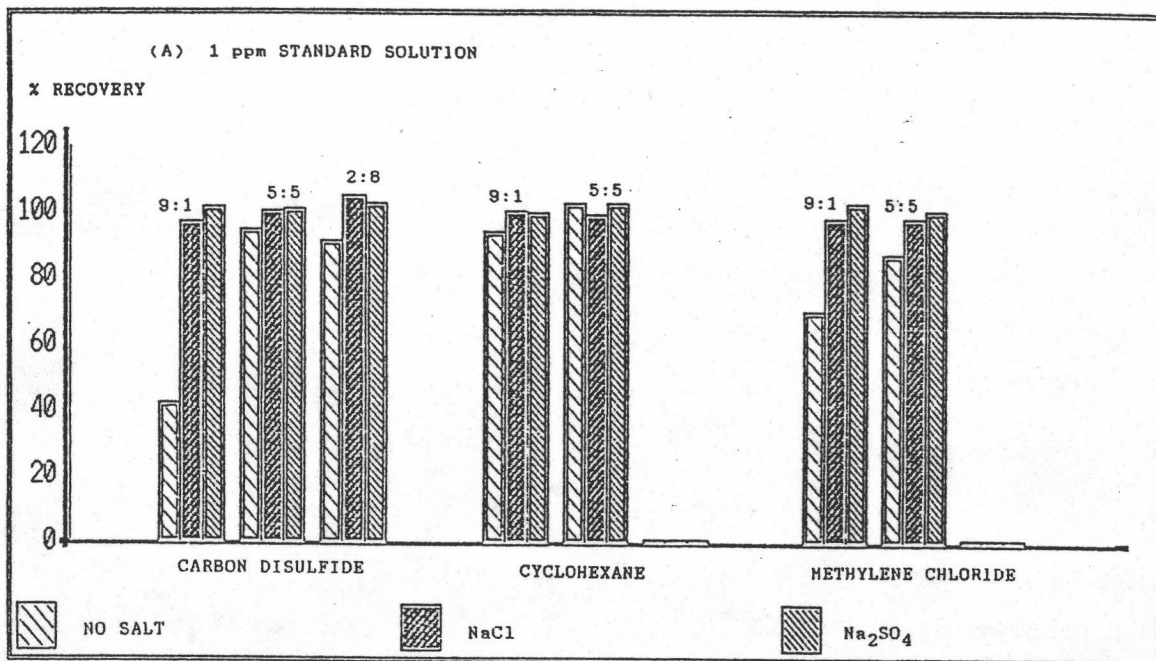


Figure 4.19 The microextraction of pyrene in mixture solution

The recoveries data of each PAH in each solvent are shown in Table 4.21-4.25. They are indicated that the microextraction using cyclohexane as solvent give the higher % recovery than carbon disulfide and methylene chloride. Therefore, cyclohexane would be selected as the appropriate solvent for microextraction of PAHs.

The salting out with sodium chloride and sodium sulfate having the effect on % recovery of the extraction of each PAH are evaluated. The results of % recovery of each PAH in each extracting solvent and each sample to solvent ratio which can be seen in Table 4.21-4.25 show the higher % recovery of each PAH with sodium sulfate than sodium chloride and nonsalting out, respectively. The reason of this is that sodium sulfate added into the solution results in the higher ionic strength than the sodium chloride and nonsalting out do. Therefore, sodium sulfate seems to be the most suitable salt for this microextraction technique.

According to % recoveries show in Table 4.16-4.25, the % recovery of each PAH in the single component solutions range from 47.13-104.40 % with % RSD 0.00-9.72 % and % recovery of each PAH in the mixture solutions range from 27.79-105.70 % with % RSD 0.11-9.24 %. It can be seen that the % recovery of each PAH in the single component solutions are higher than mixture solutions. This means that other compounds which are in the solution have the effect on % recovery of each PAH.

4.6 THE MINIMUM DETECTABLE LEVEL (MDL) OF PAHs

The minimum detectable level is defined as amount of the component which give a detector response equal to twice the average noise level (46). The minimum detectable level of each PAH is determined by injecting standard PAH with a concentration varied from 20 ppb to 2 ppm into the GC. The minimum detectable level of each PAH in single component solutions and in mixture solutions are presented in Table 4.26 and Table 4.27.

They are found that the detection limit of each PAH in carbon disulfide are lower than in cyclohexane and methylene chloride. Carbon disulfide does not give any response to FID, thus, more than 1 uL of carbon disulfide can be injected into GC. Since, only 1 uL of cyclohexane and methylene chloride can be injected to GC and they cannot be injected more than 1 uL due to the resolution of solvent peak and the first peak of the interested compound.

The minimum detectable level of each PAH in the mixture solutions are limited by the baseline drift when the temperature programme is used. Then, the minimum detectable level for single component solutions are lower than mixture solutions.



Table 4.26 The minimum detectable level of PAHs in various solvents

STANDARD	MINIMUM DETECTABLE LEVEL (ppm)		
	CS ₂	CH ₂ Cl ₂	CYCLOHEXANE
ACENAPHTHENE	0.05	0.10	0.10
FLUORENE	0.06	0.12	0.12
PHENANTHRENE	0.07	0.14	0.14
FLUORANTHENE	0.15	0.30	0.30
PYRENE	0.15	0.30	0.30

Table 4.27 The minimum detectable level of PAHs mixture in various solvents

STANDARD	MINIMUM DETECTABLE LEVEL (ppm)		
	CS ₂	CH ₂ Cl ₂	CYCLOHEXANE
ACENAPHTHENE	0.05	0.50	0.50
FLUORENE	0.06	0.60	0.60
PHENANTHRENE	0.07	0.70	0.70
FLUORANTHENE	0.15	1.50	1.50
PYRENE	0.15	1.50	1.50

Triplicate analyses

4.7 THE ACCURACY OF MICROEXTRACTION METHOD

The microextraction with carbon disulfide in the sample to solvent ratio of 9:1 and salting out with sodium sulfate are selected as suitable combination for analysis of PAHs. Carbon disulfide is found to be a most desirable solvent for the extraction of PAHs because it does not give any response to FID, then the volume of the extract injected into GC can be increased. The accuracy of microextraction is evaluated by comparing the results of concentration of each PAH obtained from the analysis with the true concentration of each PAH in synthetic unknown mixture solutions. The unknowns are prepared in methanol. It was diluted with distilled water and then it was analyzed by the microextraction procedure as described in section 3.4.4. The results of the concentration of each PAH and % error are shown in Table 4.28.

It is found that this microextraction technique gives the high precision and high accuracy. Thus, this microextraction technique should be considered as a available method for the determination of PAHs in water sample.

Table 4.28 The results of the analysis of synthetic unknown solutions

STANDARD	CONCENTRATION(ppm)		% ERROR
	TRUE	EXPERIMENT	
ACENAPHTHENE			
NO.1	8.63	8.64	0.12
NO.2	4.62	4.63	0.22
FLUORENE			
NO.1	4.86	4.87	0.21
NO.2	6.62	6.59	0.45
PHENANTHRENE			
NO.1	7.59	7.72	1.72
NO.2	8.21	8.19	0.24
FLUORANTHENE			
NO.1	5.11	5.15	0.78
NO.2	8.89	8.95	0.68
PYRENE			
NO.1	3.12	3.16	1.28
NO.2	4.33	4.39	1.34

Triplicate analyses

4.8 THE DETERMINATION OF PAHs IN REAL WATER SAMPLES.

Three water samples collected from various sites were analyzed by microextraction procedure which is the same as described in section 4.7 and GC equipped with FID. The gas chromatograms are shown in Figure 4.20-4.22. The unknown peak is identified by means of absolute retention time method. The retention times of the peaks obtained from the injecting of extracts into the two different columns, i.e., a 2 m x 3/8" O.D. stainless steel column packed with 5 % OV-17 on chromosorb WAW/DMCS 60-80 mesh and another column, a 6' x 1/8" I.D. stainless steel column packed with 10 % FFAP on chromosorb WAW/DMCS 60-80 mesh are the same as phenanthrene compound as can be seen in Figure 4.23. Therefore, it seems to be that phenanthrene is present in the water sample. Then, the identified compound in the water sample which is phenanthrene is quantified by the internal standard method and the result of concentration of phenanthrene is 65 ppb.

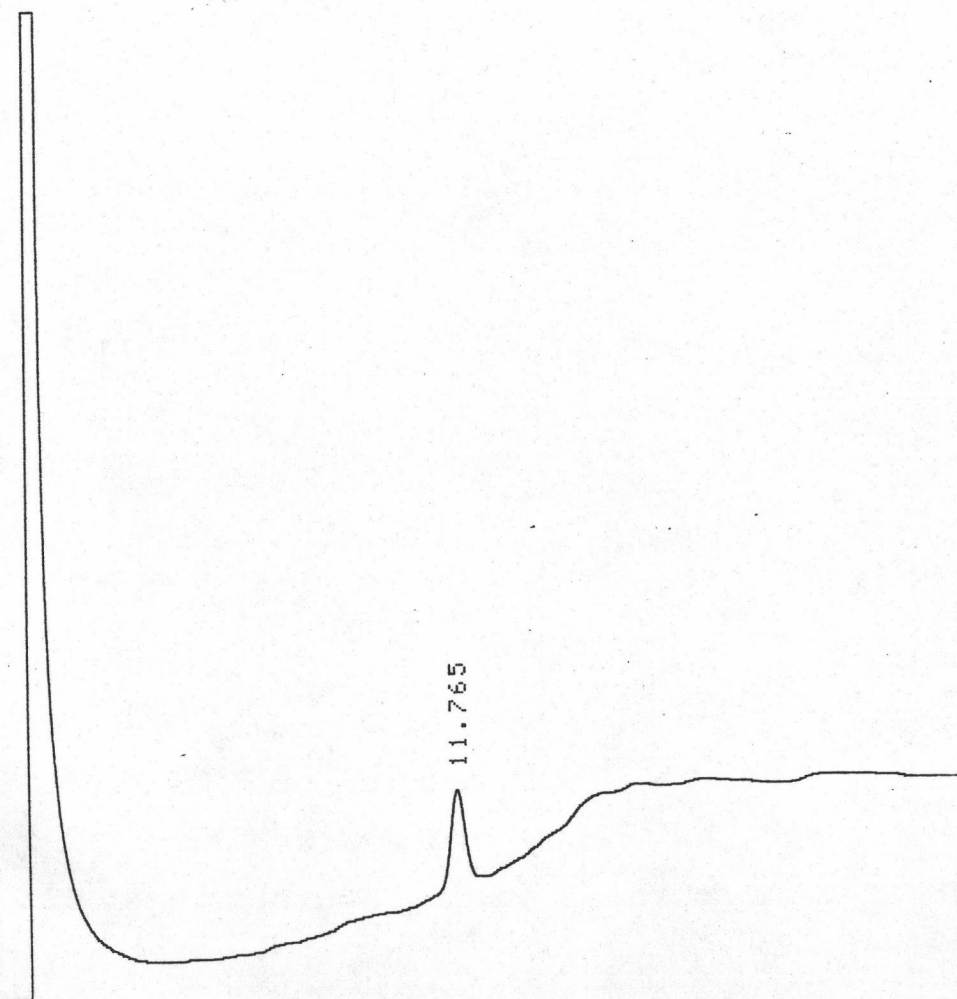


Figure 4.20 Gas chromatogram of a real sample¹

Conditions: column, 1 min hold at 185°C then programmed at a rate 4 °C/min to 240 °C and hold until the last peak eluted; injector and FID, 350 °C; N₂ carrier gas, 30 mL/min; sample size, 1 µL; detector range, $\times 10^1$; attenuation, 5; chart speed, 5 mm/min

¹collected from Sam Lae Station

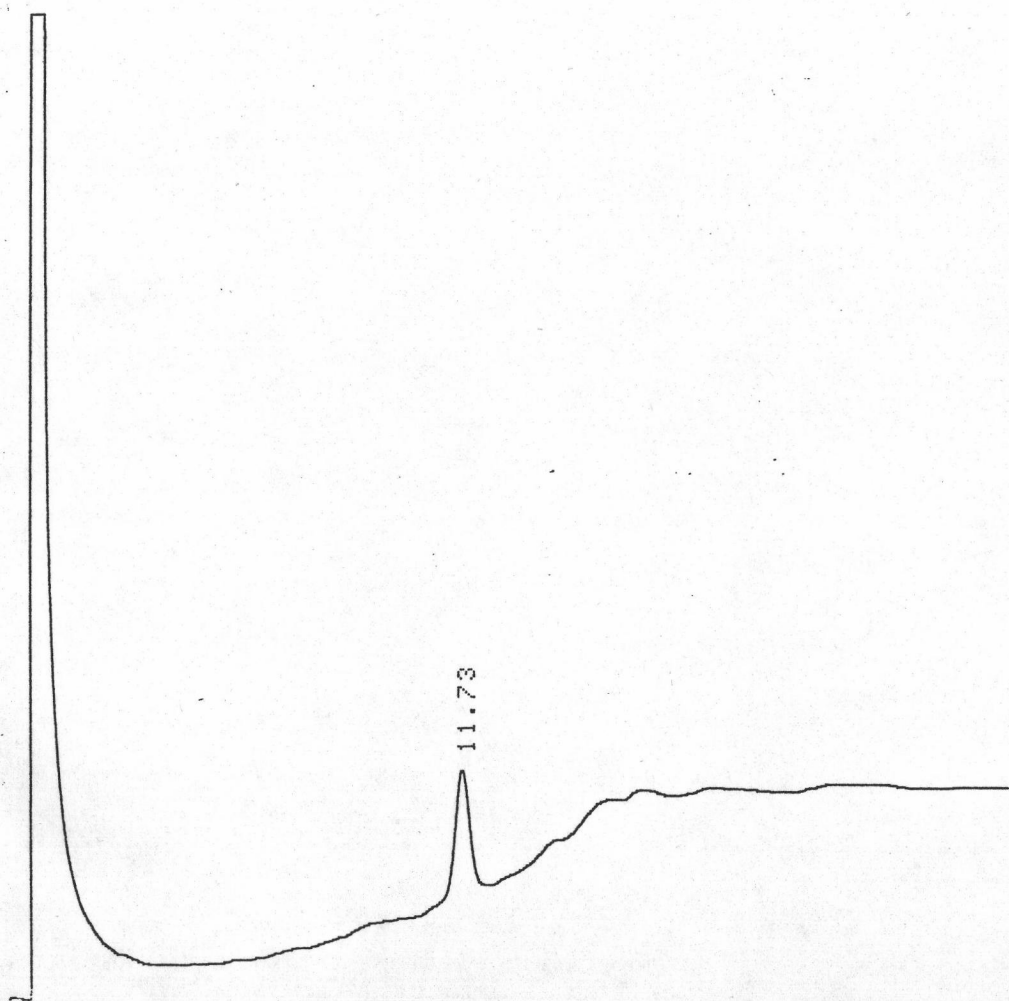


Figure 4.21 Gas chromatogram of a real sample²

Conditions: column, 1 min hold at 185°C then programmed at a rate 4 °C/min to 240 °C and hold until the last peak eluted; injector and FID, 350 °C; N₂ carrier gas, 30 mL/min; sample size, 1 uL; detector range, x10¹; attenuation, 5; chart speed, 5 mm/min

²collected from Bangkok Noi Station

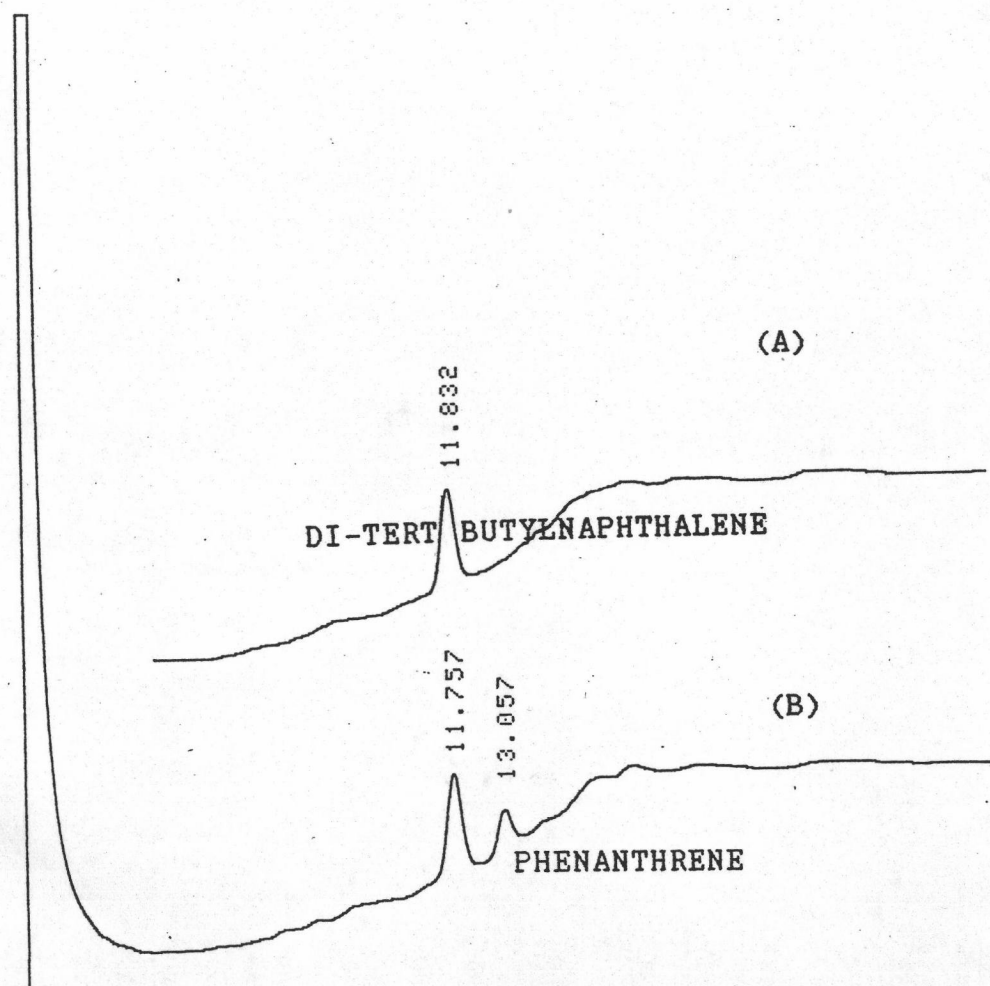


Figure 4.22 Gas chromatograms of blank solution (A) and a real sample³(B) in CS₂

Conditions: column, 1 min hold at 185°C then programmed at a rate 4 °C/min to 240 °C until the last peak eluted; injector and FID, 350 °C; N₂ carrier gas, 30 mL/min; sample size, 1 uL; detector range, $\times 10^1$; attenuation, 5; chart speed, 5 mm/min

³collected from Samsen Station

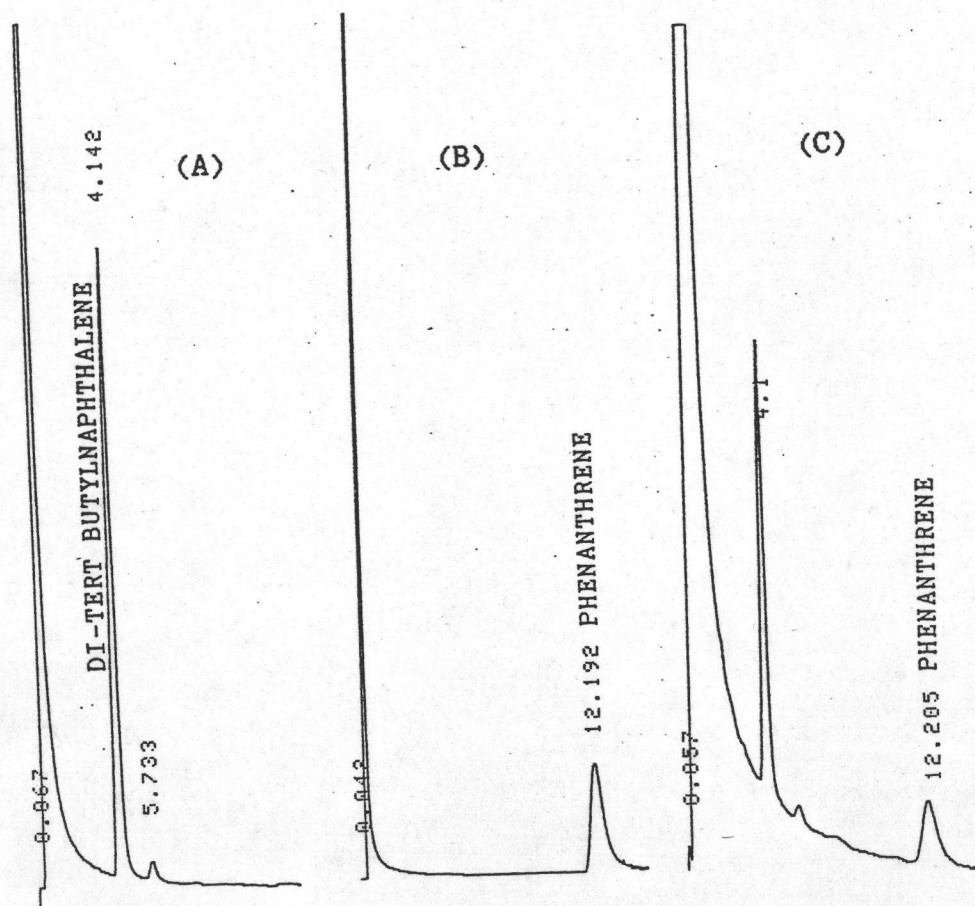


Figure 4.23 Gas chromatograms of di-tert butylnaphthalene (A), phenanthrene (B) and a real sample³ (C)

Conditions: column, 10% FFAP, 200 °C; injector and FID, 350 °C; N₂ carrier gas, 30 mL/min; sample size, 1 uL; detector range, x10⁰; attenuation, 5; chart speed, 3 mm/min

³collected from Samsen Station