

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The Study of Gas Chromatographic Separation of Phthalate Esters on Two GC Columns

From the results of gas chromatographic separation of phthalate esters on two GC columns in Figures 4.1-4.2 show that HP-1(Crosslinked Methyl Silicone Gum) capillary column is better separation than HP-17 (Crosslinked 50% Phenyl Methyl Silicone) capillary column. Therefore, HP-1(Crosslinked Methyl Silicone Gum) capillary column is considered to be chosen to analyze some phthalate esters, i.e, DMP, DEP, DBP, BBP, DEHP and DOP because it can give better separation of phthalate esters and less analysis time.

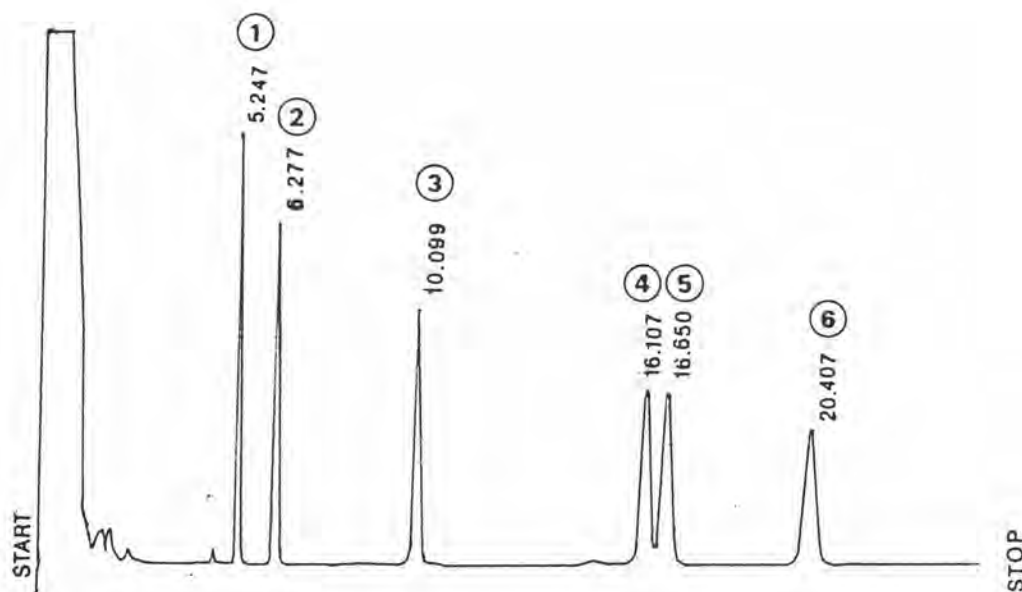


Figure 4.1 The gas chromatogram of some phthalate esters in hexane on HP-17 (Crosslinked 50% Phenyl Methyl Silicone) capillary column. The GC conditions were described in Table 3.1

- (1) Dimethylphthalate (DMP)
- (2) Diethylphthalate (DEP)
- (3) Di-n-butylphthalate (DBP)
- (4) Butylbenzylphthalate (BBP)
- (5) Di(2-ethylhexyl)phthalate (DEHP)
- (6) Di-n-octylphthalate (DOP)

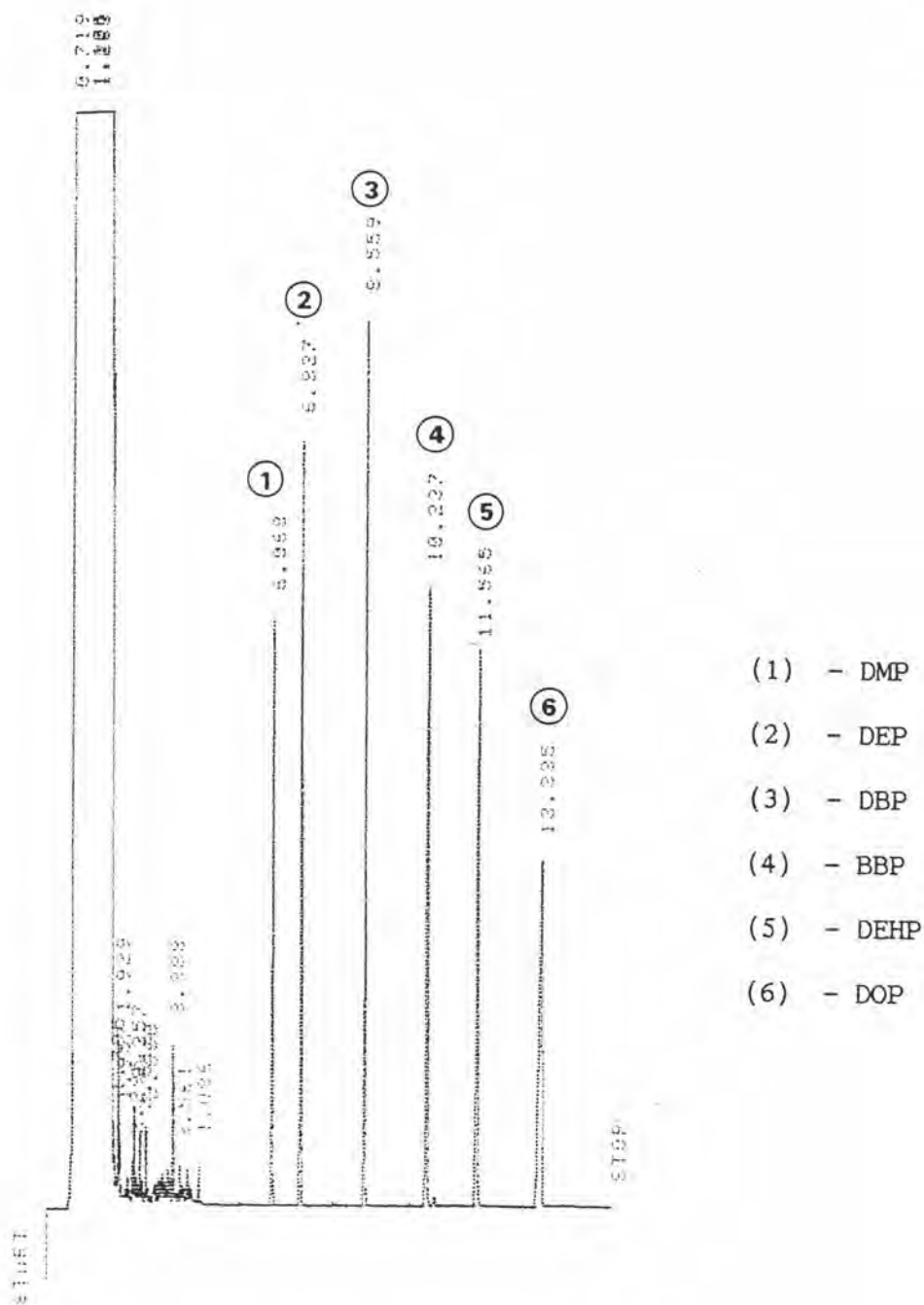


Figure 4.2 The gas chromatogram of some phthalate esters in hexane on HP-1 (Crosslinked Methyl Silicone Gum) capillary column. The GC conditions were described in Table 3.2.

4.2 The Study of Various Parameters on Sensitivity of GC

Various parameters, i.e., purge time, split ratio, and make-up gas flow rate were studied and DEHP was used as a model compound.

4.2.1 The Study of Purge Time

The purge time is the time between the start of sample injection and the time at which the sample/solvent residual vapors are purged out of the injection (103).

The result of the study of effect of purge time on the sensitivity of GC according to experimental section 3.5.1 are presented in Table 4.1. The graph plotted the peak area of DEHP against purge time are shown in Figure 4.3. It is found that the optimum purge time obtained from the study is 1.0 minute. Therefore, the purge time of 1.0 minute is chosen as the optimum purge time for the studied phthalate ester compounds.

Table 4.1 The result of the effect of purge time on the peak area of DEHP

Purge time (min)	Peak area	%RSD
0.2	380674	±2.85
0.4	402562	±1.19
0.6	421354	±0.44
0.8	472726	±4.75
1.0	477067	±0.95
2.0	476332	±0.13
3.0	478119	±2.23
4.0	470019	±0.93

Triplicate analyzes

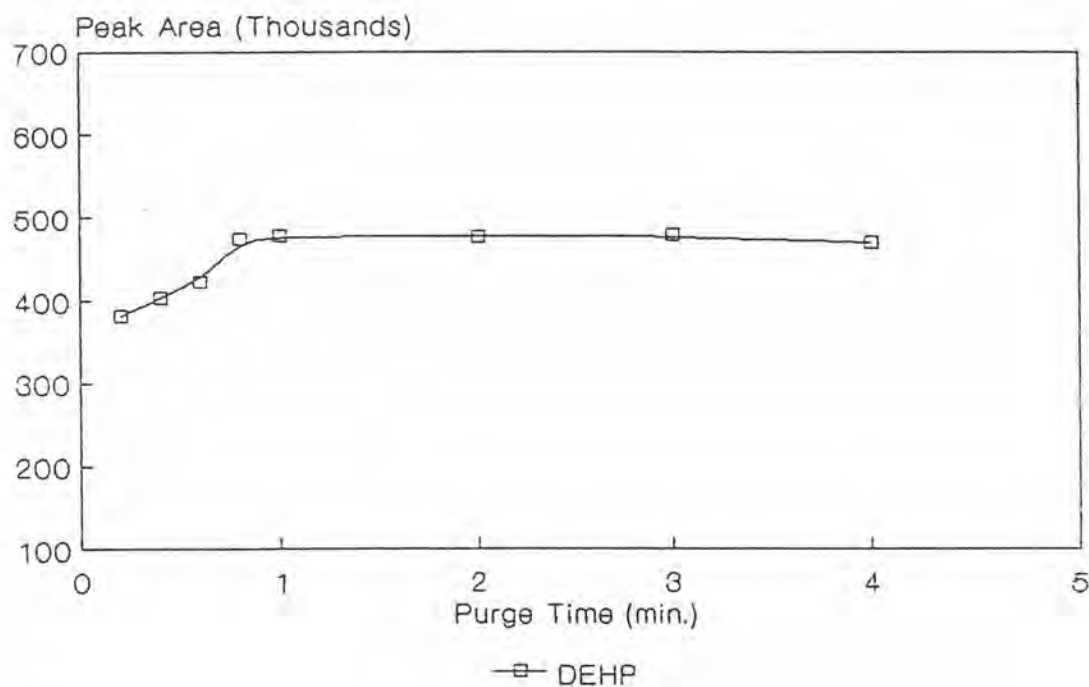


Figure 4.3 The effect of purge time on the peak area of DEHP

4.2.2 The Study of Split Ratio

A capillary inlet splitter splits the sample into two unequal portions, the smaller of which goes onto the column. This reduces the amount of sample going onto the column and prevents column overloading. the split ratio is calculated :

$$\text{Split ratio} = \frac{\text{inlet flow}}{\text{column flow}} \quad (4.3)$$

Split ratios typically range from 10 : 1 to 500 : 1 depending on the column characteristics and the analysis problem (83).

The result of the study of effect of split ratio on the sensitivity of GC according the experimental section 3.5.2 are listed in Table 4.2. The graph plotted the peak area of DEHP against split ratio are shown in Figure 4.4. It can be seen that the peak area of DEHP increases when the split ratio decreases. The increase in the value of peak area will continue until the split ratio reaches 25:1 and it will remain constant. Therefore, the split ratio of 25:1 is chosen as a suitable ratio for the studied phthalate ester compounds.

Table 4.2 The result of the effect of split ratio on the peak area of DEHP

Split ratio	Peak area	%RSD
16.4 : 1	442401	±1.96
24.7 : 1	446561	±1.03
30.6 : 1	440797	±1.83
40.5 : 1	438657	±1.06
45.3 : 1	425728	±3.20
59.6 : 1	409561	±3.58
77.3 : 1	361740	±2.63

Triplicate analyzes

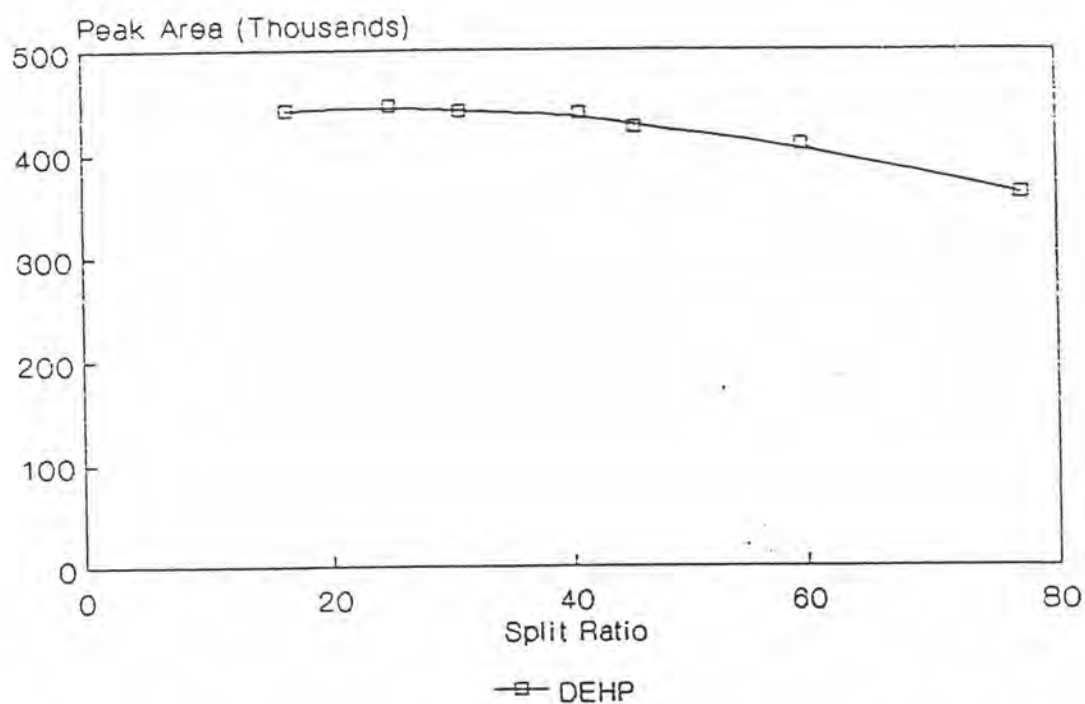


Figure 4.4 The effect of split ratio on the peak area of DEHP

4.2.3 The Study of Make-up Gas (N₂) Flow Rate

By using a make-up gas, the combined (make-up and carrier) flow permits the detector sensitivity to be optimized. A FID gives the greatest response when nitrogen is used as the make-up gas (83).

The result of the study of effect of make-up gas flow rate on the sensitivity of GC according to experimental section 3.5.3 are presented in Table 4.3. The graph plotted the peak area of DEHP against make-up gas flow rate are depicted in Figure 4.5. The result shows that the peak area of DEHP increases linearly with make-up gas flow rate. The maximum sensitivity (peak area) occurs when the make-up gas flow rate is around 60.0. Hence, the make-up gas flow rate of 60.0 mL/min is selected as the optimum flow for the study phthalate ester compounds.

Table 4.3 The results of the effect of make-up gas flow rate on the peak area of DEHP

Make-up gas flow rate (ml/min)	Peak area	% RSD
0.00	254745	±2.78
20.39	387407	±1.84
28.49	458433	±0.53
39.29	516373	±2.64
49.21	580471	±3.06
54.51	599921	±3.65
59.79	614541	±0.87
66.22	600011	±1.67
73.31	579324	±1.44

Triplicate analyzes

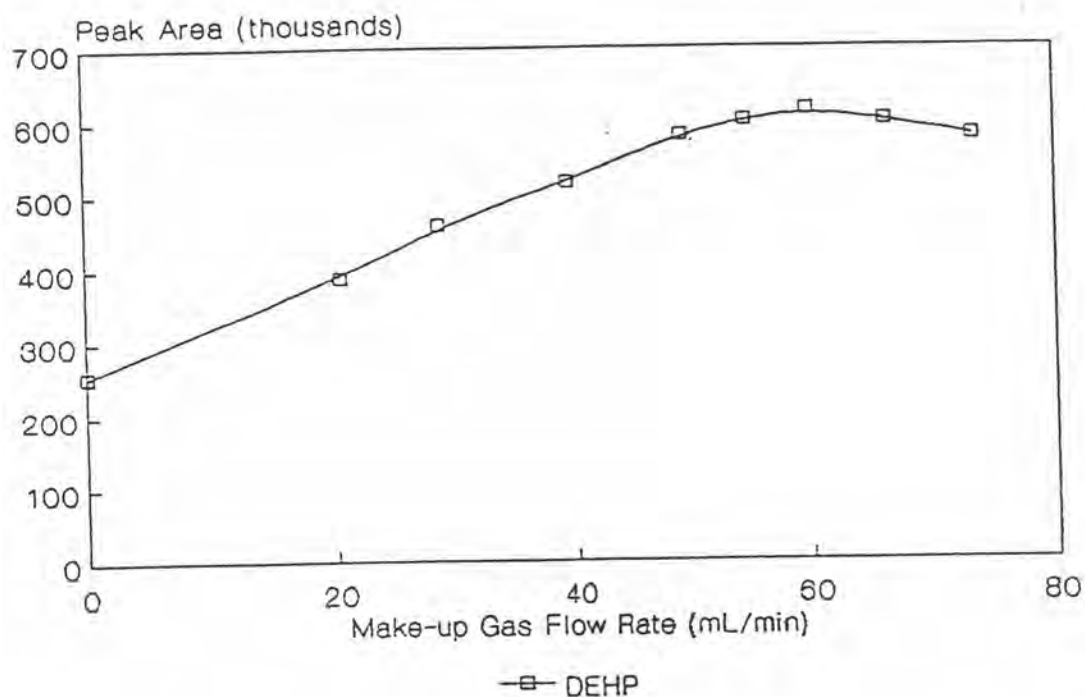


Figure 4.5 The effect of make-up gas flow rate on the peak area of DEHP

The suitable GC conditions for the study of phthalate ester compounds can be performed by using the selected condition from the previous studies and are shown in Table 4.4.

Table 4.4 The suitable GC conditions for the study of the phthalate ester compounds as single and mixture component solution.

GC Parameter	GC Conditions
Analytical Column	12 m x 0.2 mm ID. x 0.33 μ m film thickness, HP-1 (Methyl Silicone Gum) capillary column
Splitless Time	1 min
Split Ratio	25 : 1
Flow Rate of Carrier Gas (He)	1.12 mL/min
H ₂	45.0 mL/min
Air	320.0 mL/min
N ₂	60.0 mL/min
Detector	FID
Detector Temperature	300°C
Inlet Temperature	280°C
Temperature Program	: 36°C (1 min) to 260°C (5 min) at 25°C/min for methylene chloride solvent
	: 60°C (1 min) to 260°C (5 min) at 25°C/min for hexane and ethyl acetate solvent
	: 90°C (1 min) to 260°C (5 min) at 25°C/min for toluene solvent

4.3 The Study of Various Effects on the Percent Recovery of Solid Phase Extraction Technique

4.3.1 The Study of pH Effect in Single Component Solution

The results of pH effect of extracted solution on the percent recovery of each phthalate ester i.e., DMP, DEP, DBP, BBP, DEHP and DOP in single component solution at two concentration levels are presented in Tables 4.5-4.8. The graphs plotted the percent recovery against pH of the extracted solution are shown in Figures 4.6-4.19. It is found that the phthalate esters, i.e., DMP, DEP, DBP and BBP are extracted equally well at pH 2.0-8.0 and the phthalate esters i.e., DEHP and DOP are extracted into organic solvent very well at pH 2.0-3.0. This can be suggested that at pH 2.0-3.0 non-polar interactions can be very strong with non polar isolates of high molecular weight compounds, i.e., DEHP and DOP. The increasing polarity of these compounds can be performed by extracting them in acid solution (pH 2.0-3.0) and they can be removed from the sorbent more easily.

Table 4.5 The results of the effect of pH extracted solution on the percent recovery of DMP, DEP, and DBP in single component solution with concentration of aqueous standard solution in lower level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	2.09	0.295	13.78	93.42	±1.11
	3.09	0.295	13.49	91.51	±3.39
	4.02	0.295	13.66	92.60	±3.07
	5.05	0.295	13.58	92.06	±2.19
	6.08	0.295	13.38	90.68	±3.53
	7.05	0.295	13.86	93.96	±1.07
	8.02	0.295	13.80	93.59	±2.39
DEP	2.03	0.265	12.38	93.57	±1.69
	3.02	0.265	12.34	93.28	±4.89
	4.04	0.265	12.15	91.84	±1.05
	5.04	0.265	12.29	92.87	±2.02
	5.65	0.265	12.31	93.06	±4.97
	7.05	0.265	12.18	92.08	±1.82
	8.04	0.265	12.07	91.26	±5.77
DBP	2.02	0.196	9.01	91.98	±1.89
	3.03	0.196	8.84	90.25	±1.78
	4.06	0.196	8.87	90.53	±3.03
	5.09	0.196	8.99	91.77	±5.37
	5.56	0.196	8.88	90.64	±4.17
	7.03	0.196	8.62	87.95	±2.34
	8.01	0.196	8.72	88.93	±2.99

Triplicate analyzes

Table 4.6 The results of the effect of pH extracted solution on the percent recovery of DMP, DEP, and DBP in single component solution with concentration of aqueous standard solution in higher level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	2.09	1.48	68.83	93.33	±0.92
	3.09	1.48	67.64	91.72	±1.67
	4.07	1.48	68.21	92.49	±1.79
	5.09	1.48	68.68	93.13	±1.90
	5.91	1.48	67.79	91.92	±1.38
	7.02	1.48	69.11	93.71	±0.91
	8.02	1.48	68.51	92.89	±1.72
DEP	2.07	1.32	61.70	93.28	±3.32
	3.06	1.32	62.01	93.74	±0.25
	4.07	1.32	59.54	90.00	±2.55
	5.08	1.32	60.05	90.78	±2.20
	5.91	1.32	60.22	91.03	±0.80
	7.14	1.32	60.43	91.35	±2.33
	8.15	1.32	60.36	91.25	±2.31
DBP	2.05	0.980	44.88	91.59	±2.97
	3.05	0.980	43.85	89.48	±4.51
	4.04	0.980	43.65	89.09	±3.76
	5.05	0.980	44.63	91.08	±1.97
	5.79	0.980	44.01	89.81	±4.37
	7.05	0.980	43.99	89.77	±1.34
	8.08	0.980	44.46	90.74	±1.06

 Triplicate analyzes

Table 4.7 The results of the effect of pH extracted solution on the percent recovery of BBP, DEHP, and DOP in single component solution with concentration of aqueous standard solution in lower level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
BBP	2.04	0.204	9.22	90.52	±1.82
	3.02	0.204	9.17	90.00	±2.72
	4.04	0.204	9.20	90.28	±3.48
	5.02	0.204	9.21	90.41	±2.48
	5.69	0.204	9.18	90.06	±1.83
	7.00	0.204	9.18	90.05	±3.77
	8.00	0.204	9.11	89.41	±1.08
	DEHP	2.03	0.203	8.84	87.05
3.05		0.203	8.81	86.75	±1.10
4.02		0.203	4.61	45.37	±6.17
5.03		0.203	1.57	15.48	±9.62
5.96		0.203	1.68	16.52	±4.95
7.05		0.203	1.26	12.36	±7.23
8.03		0.203	1.32	13.04	±8.31
DOP		2.02	0.281	12.31	87.59
	3.04	0.281	12.25	87.19	±1.89
	4.03	0.281	4.85	34.55	±3.82
	5.03	0.281	1.89	13.45	±4.95
	5.84	0.281	1.44	10.28	±5.35
	7.02	0.281	1.68	11.94	±7.70
	8.02	0.281	1.69	12.05	±8.42

Triplicate analyzes

Table 4.8 The results of the effect of pH extracted solution on the percent recovery of BBP, DEHP, and DOP in single component solution with concentration of aqueous standard solution in higher level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
BBP	2.03	1.02	46.35	90.97	±1.65
	3.04	1.02	45.56	89.42	±2.27
	4.03	1.02	46.34	90.95	±1.07
	5.01	1.02	45.31	88.93	±1.86
	5.65	1.02	46.29	90.85	±2.75
	7.01	1.02	45.83	89.96	±4.47
	8.01	1.02	44.37	87.08	±4.57
	DEHP	2.04	1.02	43.52	85.66
3.05		1.02	43.43	85.49	±1.73
4.02		1.02	22.45	44.19	±3.34
5.02		1.02	8.05	15.85	±10.41
5.91		1.02	8.03	15.80	±3.65
7.01		1.02	5.88	11.58	±7.57
8.01		1.02	6.51	12.82	±5.27
DOP		2.03	1.41	62.09	88.38
	3.05	1.41	61.27	87.21	±4.76
	4.02	1.41	25.16	35.81	±1.25
	5.03	1.41	8.93	12.71	±4.35
	6.05	1.41	8.24	11.73	±1.68
	7.06	1.41	8.58	12.22	±7.04
	8.04	1.41	8.61	12.25	±5.95

Triplicate analyzes

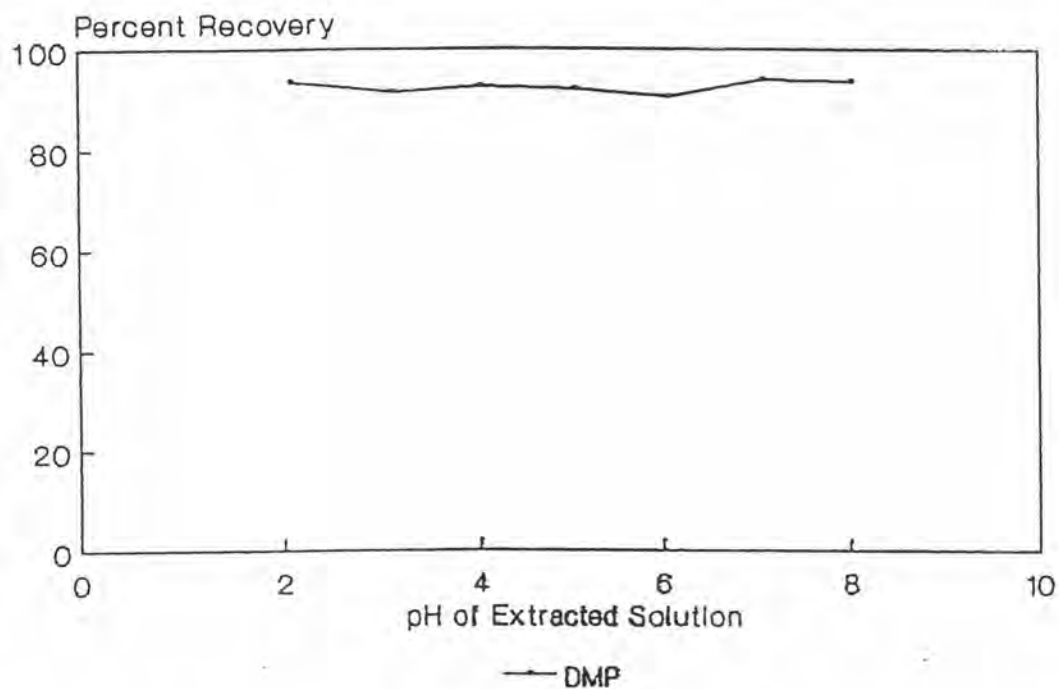


Figure 4.6 The effect of pH of extracted solution on the percent recovery of DMP in single component solution with concentration of aqueous standard solution in lower level of ppm

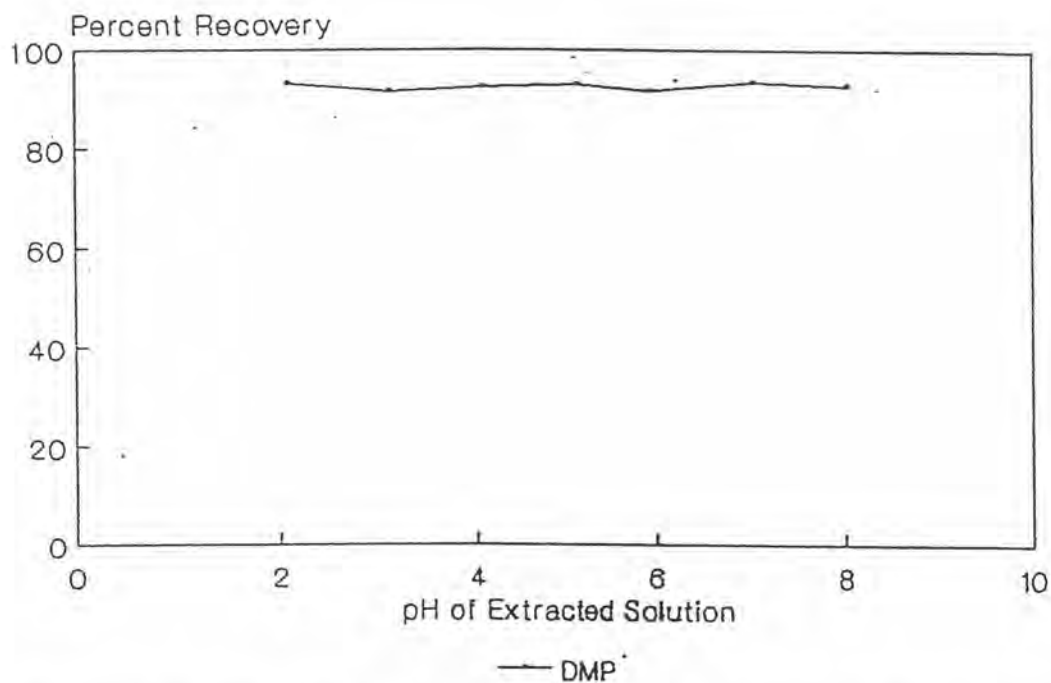


Figure 4.7 The effect of pH of extracted solution on the percent recovery of DMP in single component solution with concentration of aqueous standard solution in higher level of ppm

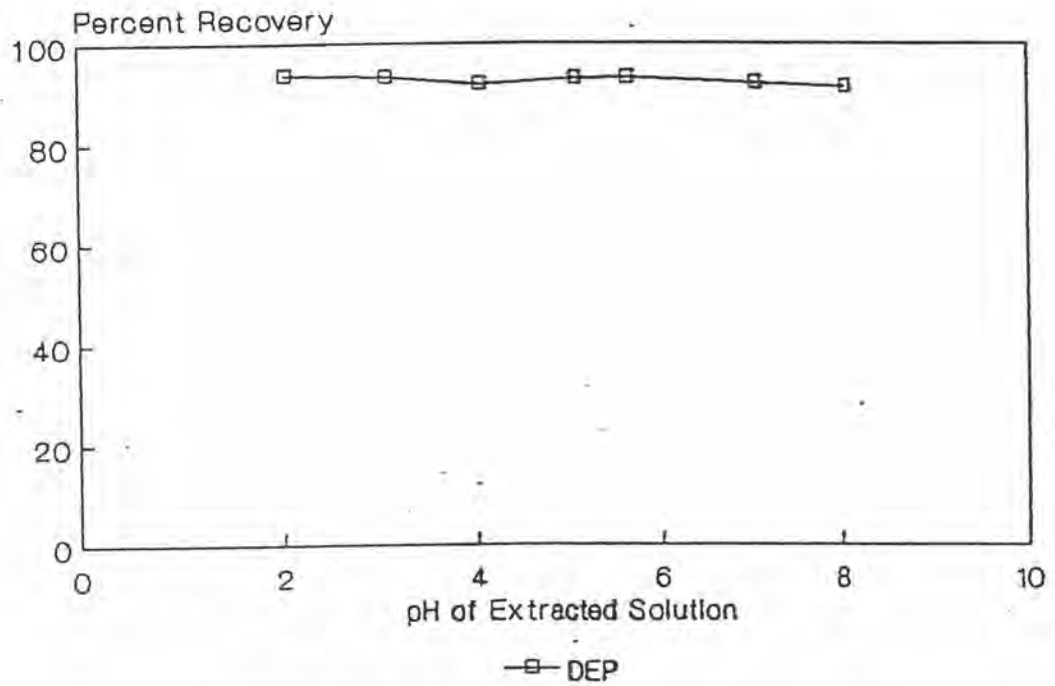


Figure 4.8 The effect of pH of extracted solution on the percent recovery of DEP in single component solution with concentration of aqueous standard solution in lower level of ppm

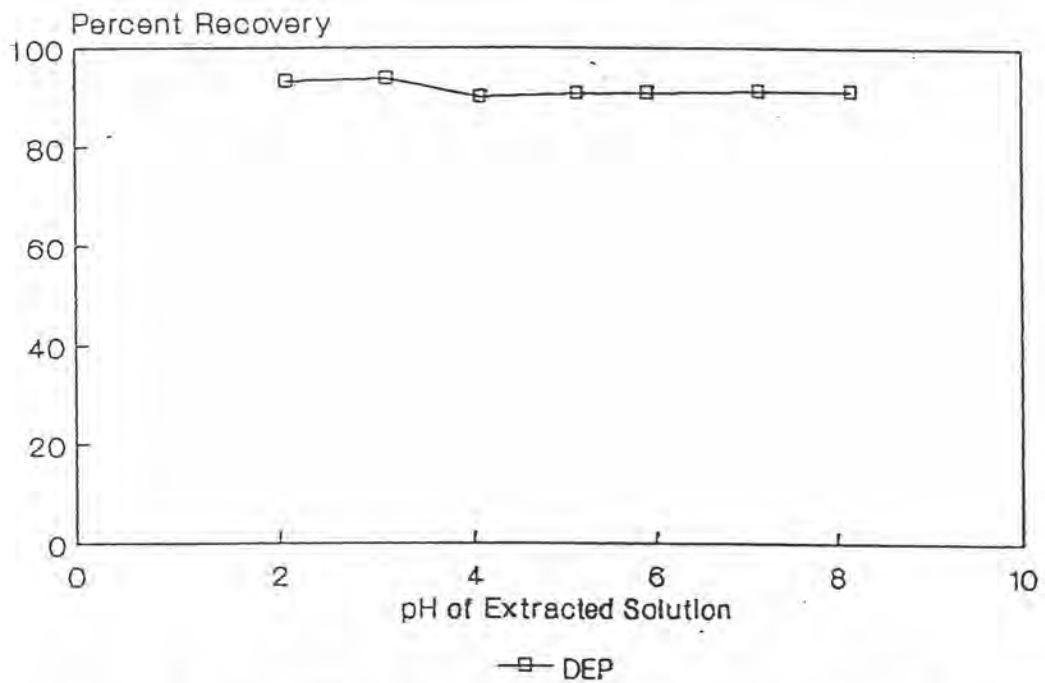


Figure 4.9 The effect of pH of extracted solution on the percent recovery of DEP in single component solution with concentration of aqueous standard solution in higher level of ppm

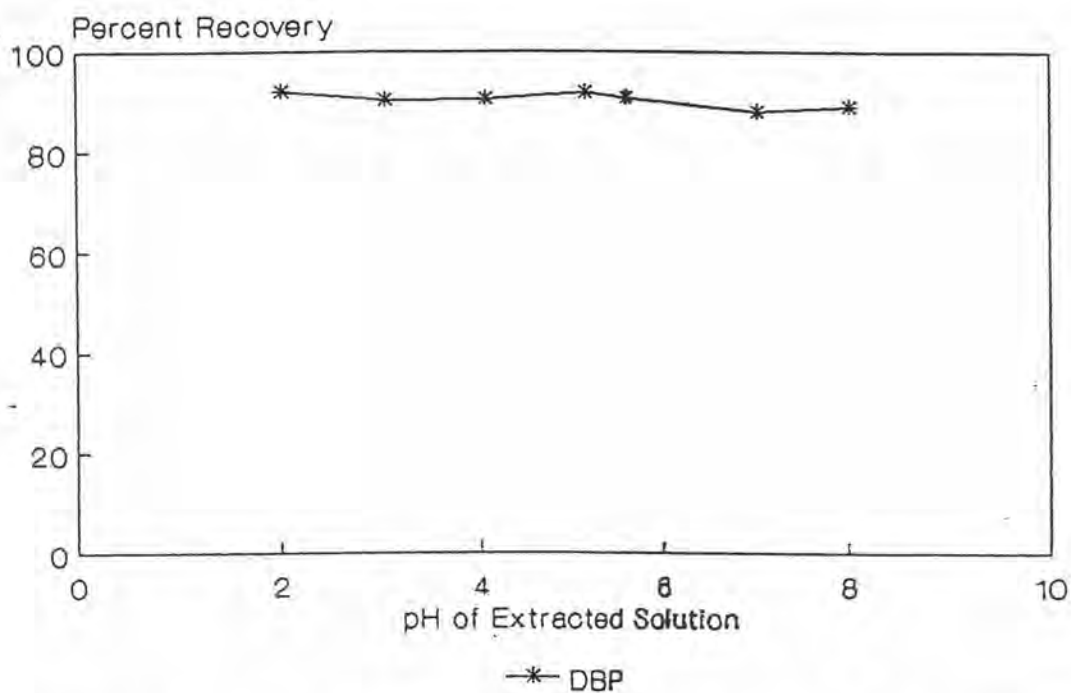


Figure 4.10 The effect of pH of extracted solution on the percent recovery of DBP in single component solution with concentration of aqueous standard solution in lower level of ppm

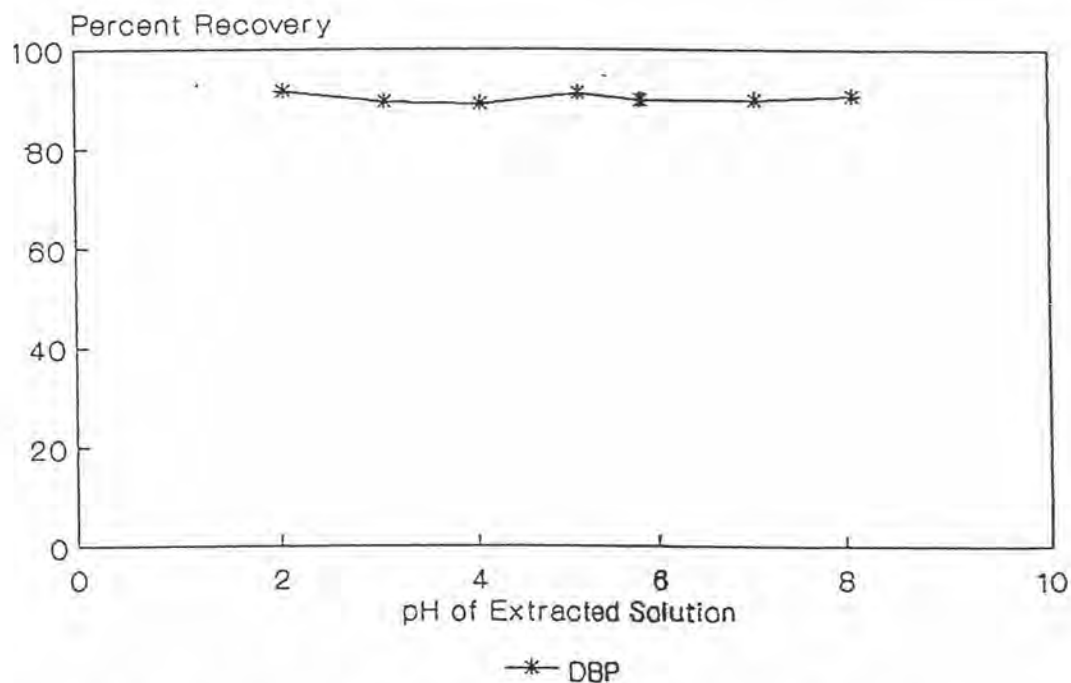


Figure 4.11 The effect of pH of extracted solution on the percent recovery of DBP in single component solution with concentration of aqueous standard solution in higher level of ppm

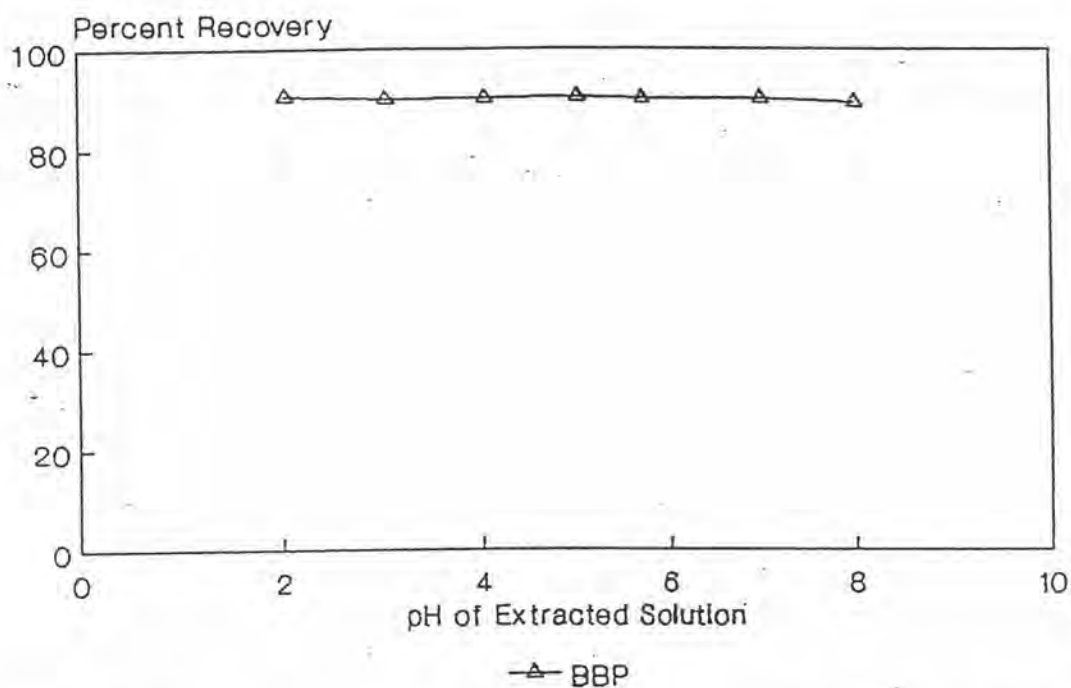


Figure 4.12 The effect of pH of extracted solution on the percent recovery of BBP in single component solution with concentration of aqueous standard solution in lower level of ppm

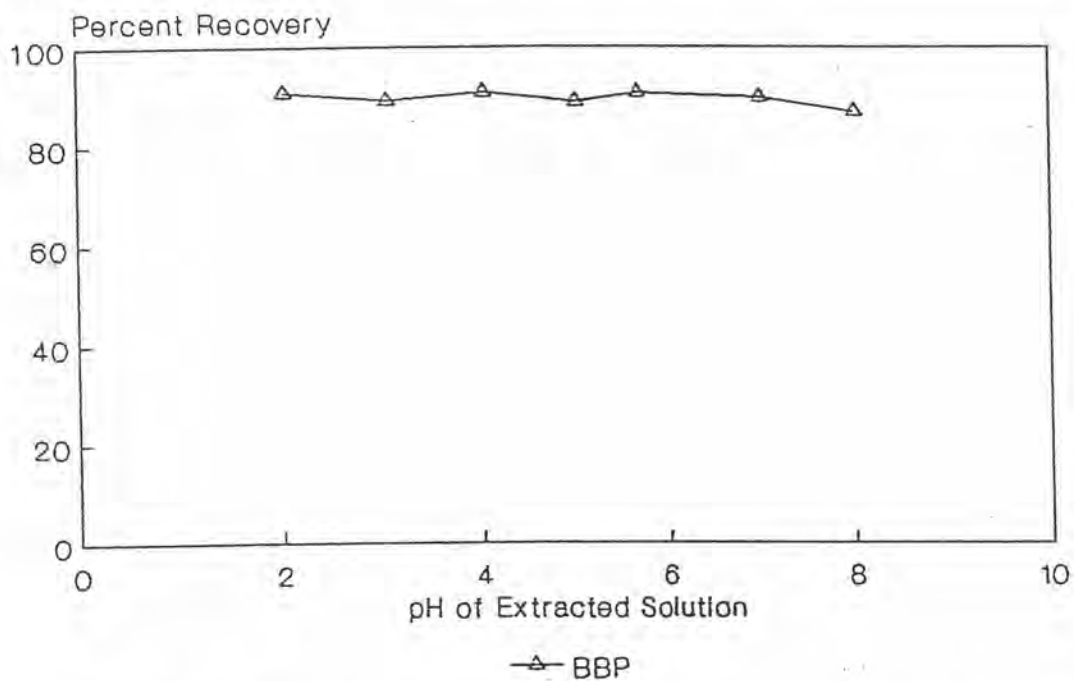


Figure 4.13 The effect of pH of extracted solution on the percent recovery of BBP in single component solution with concentration of aqueous standard solution in higher level of ppm

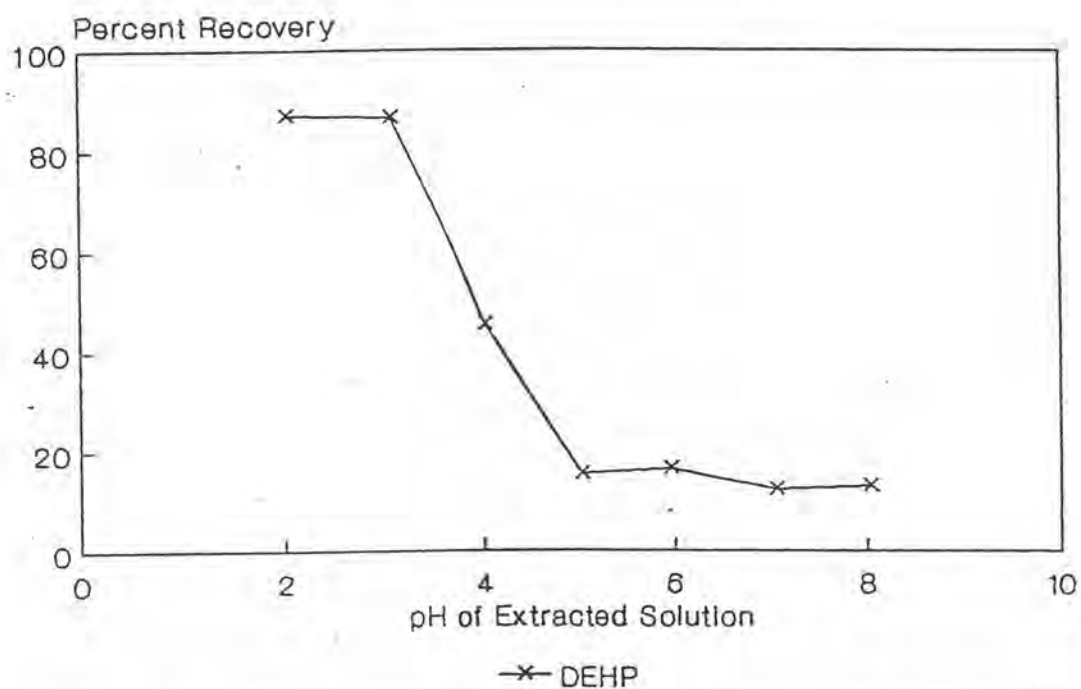


Figure 4.14 The effect of pH of extracted solution on the percent recovery of DEHP in single component solution with concentration of aqueous standard solution in lower level of ppm

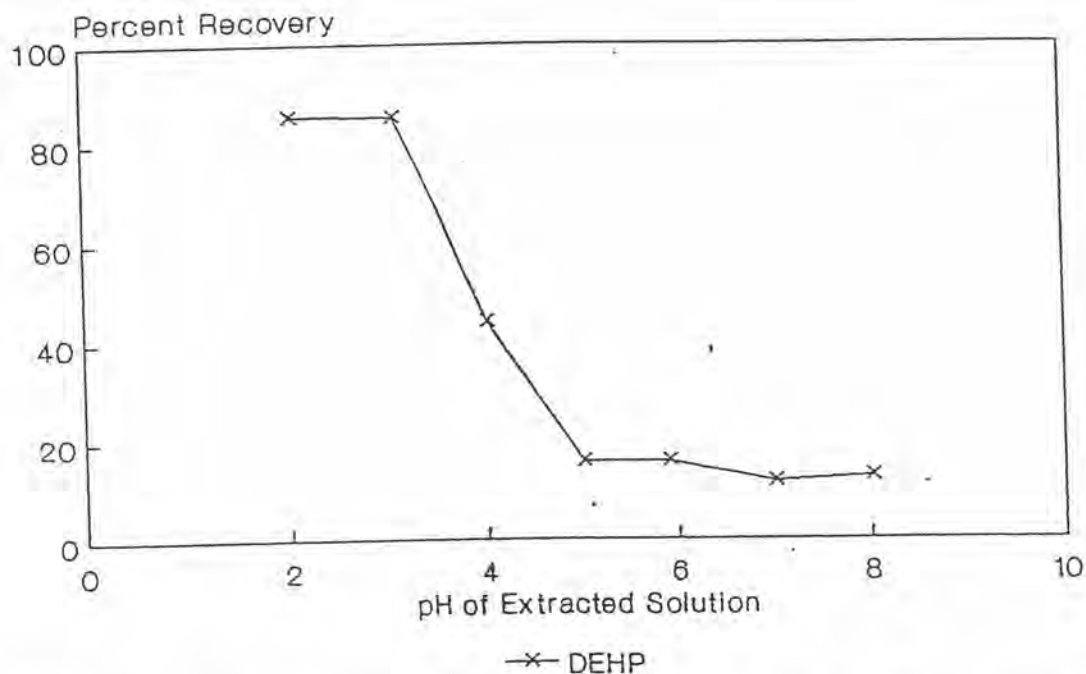


Figure 4.15 The effect of pH of extracted solution on the percent recovery of DEHP in single component solution with concentration of aqueous standard solution in higher level of ppm

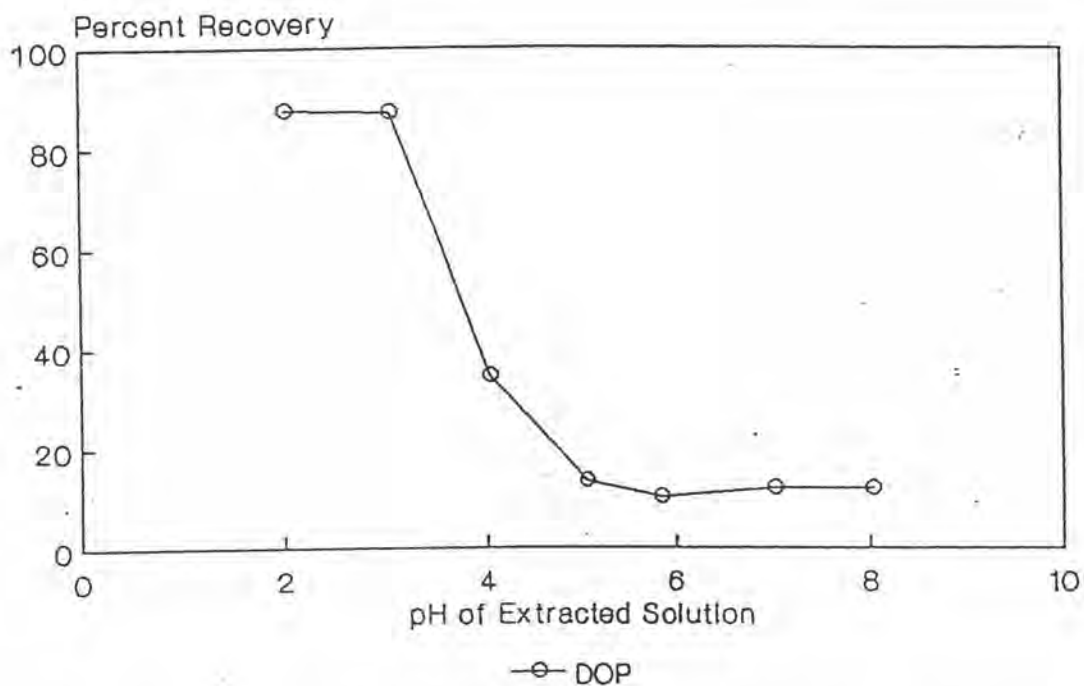


Figure 4.16 The effect of pH of extracted solution on the percent recovery of DOP in single component solution with concentration of aqueous standard solution in lower level of ppm

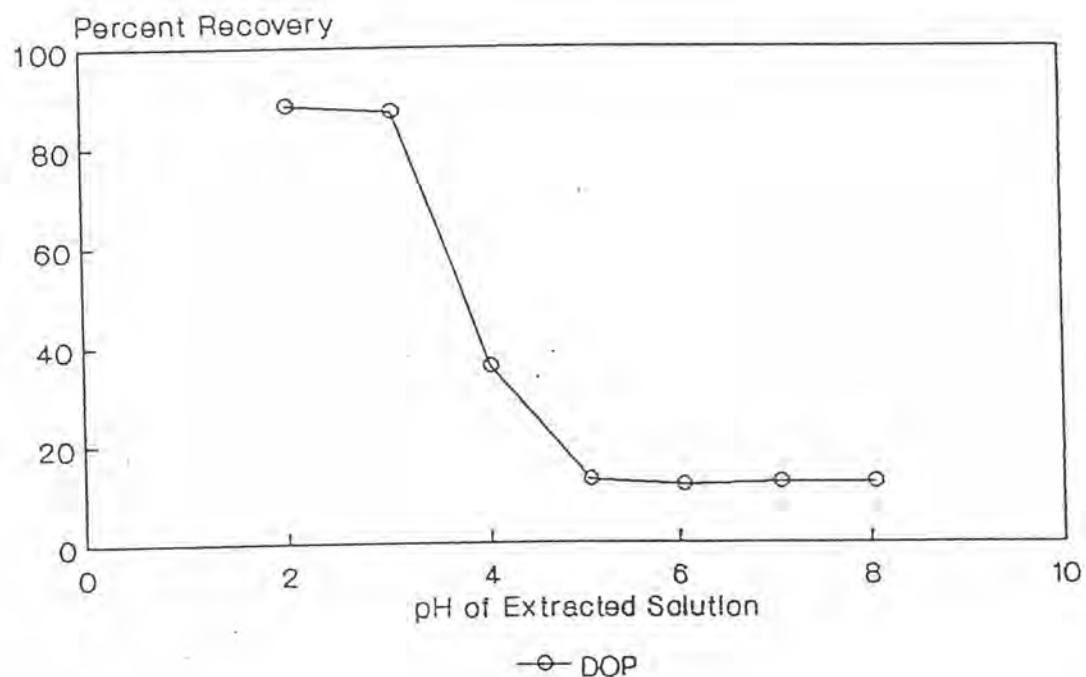


Figure 4.17 The effect of pH of extracted solution on the percent recovery of DOP in single component solution with concentration of aqueous standard solution in higher level of ppm

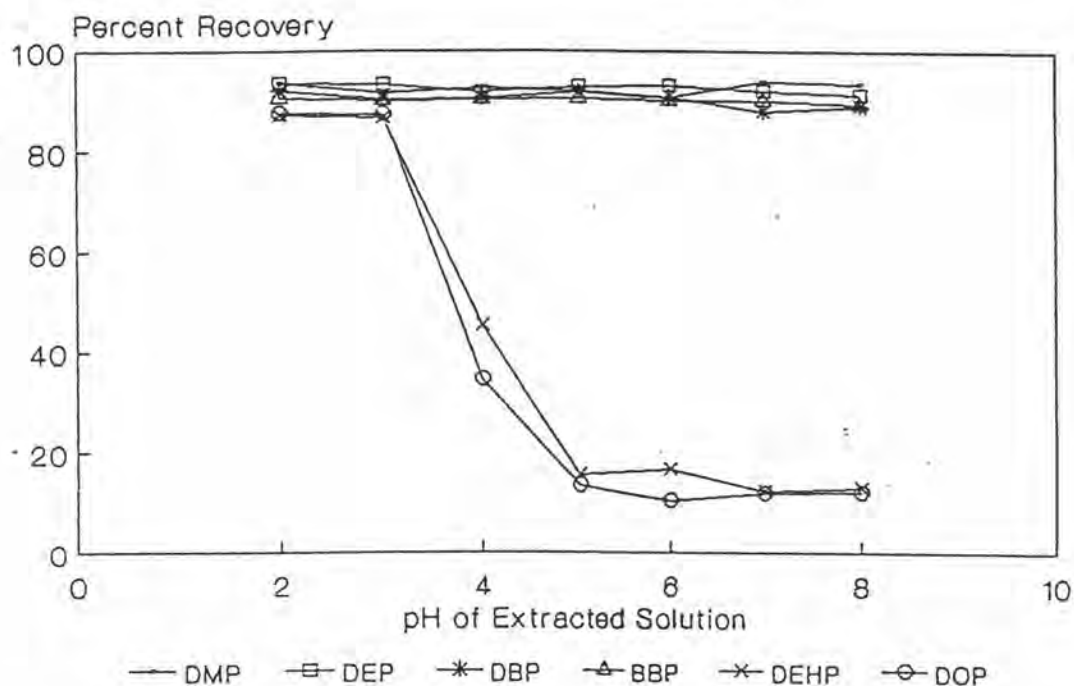


Figure 4.18 The effect of pH of extracted solution on the percent recovery of each phthalate ester in single component solution with concentration of aqueous standard solution in lower level of ppm

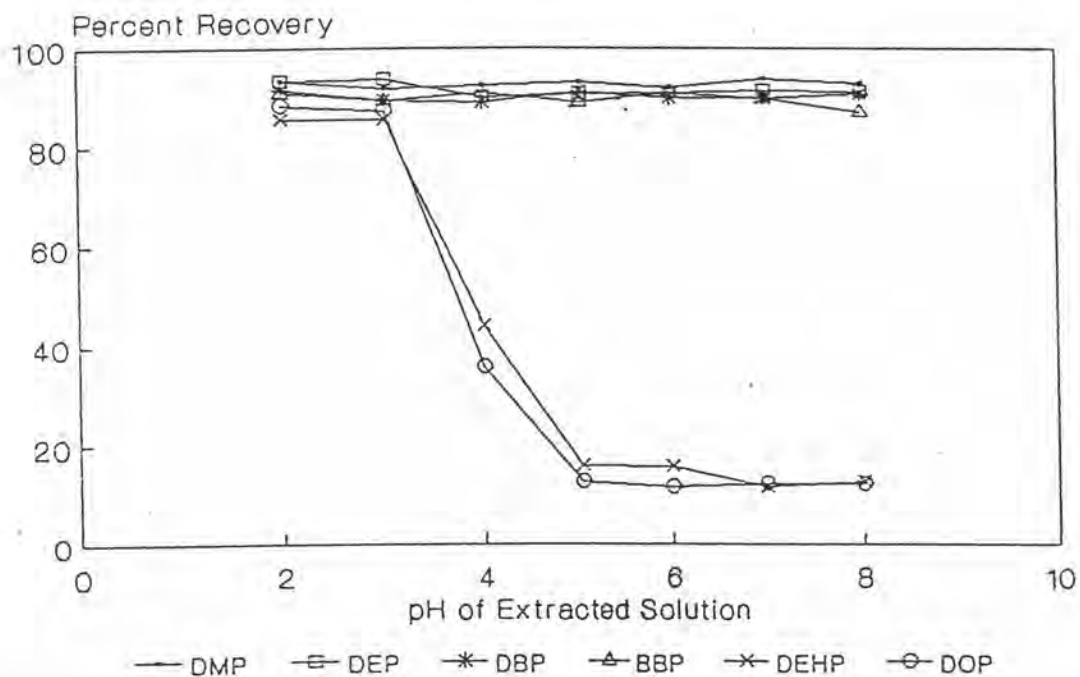


Figure 4.19 The effect of pH of extracted solution on the percent recovery of each phthalate ester in single component solution with concentration of aqueous standard solution in higher level of ppm

4.3.2 The Study of pH Effect in Mixture Solution

The results of pH effect on the percent recovery of each phthalate ester i.e., DMP, DEP, DBP, BBP, DEHP and DOP in mixture solution at two concentration levels are presented in Tables 4.9-4.12. The graphs plotted the percent recovery against pH of the extracted solution are shown in Figures 4.20-4.33. From these study of pH effect indicated that the results of the pH effect on the percent recovery in single component and mixture solutions are similar. The phthalate esters, i.e., DMP, DEP, DBP and BBP are extracted equally well at pH 2.0-8.0 and the phthalate esters i.e., DEHP and DOP are extracted very well at pH 2.0-3.0. Hence, the pH value of 2.0 is chosen as the suitable pH for the SPE study of phthalate esters.

Table 4.9 The results of the effect of pH extracted solution on the percent recovery of DMP, DEP, and DBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	2.02	0.280	13.48	95.17	±0.83
	3.04	0.280	13.37	94.39	±2.77
	4.01	0.280	13.49	95.31	±1.92
	5.02	0.280	13.41	94.68	±1.85
	5.72	0.280	13.32	94.09	±2.95
	7.02	0.280	13.34	94.18	±5.27
	8.01	0.280	13.31	94.00	±3.80
DEP	2.02	0.270	12.94	95.45	±1.34
	3.04	0.270	12.85	94.77	±2.31
	4.01	0.270	12.83	94.62	±1.17
	5.02	0.270	12.79	94.33	±4.79
	5.72	0.270	12.85	94.74	±4.31
	7.02	0.270	12.76	94.12	±1.76
	8.01	0.270	12.77	94.19	±3.90
DBP	2.02	0.190	8.90	91.59	±1.45
	3.04	0.190	8.91	91.63	±3.68
	4.01	0.190	8.85	91.01	±2.29
	5.02	0.190	8.86	91.17	±4.49
	5.72	0.190	8.88	91.35	±2.71
	7.02	0.190	8.87	91.29	±1.58
	8.01	0.190	8.89	91.46	±5.19

Triplicate analyzes

Table 4.10 The results of the effect of pH extracted solution on the percent recovery of DMP, DEP, and DBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	2.02	1.42	67.86	95.85	±2.26
	3.04	1.42	67.52	95.37	±3.19
	4.02	1.42	67.56	95.42	±3.85
	5.04	1.42	67.39	95.18	±1.89
	5.72	1.42	67.52	95.37	±2.99
	7.01	1.42	67.89	95.89	±3.03
	8.01	1.42	67.32	95.08	±2.93
	DEP	2.02	1.36	64.92	95.75
3.04		1.36	64.48	95.10	±1.19
4.02		1.36	64.59	95.27	±1.11
5.04		1.36	64.14	94.60	±2.55
5.72		1.36	63.89	94.23	±4.42
7.01		1.36	64.22	94.72	±3.37
8.01		1.36	63.90	94.25	±4.11
DBP		2.02	0.970	45.15	92.91
	3.04	0.970	44.75	92.08	±3.95
	4.02	0.970	45.02	92.64	±4.96
	5.04	0.970	43.87	90.27	±4.39
	5.72	0.970	44.67	91.92	±1.32
	7.01	0.970	45.04	92.67	±4.96
	8.01	0.970	44.58	91.72	±5.41

Triplicate analyzes

Table 4.11 The results of the effect of pH extracted solution on the percent recovery of BBP, DEHP, and DOP in mixture solution with concentration of aqueous standard solution in lower level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
BBP	2.02	0.210	9.57	92.35	±1.37
	3.04	0.210	9.49	91.66	±0.29
	4.01	0.210	9.48	91.51	±3.42
	5.02	0.210	9.41	90.81	±3.76
	5.72	0.210	9.47	91.37	±2.78
	7.02	0.210	9.39	90.71	±5.71
	8.01	0.210	9.42	90.90	±3.83
	DEHP	2.02	0.210	9.13	88.49
3.04		0.210	9.18	88.96	±0.78
4.01		0.210	3.52	34.12	±6.64
5.02		0.210	1.82	17.68	±8.69
5.72		0.210	1.65	16.01	±6.31
7.02		0.210	1.22	11.81	±9.52
8.01		0.210	1.40	13.56	±5.87
DOP		2.02	0.280	12.49	87.87
	3.04	0.280	12.38	87.04	±2.19
	4.01	0.280	5.05	35.48	±3.68
	5.02	0.280	2.31	16.27	±8.89
	5.72	0.280	2.11	14.83	±6.95
	7.02	0.280	1.66	11.67	±8.09
	8.01	0.280	1.81	12.76	±5.64

Triplicate analyzes

Table 4.12 The results of the effect of pH extracted solution on the percent recovery of BBP, DEHP, and DOP in mixture solution with concentration of aqueous standard solution in higher level of ppm

Compounds	pH	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
BBP	2.02	1.04	47.69	92.06	±1.03
	3.04	1.04	47.24	91.19	±2.84
	4.02	1.04	47.26	91.33	±5.32
	5.04	1.04	46.39	89.57	±1.24
	5.72	1.04	47.10	90.93	±4.46
	7.01	1.04	46.49	89.76	±6.51
	8.01	1.04	47.02	90.77	±4.90
DEHP	2.02	1.03	45.39	87.96	±0.45
	3.04	1.03	46.11	89.37	±2.30
	4.02	1.03	17.76	34.41	±4.96
	5.04	1.03	7.48	14.50	±4.87
	5.72	1.03	8.02	15.55	±5.37
	7.01	1.03	5.65	10.94	±8.98
	8.01	1.03	7.68	14.88	±5.06
DOP	2.02	1.42	62.23	87.52	±0.76
	3.04	1.42	63.73	89.64	±2.84
	4.02	1.42	23.73	33.37	±3.09
	5.04	1.42	9.58	13.48	±5.84
	5.72	1.42	10.24	14.40	±3.61
	7.01	1.42	7.93	11.15	±8.61
	8.01	1.42	10.41	14.64	±7.89

Triplicate analyzes

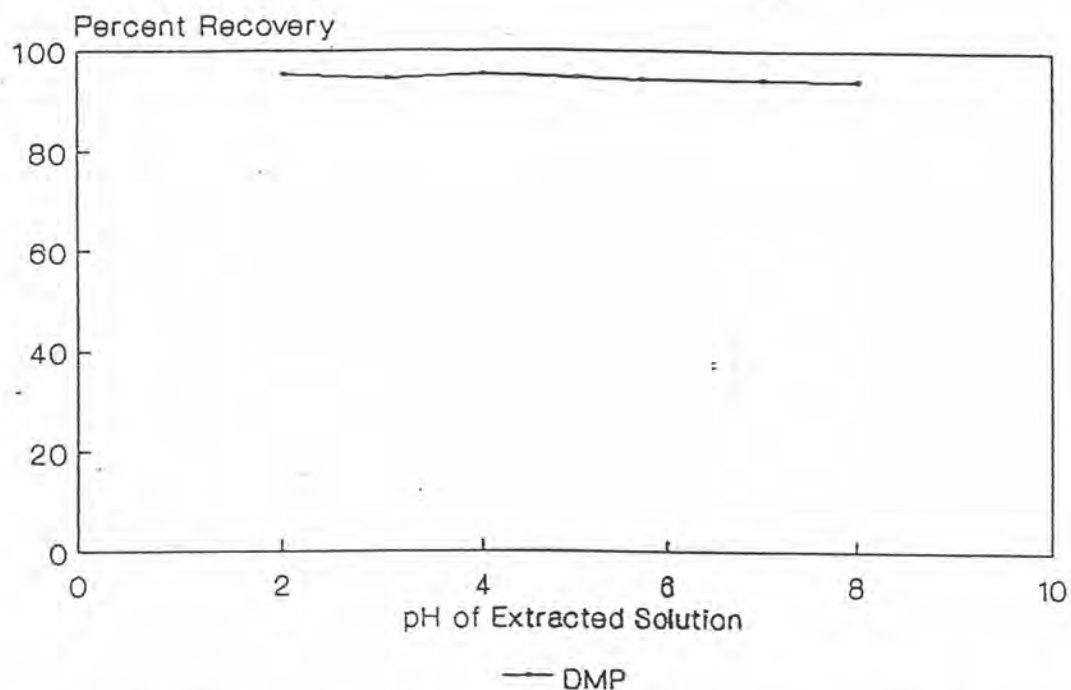


Figure 4.20 The effect of pH of extracted solution on the percent recovery of DMP in mixture solution with concentration of aqueous standard solution in lower level of ppm

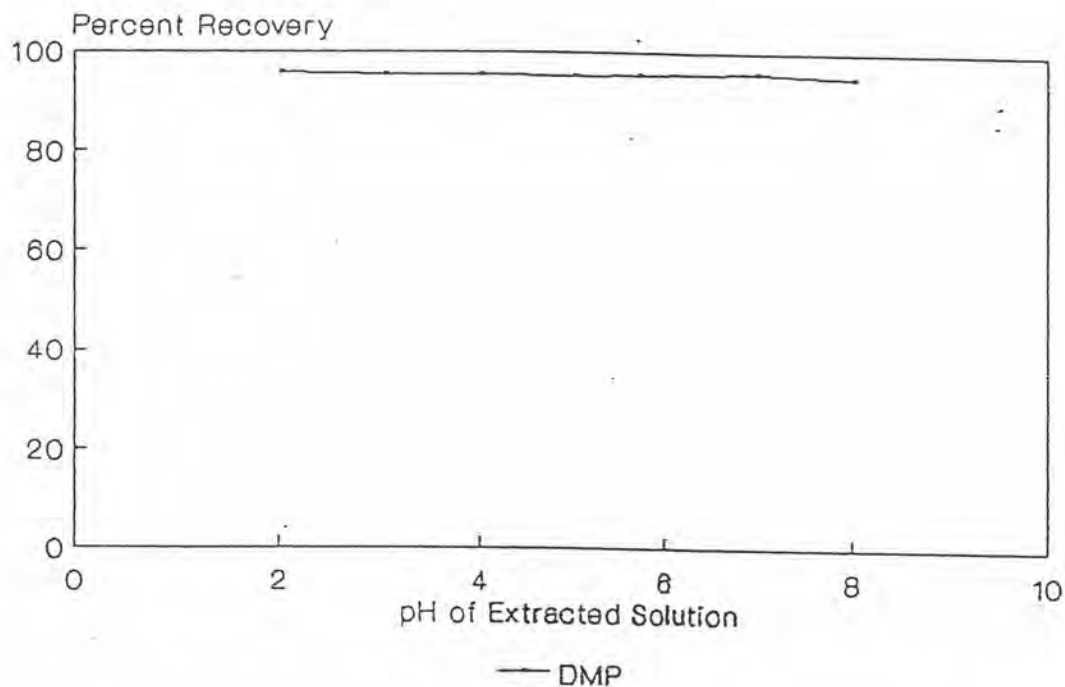


Figure 4.21 The effect of pH of extracted solution on the percent recovery of DMP in mixture solution with concentration of aqueous standard solution in higher level of ppm

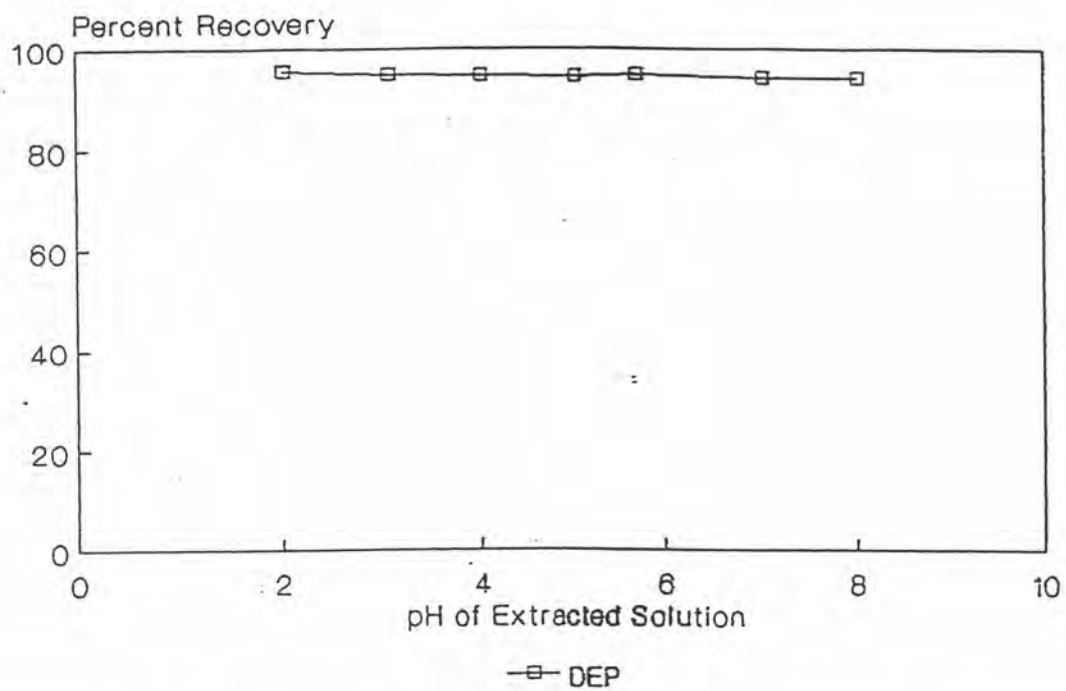


Figure 4.22 The effect of pH of extracted solution on the percent recovery of DEP in mixture solution with concentration of aqueous standard solution in lower level of ppm

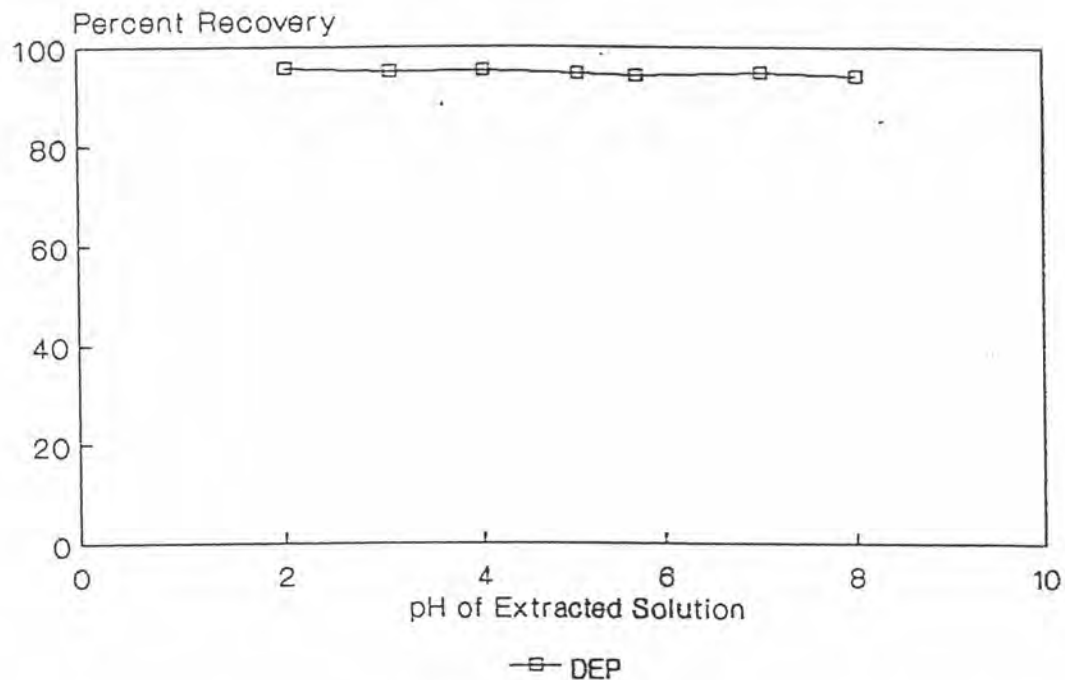


Figure 4.23 The effect of pH of extracted solution on the percent recovery of DEP in mixture solution with concentration of aqueous standard solution in higher level of ppm

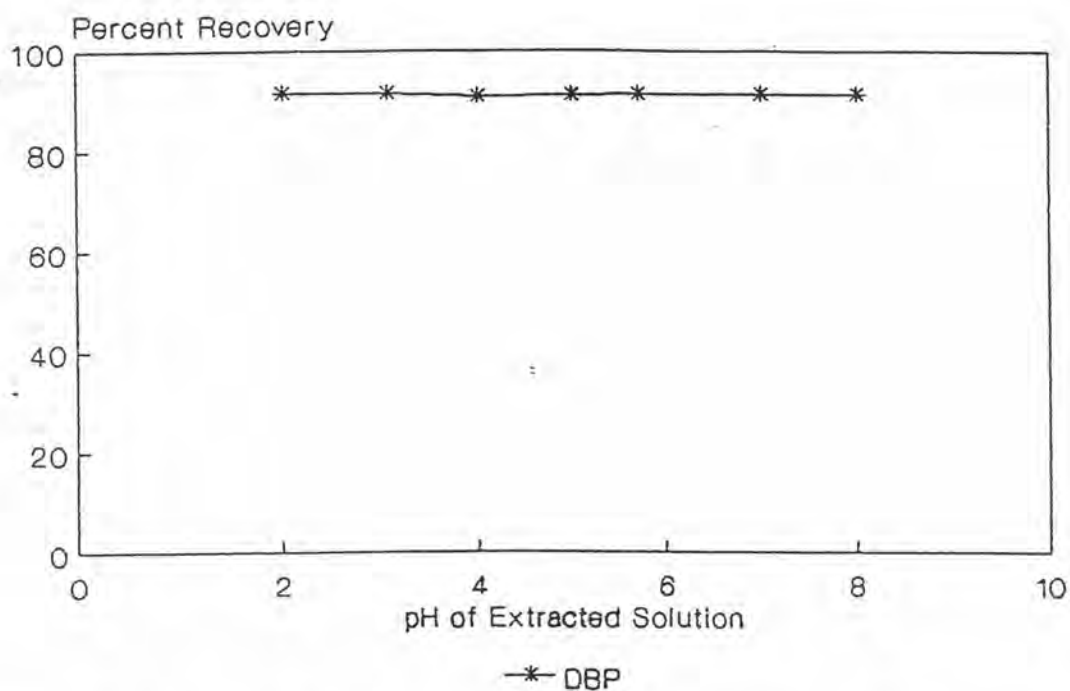


Figure 4.24 The effect of pH of extracted solution on the percent recovery of DBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

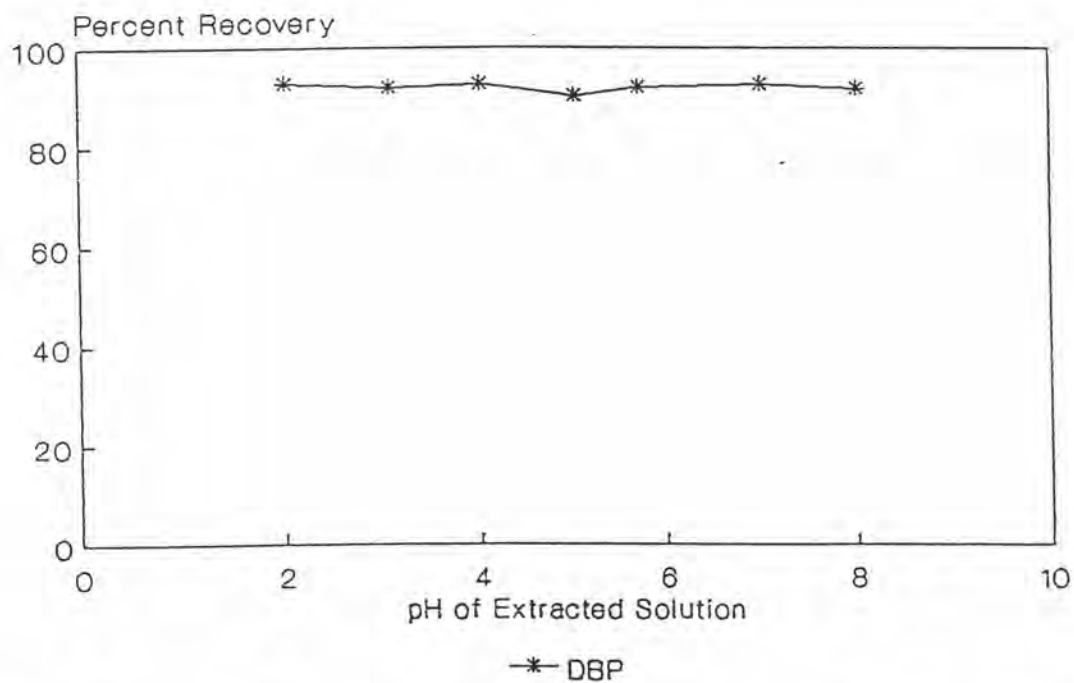


Figure 4.25 The effect of pH of extracted solution on the percent recovery of DBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

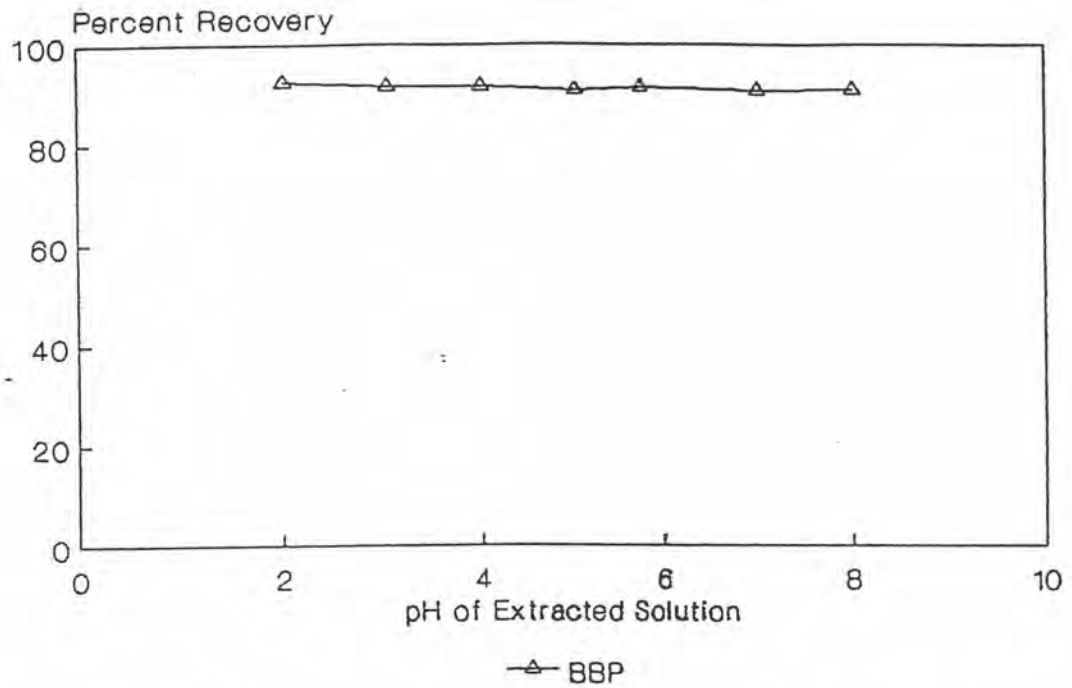


Figure 4.26 The effect of pH of extracted solution on the percent recovery of BBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

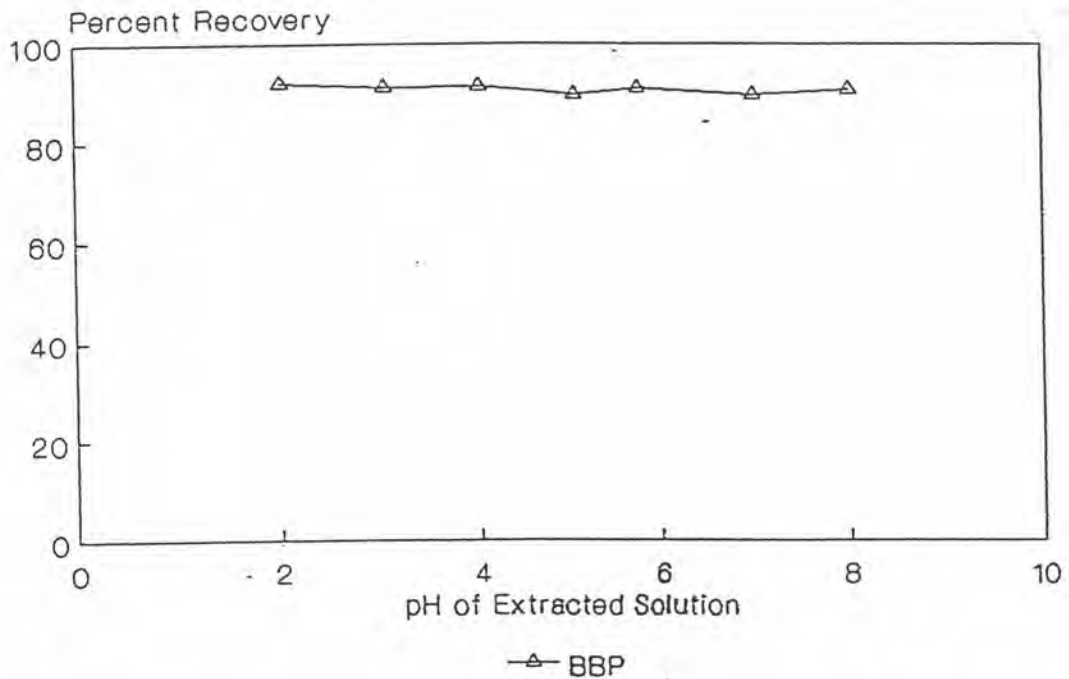


Figure 4.27 The effect of pH of extracted solution on the percent recovery of BBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

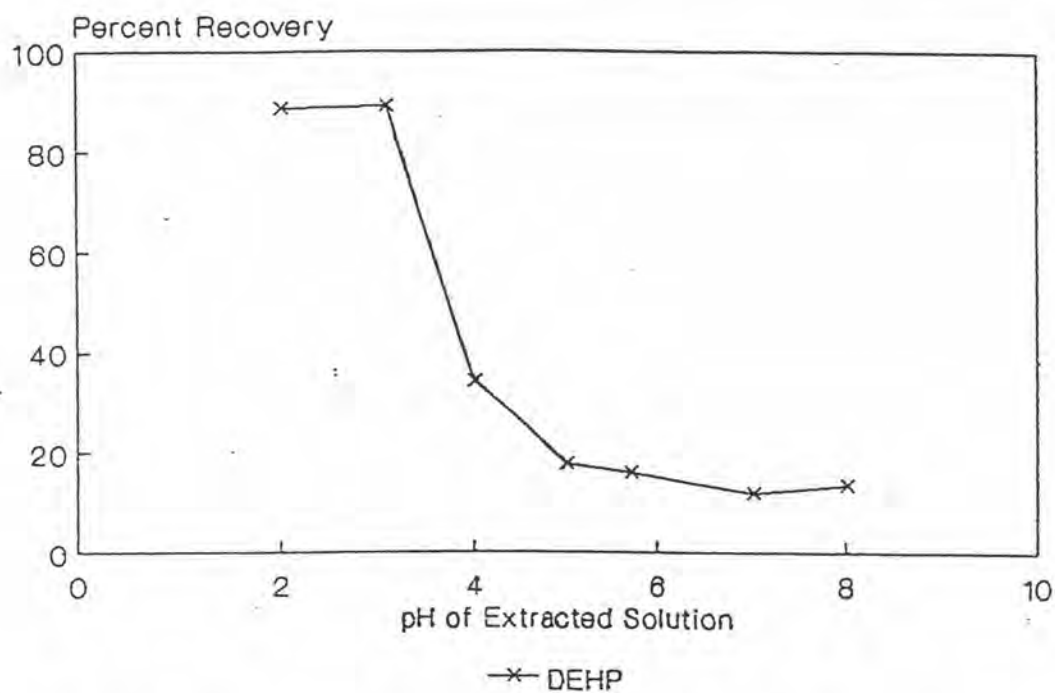


Figure 4.28 The effect of pH of extracted solution on the percent recovery of DEHP in mixture solution with concentration of aqueous standard solution in lower level of ppm

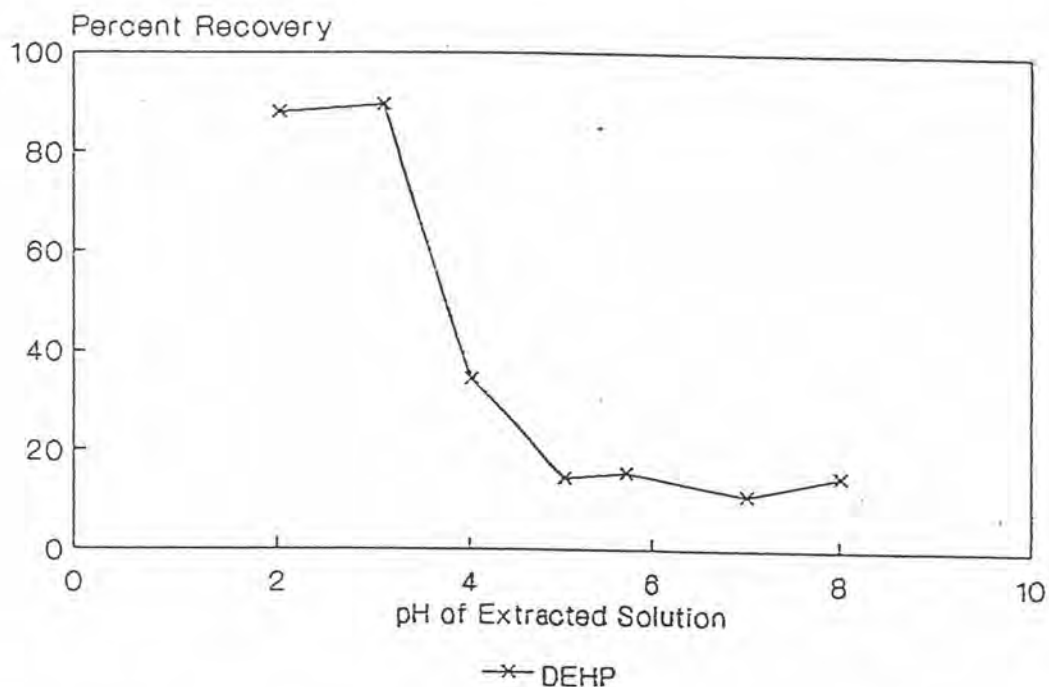


Figure 4.29 The effect of pH of extracted solution on the percent recovery of DEHP in mixture solution with concentration of aqueous standard solution in higher level of ppm

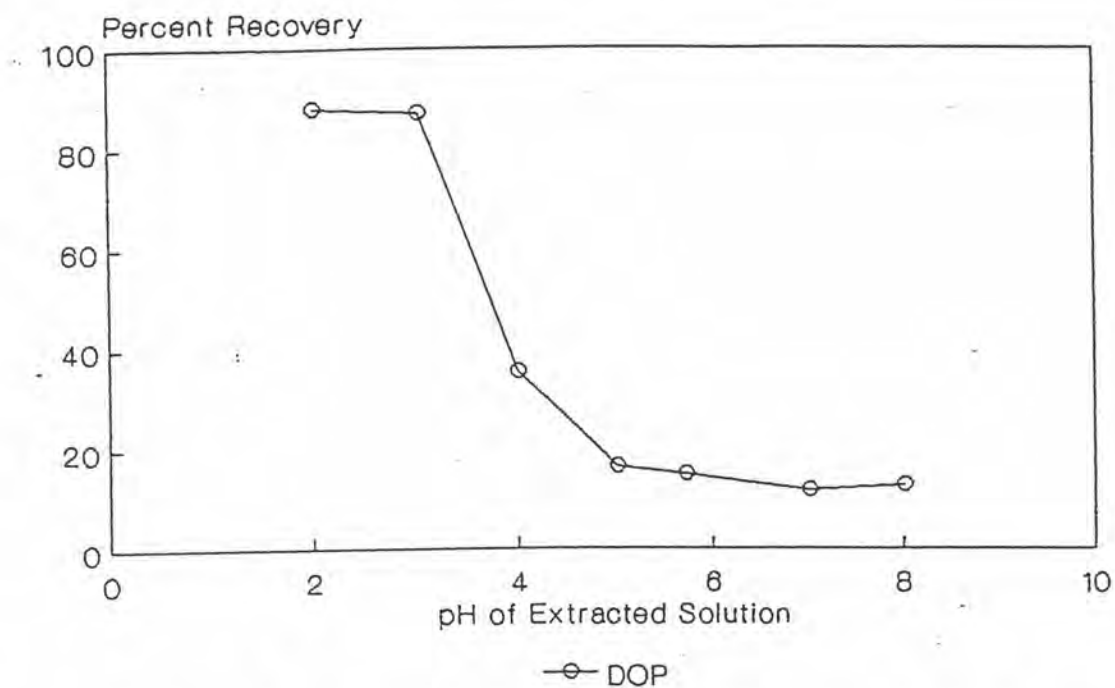


Figure 4.30 The effect of pH of extracted solution on the percent recovery of DOP in mixture solution with concentration of aqueous standard solution in lower level of ppm

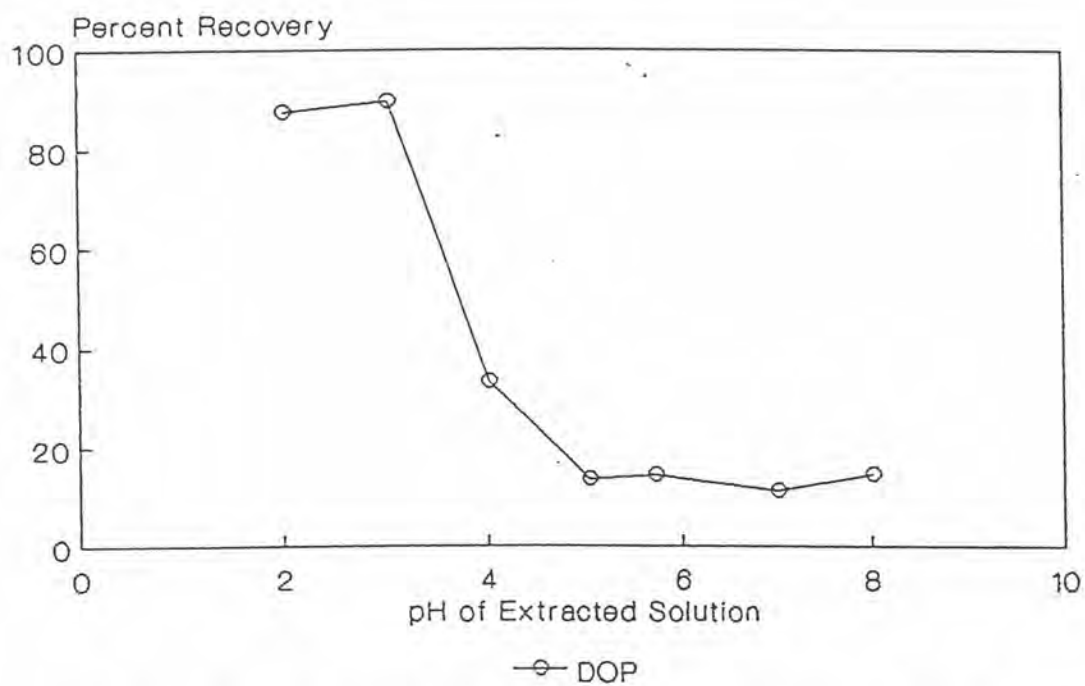


Figure 4.31 The effect of pH of extracted solution on the percent recovery of DOP in mixture solution with concentration of aqueous standard solution in higher level of ppm

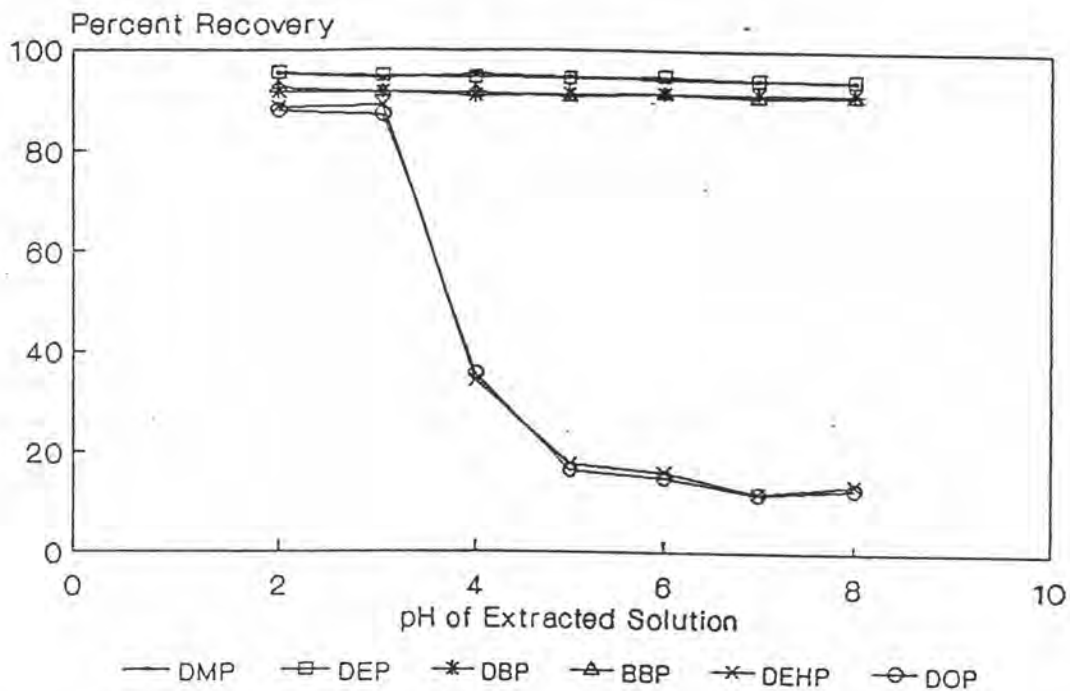


Figure 4.32 The effect of pH of extracted solution on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

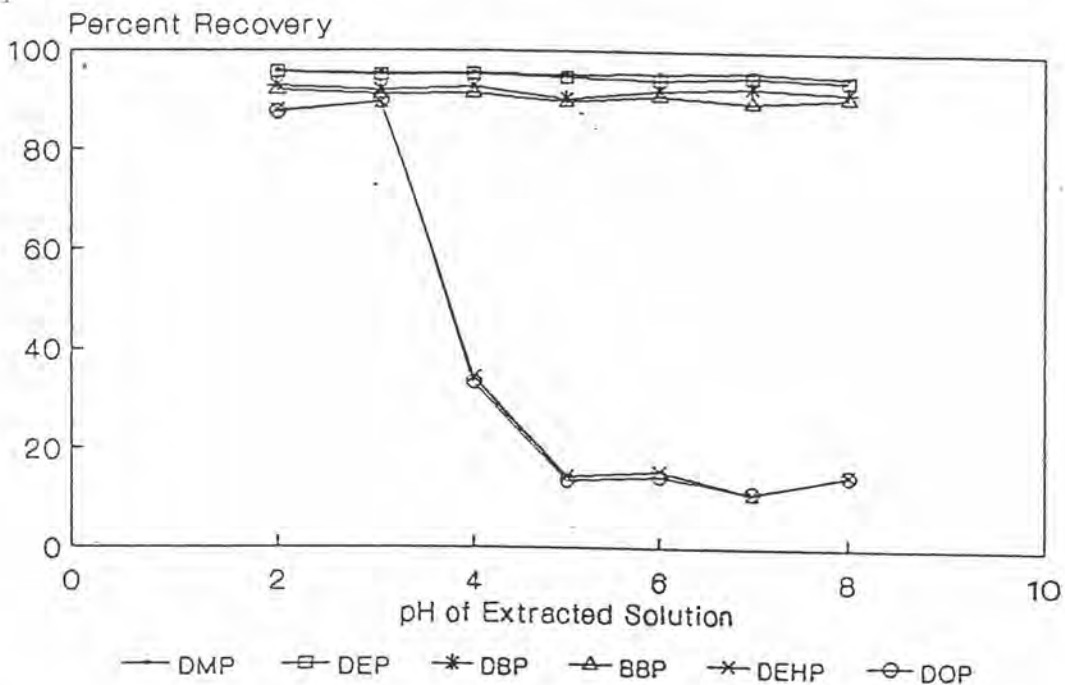


Figure 4.33 The effect of pH of extracted solution on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher level of ppm

4.3.3 The Study of Sorbent Mass

The data for the effect of sorbent mass on the percent recovery of each phthalate ester i.e., DMP, DEP, DBP, BBP, DEHP and DOP at concentration of 1.00 ppm in mixture solution are presented in Table 4.13. The graphs plotted the percent recovery of each phthalate ester against sorbent mass are depicted in Figures 4.34-4.40. It is found that the minimal sorbent mass obtained from this study is 500 mg for DMP and 100 mg for DEP, DBP, BBP, DEHP and DOP. The reason of this is that DMP is more polar and soluble than other phthalate esters. and the interaction of DMP with C₁₈ is not as strong as other phthalate esters. When the extent of C₁₈ is little (100-300 mg), the DMP will contact and interact with C₁₈ very quickly, the percent recovery is low. However, the more extent of C₁₈ is around 400-500 mg, the more extent of C₁₈ contacts and interacts with DMP, the percent recovery is increasing. Therefore, the sorbent mass at 500 mg is chosen as the optimal mass for the SPE study of phthalate esters.

Table 4.13 The results of the effect of sorbent mass on the percent recovery of each phthalate ester in mixture solution

Compounds	C SPE mass (mg)	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	100	1.22	43.85	71.89	±2.94
	200	1.22	51.98	85.22	±1.49
	300	1.22	54.88	89.97	±1.49
	400	1.22	56.73	93.00	±0.18
	500	1.22	58.35	95.65	±0.91
DEP	100	1.07	50.39	94.37	±1.13
	200	1.07	50.63	94.81	±0.48
	300	1.07	50.95	95.41	±2.03
	400	1.07	50.68	94.91	±2.26
	500	1.07	50.79	95.12	±0.93
DBP	100	1.01	46.23	91.36	±1.41
	200	1.01	46.49	91.88	±1.42
	300	1.01	46.73	92.36	±1.79
	400	1.01	46.27	91.44	±1.47
	500	1.01	46.84	92.56	±1.85
BBP	100	1.11	50.71	91.53	±2.01
	200	1.11	50.42	91.01	±1.73
	300	1.11	51.12	92.27	±0.97
	400	1.11	50.55	91.24	±1.92
	500	1.11	50.89	91.86	±1.95
DEHP	100	1.09	47.52	86.72	±2.62
	200	1.09	47.97	87.53	±0.83
	300	1.09	48.89	89.22	±1.43
	400	1.09	48.41	88.34	±1.89
	500	1.09	48.11	87.79	±2.84
DOP	100	1.36	59.70	87.54	±2.85
	200	1.36	59.50	87.25	±2.37
	300	1.36	59.99	87.96	±2.78
	400	1.36	60.40	88.57	±0.96
	500	1.36	60.02	88.01	±0.53

Duplicate analyzes

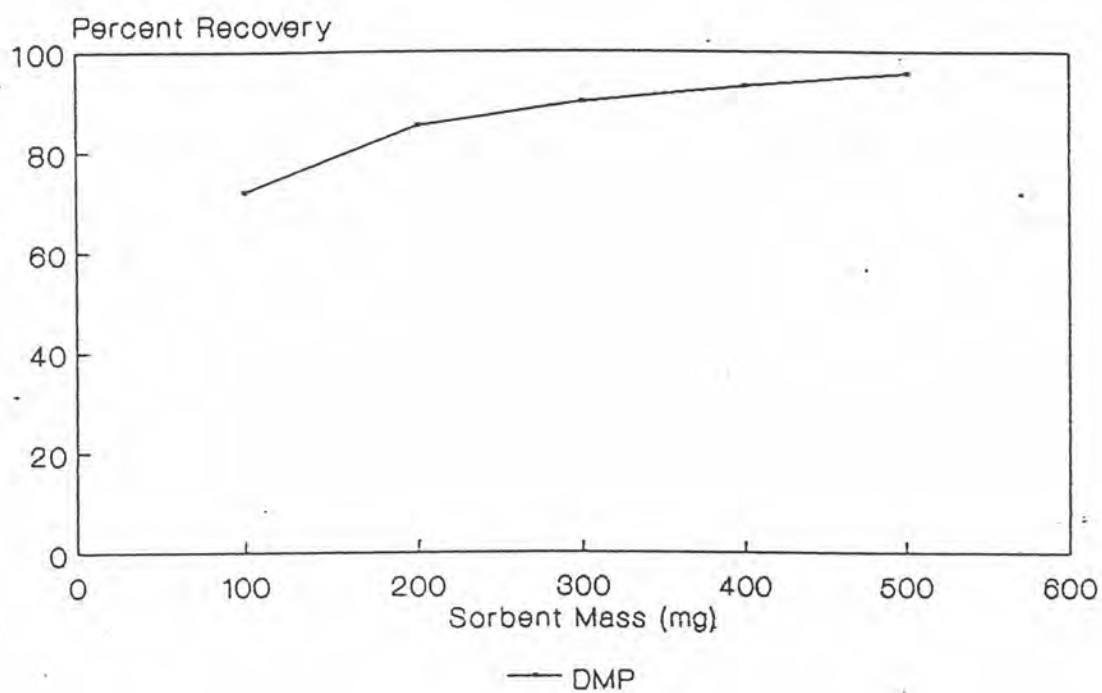


Figure 4.34 The effect of sorbent mass on the percent recovery of DMP in mixture solution

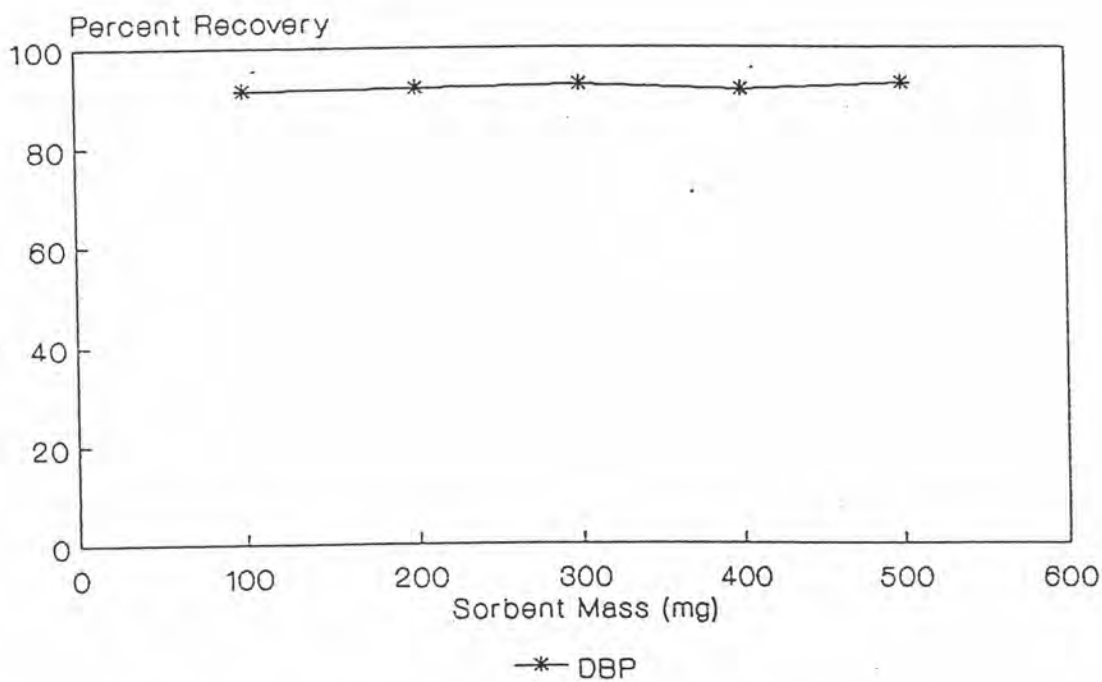


Figure 4.35 The effect of sorbent mass on the percent recovery of DEP in mixture solution

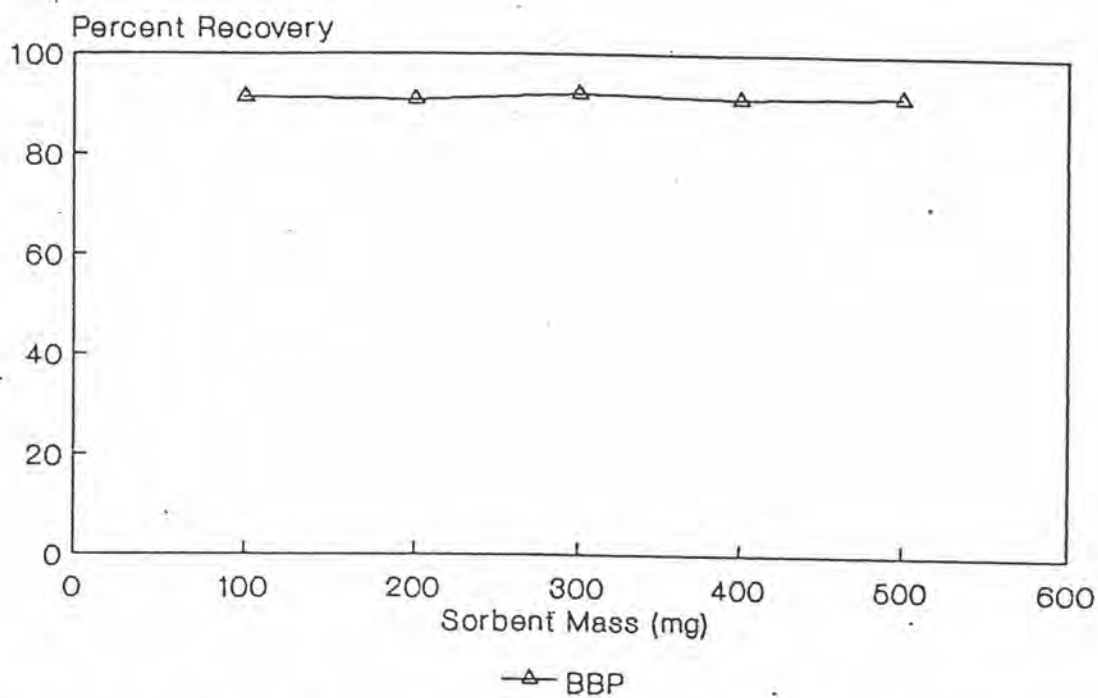


Figure 4.36 The effect of sorbent mass on the percent recovery of DBP in mixture solution

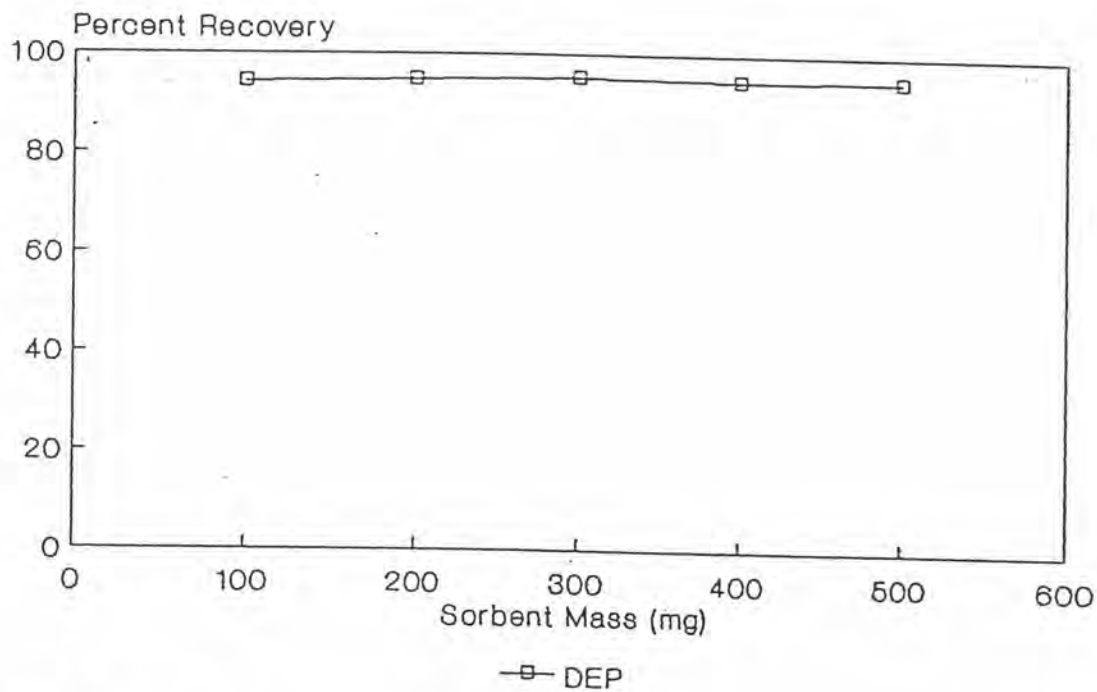


Figure 4.37 The effect of sorbent mass on the percent recovery of BBP in mixture solution

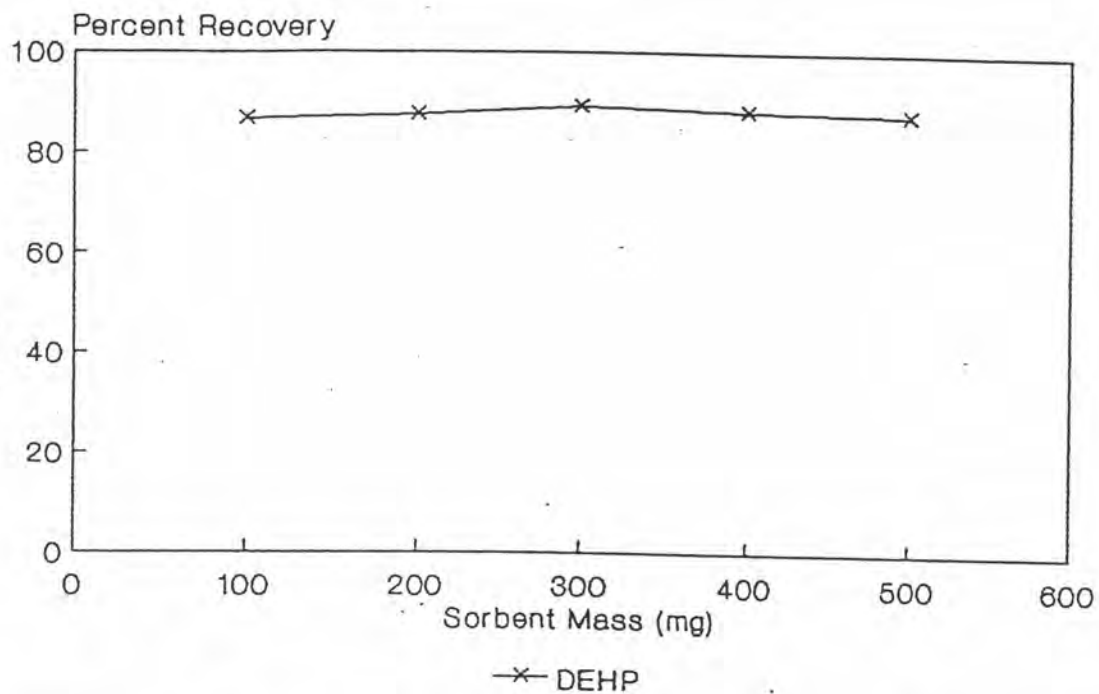


Figure 4.38 The effect of sorbent mass on the percent recovery of DEHP in mixture solution

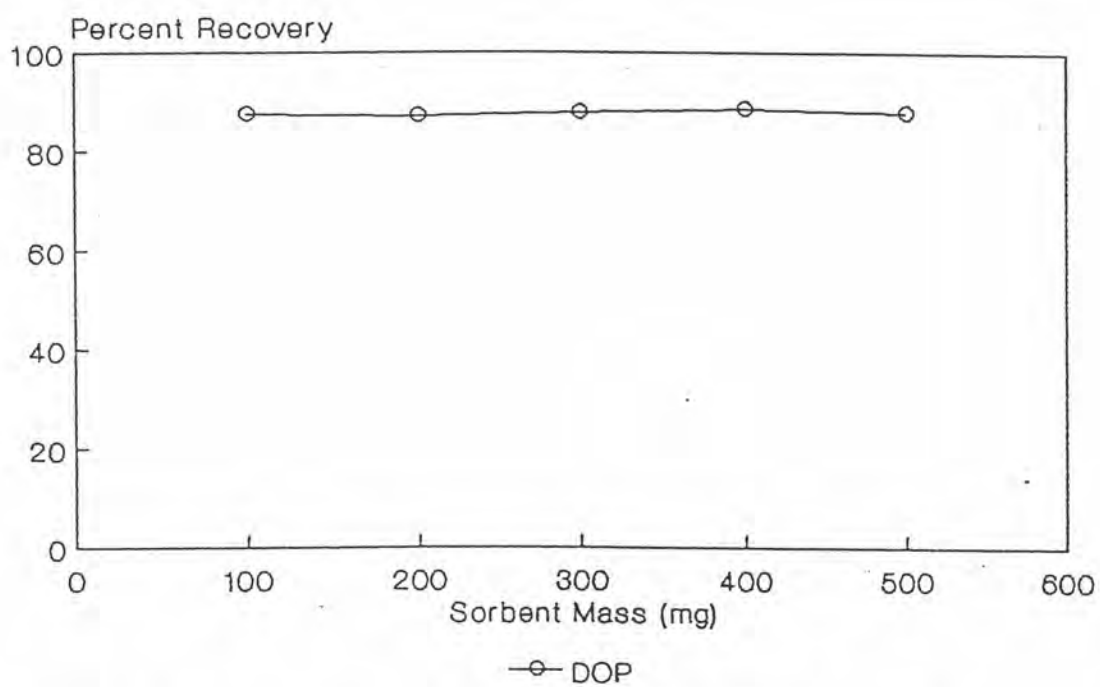


Figure 4.39 The effect of sorbent mass on the percent recovery of DOP in mixture solution

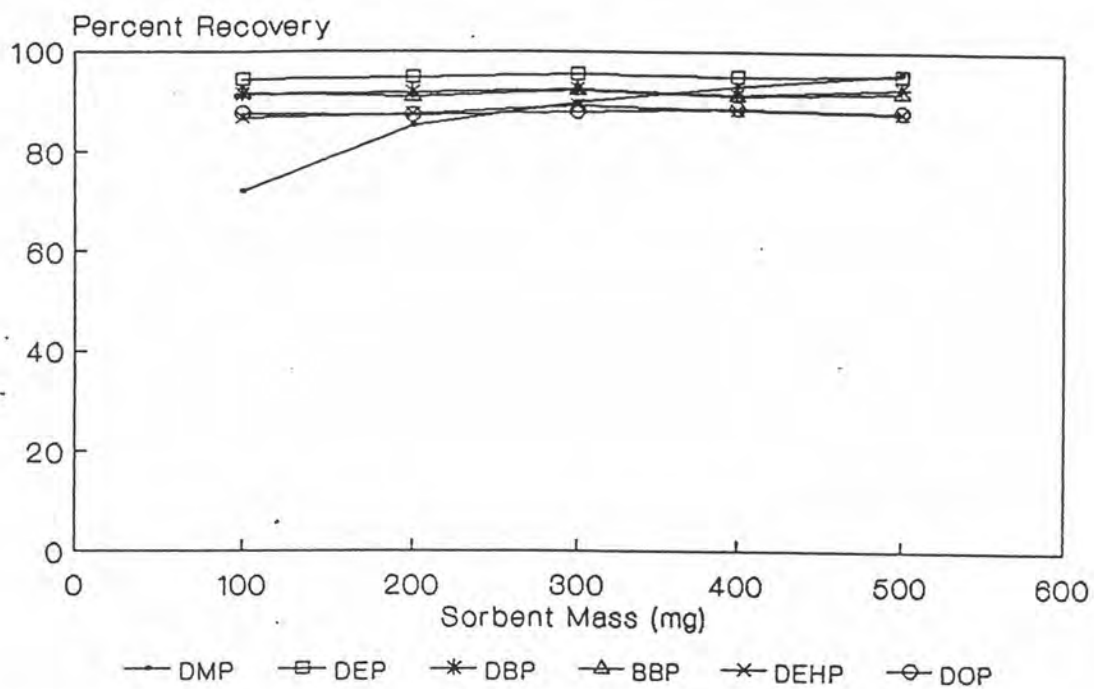


Figure 4.40 The effect of sorbent mass on the percent recovery of each phthalate ester in mixture solution

4.3.4 The Study of Elution Solvent in Single Component Solution

The results of the effect of elution solvent i.e., toluene, ethyl acetate, methylene chloride, isooctane and hexane on the percent recovery of each phthalate ester in single component solution at two concentration levels are demonstrated in Tables 4.14-4.15. The graphs plotted the percent recovery of each phthalate ester against elution solvent are shown in Figures 4.41-4.42. It is found that toluene is the best eluting solvent giving the highest percent recovery comparing with other eluting solvent i.e., ethyl acetate, methylene chloride, isooctane and hexane. The eluting solvents in order of decreasing polarity are ethyl acetate, methylene chloride, toluene, isooctane and hexane, respectively. As phthalate esters are moderately non-polar and toluene is similar polarity to them. So it should be the most suitable eluting solvent as the basic of "like dissolve like".

Table 4.14 The results of the effect of elution solvent on the percent recovery of each phthalate ester in single component solution with concentration of aqueous standard solution in lower level of ppm

Compounds	Elution solvent	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	Toluene	0.283	14.27	100.76	±1.99
	Ethyl acetate	0.295	13.78	93.42	±1.11
	Methylene chloride	0.283	13.19	93.19	±2.73
	Hexane	0.283	ND	ND	ND
	Isooctane	0.283	ND	ND	ND
DEP	Toluene	0.271	13.95	102.85	±0.60
	Ethyl acetate	0.265	12.38	93.57	±1.69
	Methylene chloride	0.271	12.56	92.59	±1.05
	Hexane	0.271	ND	ND	ND
	Isooctane	0.271	ND	ND	ND
DBP	Toluene	0.194	9.37	96.36	±1.51
	Ethyl acetate	0.196	9.01	91.98	±1.89
	Methylene chloride	0.194	8.91	91.63	±1.44
	Hexane	0.194	ND	ND	ND
	Isooctane	0.194	ND	ND	ND
BBP	Toluene	0.207	9.98	96.36	±1.68
	Ethyl acetate	0.204	9.37	91.98	±1.82
	Methylene chloride	0.204	9.34	91.63	±2.42
	Hexane	0.204	ND	ND	ND
	Isooctane	0.204	ND	ND	ND
DEHP	Toluene	0.206	9.14	88.56	±1.22
	Ethyl acetate	0.203	8.84	87.05	±3.46
	Methylene chloride	0.206	9.05	87.73	±3.99
	Hexane	0.206	ND	ND	ND
	Isooctane	0.206	ND	ND	ND
DOP	Toluene	0.284	12.39	87.19	±2.05
	Ethyl acetate	0.281	12.31	87.59	±1.79
	Methylene chloride	0.284	12.33	86.71	±2.29
	Hexane	0.284	ND	ND	ND
	Isooctane	0.284	ND	ND	ND

Remark: 1. ND = Not Detectable
2. Duplicate analyzes

Table 4.15 The results of the effect of elution solvent on the percent recovery of each phthalate ester in single component solution with concentration of aqueous standard solution in higher level of ppm

Compounds	Elution solvent	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	Toluene	1.42	71.64	101.19	±1.24
	Ethyl acetate	1.48	68.83	93.33	±0.92
	Methylene chloride	1.42	65.44	92.43	±2.81
	Hexane	1.42	ND	ND	ND
	Isooctane	1.42	ND	ND	ND
DEP	Toluene	1.36	70.88	104.55	±1.02
	Ethyl acetate	1.32	61.70	93.28	±3.32
	Methylene chloride	1.36	63.32	93.39	±3.05
	Hexane	1.36	ND	ND	ND
	Isooctane	1.36	ND	ND	ND
DBP	Toluene	0.972	46.33	95.33	±1.42
	Ethyl acetate	0.980	44.88	91.59	±2.97
	Methylene chloride	0.972	44.19	90.92	±2.36
	Hexane	0.972	ND	ND	ND
	Isooctane	0.972	ND	ND	ND
BBP	Toluene	1.04	48.27	93.18	±3.45
	Ethyl acetate	1.02	46.35	90.97	±1.65
	Methylene chloride	1.04	46.94	90.62	±0.27
	Hexane	1.04	ND	ND	ND
	Isooctane	1.04	ND	ND	ND
DEHP	Toluene	1.03	45.08	87.37	±1.59
	Ethyl acetate	1.02	43.52	85.66	±1.73
	Methylene chloride	1.03	45.42	88.02	±1.23
	Hexane	1.03	ND	ND	ND
	Isooctane	1.03	ND	ND	ND
DOP	Toluene	1.42	62.87	88.42	±3.27
	Ethyl acetate	1.41	62.09	88.38	±3.27
	Methylene chloride	1.42	63.37	89.13	±4.82
	Hexane	1.42	ND	ND	ND
	Isooctane	1.42	ND	ND	ND

Remark: 1. ND = Not Detectable
2. Duplicate analyzes

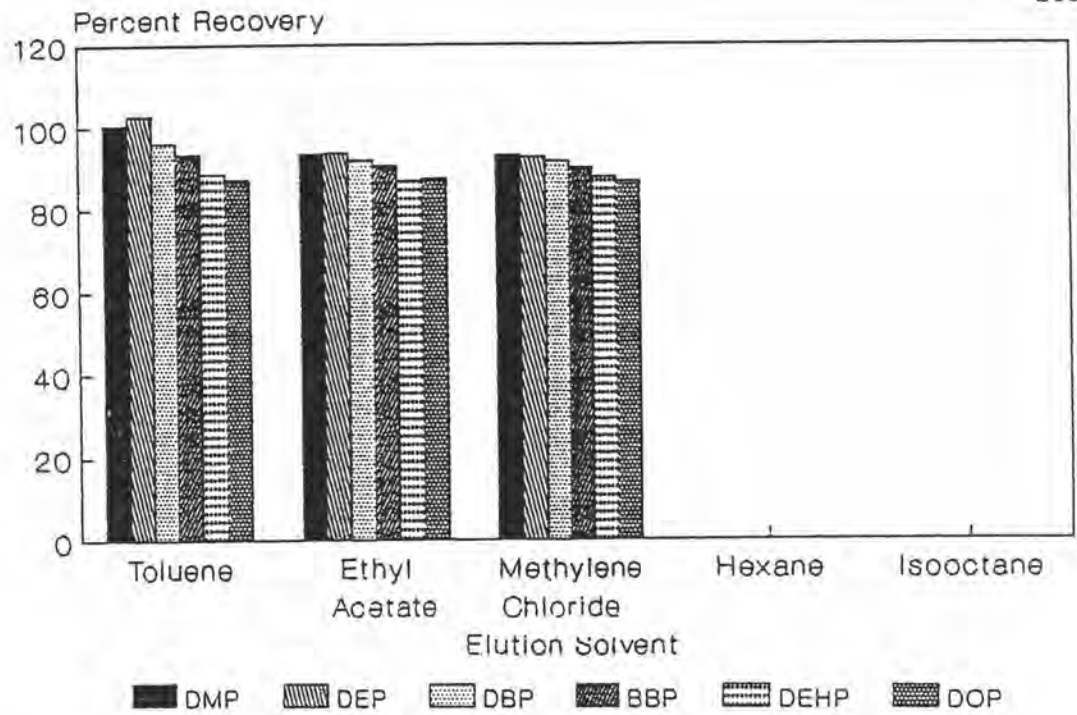


Figure 4.41 The effect of elution solvent on the percent recovery of each phthalate ester in single component solution with concentration of aqueous standard solution in lower level of ppm

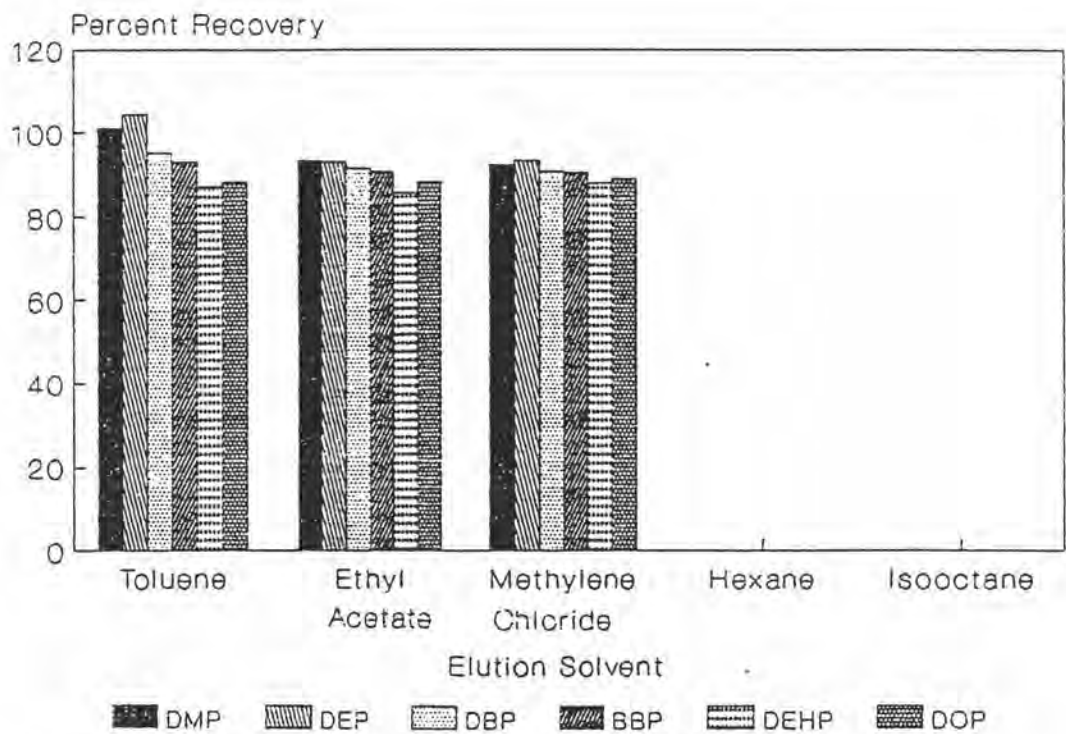


Figure 4.42 The effect of elution solvent on the percent recovery of each phthalate ester in single component solution with concentration of aqueous standard solution in higher level of ppm

4.3.5 The Study of Elution Solvent in Mixture Solution

The results of the effect of elution solvent i.e., toluene, ethyl acetate, methylene chloride, isooctane and hexane on the percent recovery of each phthalate ester in mixture solution at two concentration levels are presented in Tables 4.16-4.17. The graphs plotted the percent recovery of each phthalate ester against elution solvent are shown in Figures 4.43-4.44. A similar effect is noted in the results of the effect of elution solvent on the percent recovery in single component and mixture solutions. Toluene is the preferred elution solvent because it can give the highest percent recovery comparing with other elution solvents. Hence, toluene is chosen as the suitable elution solvent for the SPE study of phthalate esters.

Table 4.16 The results of the effect of elution solvent on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

Compounds	Elution solution	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	Toluene	0.283	14.63	103.32	±2.56
	Ethyl acetate	0.283	13.48	95.17	±0.83
	Methylene chloride	0.283	13.13	92.72	±3.17
	Hexane	0.283	ND	ND	ND
	Isooctane	0.283	ND	ND	ND
DEP	Toluene	0.271	14.04	103.56	±4.42
	Ethyl acetate	0.271	12.94	95.45	±1.34
	Methylene chloride	0.271	12.68	93.48	±1.09
	Hexane	0.271	ND	ND	ND
	Isooctane	0.271	ND	ND	ND
DBP	Toluene	0.194	9.35	96.23	±1.96
	Ethyl acetate	0.194	8.90	91.59	±1.45
	Methylene chloride	0.194	8.88	91.33	±1.62
	Hexane	0.194	ND	ND	ND
	Isooctane	0.194	ND	ND	ND
BBP	Toluene	0.207	9.84	94.97	±0.22
	Ethyl acetate	0.207	9.57	92.35	±1.37
	Methylene chloride	0.207	9.45	91.17	±3.29
	Hexane	0.207	ND	ND	ND
	Isooctane	0.207	ND	ND	ND
DEHP	Toluene	0.206	9.33	90.45	±2.53
	Ethyl acetate	0.206	9.13	88.49	±2.24
	Methylene chloride	0.206	9.09	88.07	±0.52
	Hexane	0.206	ND	ND	ND
	Isooctane	0.206	ND	ND	ND
DOP	Toluene	0.284	12.71	89.38	±2.79
	Ethyl acetate	0.284	12.49	87.87	±2.35
	Methylene chloride	0.284	12.28	86.38	±1.76
	Hexane	0.284	ND	ND	ND
	Isooctane	0.284	ND	ND	ND

Remark: 1. ND = Not Detectable
2. Duplicate analyzes

Table 4.17 The results of the effect of elution solvent on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher level of ppm

Compounds	Elution solution	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	Toluene	1.42	70.89	100.14	±0.65
	Ethyl acetate	1.42	67.86	95.85	±2.26
	Methylene chloride	1.42	66.89	94.48	±2.89
	Hexane	1.42	ND	ND	ND
	Isooctane	1.42	ND	ND	ND
DEP	Toluene	1.36	69.56	102.59	±2.21
	Ethyl acetate	1.36	64.92	95.75	±1.77
	Methylene chloride	1.36	64.24	94.75	±2.10
	Hexane	1.36	ND	ND	ND
	Isooctane	1.36	ND	ND	ND
DBP	Toluene	0.972	46.33	95.34	±1.89
	Ethyl acetate	0.972	45.15	92.91	±1.60
	Methylene chloride	0.972	44.46	91.48	±1.36
	Hexane	0.972	ND	ND	ND
	Isooctane	0.972	ND	ND	ND
BBP	Toluene	1.04	49.15	94.89	±0.11
	Ethyl acetate	1.04	47.69	92.06	±1.03
	Methylene chloride	1.04	46.92	90.57	±3.70
	Hexane	1.04	ND	ND	ND
	Isooctane	1.04	ND	ND	ND
DEHP	Toluene	1.03	46.16	89.46	±2.85
	Ethyl acetate	1.03	45.39	87.96	±0.45
	Methylene chloride	1.03	44.34	85.93	±2.81
	Hexane	1.03	ND	ND	ND
	Isooctane	1.03	ND	ND	ND
DOP	Toluene	1.42	62.75	88.25	±1.75
	Ethyl acetate	1.42	62.23	87.52	±0.76
	Methylene chloride	1.42	61.70	86.78	±4.98
	Hexane	1.42	ND	ND	ND
	Isooctane	1.42	ND	ND	ND

Remark: 1. ND = Not Detectable
2. Duplicate analyzes

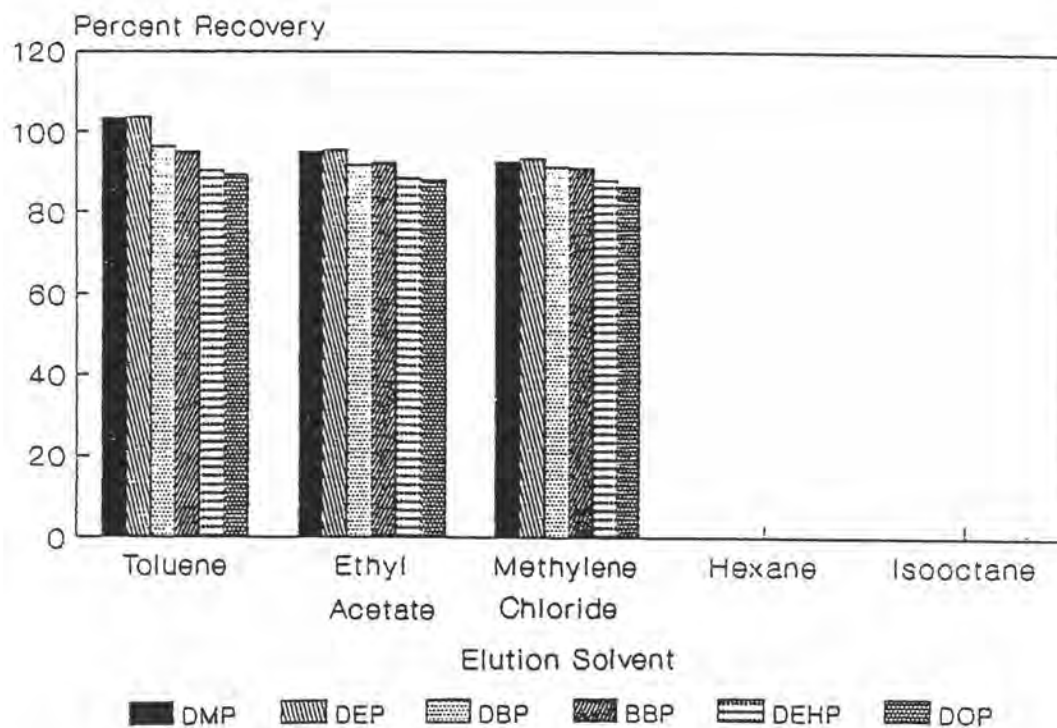


Figure 4.43 The effect of elution solvent on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

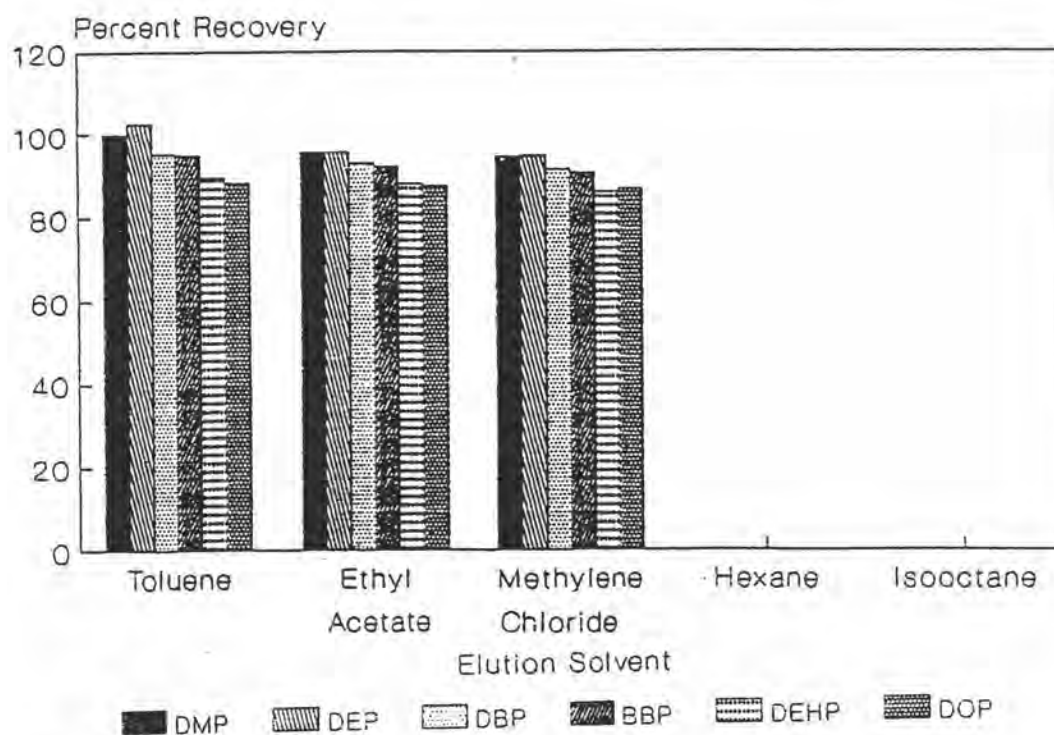


Figure 4.44 The effect of elution solvent on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher level of ppm

4.3.6 The Study of Volume of Elution Solvent

Although toluene is the elution solvent to gives the highest percent recovery, it is toxic (37,101). Ethyl acetate is less toxic and also gives the high percent recovery. Therefore, both of toluene and ethyl acetate are used as elution solvents in this study.

4.3.6.1 The Study of Volume of Elution Solvent by Using Toluene as Elution Solvent.

The results of the effect of volume of elution solvent by using toluene as elution solvent on the percent recovery of each phthalate ester in mixture solution at two concentrations are presented in Tables 4.18-4.19. The graphs plotted the percent recovery of each phthalate ester against volume of toluene are shown in Figures 4.45-4.58. It is demonstrated that the minimal volume of toluene employed in this study to obtain the maximal value of percent recovery is 3.0 mL for DMP, DEP and DBP and 1.0 mL for BBP, DEHP and DOP. Hence, the volume of toluene at 3.0 mL is chosen as the optimal volume for the SPE study of phthalate esters.

Table 4.18 The results of the effect of volume of toluene on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

Compounds	Volume of toluene (ml)	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	1	0.248	7.67	61.79	±3.72
	2	0.248	11.64	93.74	±1.99
	3	0.248	12.37	99.57	±2.64
	4	0.248	12.35	99.45	±1.44
	5	0.248	12.49	100.63	±1.75
DEP	1	0.239	7.76	64.81	±7.09
	2	0.239	11.36	94.84	±0.86
	3	0.239	11.94	99.63	±1.19
	4	0.239	12.33	102.88	±3.64
	5	0.239	12.04	100.48	±0.46
DBP	1	0.196	8.56	87.52	±1.58
	2	0.196	8.99	91.91	±0.84
	3	0.196	9.44	96.48	±2.20
	4	0.196	9.54	97.59	±4.16
	5	0.196	9.53	97.49	±1.70
BBP	1	0.201	9.16	91.09	±1.41
	2	0.201	9.21	91.51	±2.83
	3	0.201	9.38	93.27	±3.89
	4	0.201	9.32	92.66	±5.06
	5	0.201	9.19	91.43	±0.17
DEHP	1	0.203	8.89	87.56	±1.94
	2	0.203	8.79	86.56	±0.74
	3	0.203	8.99	88.56	±1.76
	4	0.203	8.77	86.28	±1.53
	5	0.203	8.93	87.91	±0.82
DOP	1	0.256	11.28	87.96	±2.72
	2	0.256	11.50	89.74	±0.24
	3	0.256	11.49	89.63	±3.34
	4	0.256	11.28	87.96	±3.31
	5	0.256	11.37	88.69	±3.10

Duplicate analyzes

Table 4.19 The results of the effect of volume of toluene on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher level of ppm

Compounds	Volume of toluene (ml)	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	1	1.24	40.14	64.64	±2.85
	2	1.24	59.52	95.84	±0.62
	3	1.24	61.79	99.51	±0.59
	4	1.24	63.07	101.57	±1.56
	5	1.24	62.24	100.23	±2.34
DEP	1	1.19	42.38	70.75	±4.38
	2	1.19	55.77	93.10	±0.95
	3	1.19	59.59	99.49	±0.81
	4	1.19	61.12	102.03	±2.04
	5	1.19	60.93	101.72	±1.66
DBP	1	0.978	43.25	88.45	±1.12
	2	0.978	44.49	90.99	±0.76
	3	0.978	46.13	94.33	±1.28
	4	0.978	46.99	96.09	±1.99
	5	0.978	46.71	95.53	±1.29
BBP	1	1.01	45.96	91.37	±3.13
	2	1.01	46.48	92.41	±2.08
	3	1.01	47.19	93.82	±0.74
	4	1.01	46.96	93.35	±3.39
	5	1.01	46.62	92.68	±3.01
DEHP	1	1.02	44.46	87.51	±3.80
	2	1.02	44.19	86.98	±2.87
	3	1.02	44.82	88.22	±2.14
	4	1.02	44.47	87.53	±1.14
	5	1.02	45.22	89.02	±3.97
DOP	1	1.28	56.66	88.40	±3.81
	2	1.28	57.77	90.12	±0.45
	3	1.28	57.62	89.89	±1.42
	4	1.28	55.63	86.78	±0.49
	5	1.28	56.89	88.75	±1.52

Duplicate analyzes

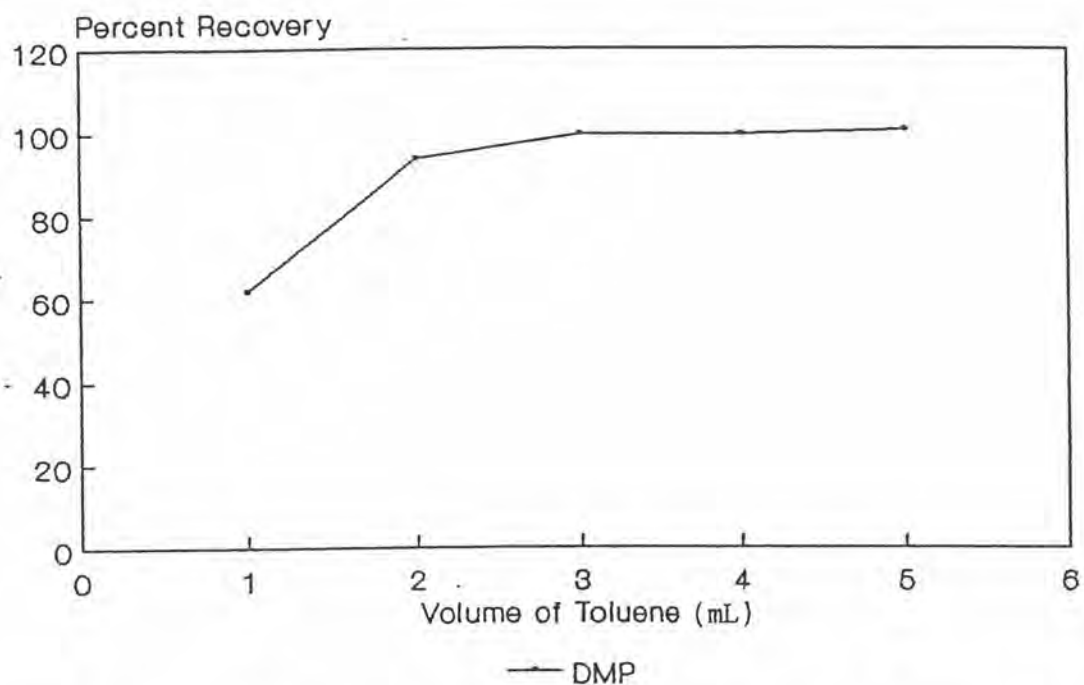


Figure 4.45 The effect of volume of toluene on the percent recovery of DMP in mixture solution with concentration of aqueous standard solution in lower level of ppm

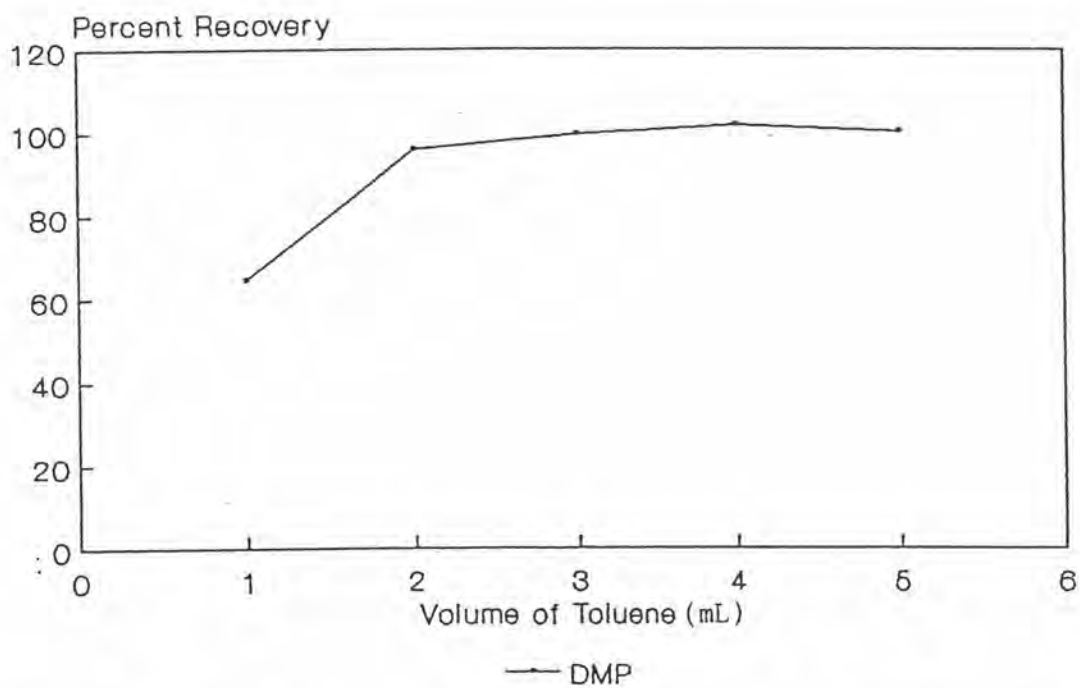


Figure 4.46 The effect of volume of toluene on the percent recovery of DMP in mixture solution with concentration of aqueous standard solution in higher level of ppm

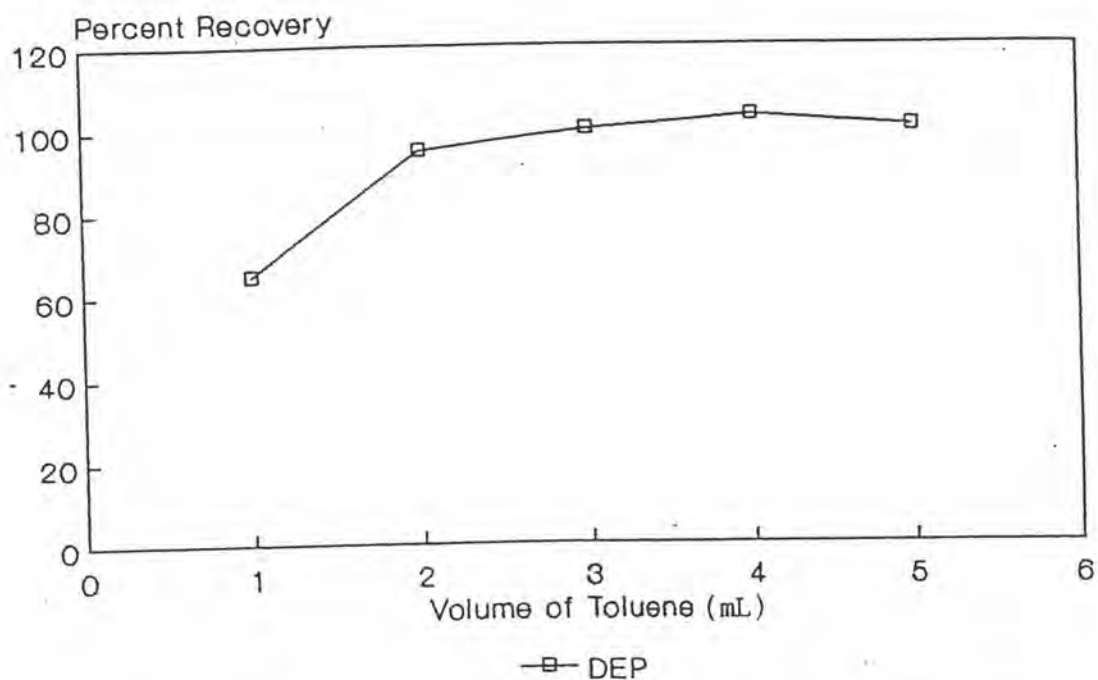


Figure 4.47 The effect of volume of toluene on the percent recovery of DEP in mixture solution with concentration of aqueous standard solution in lower level of ppm

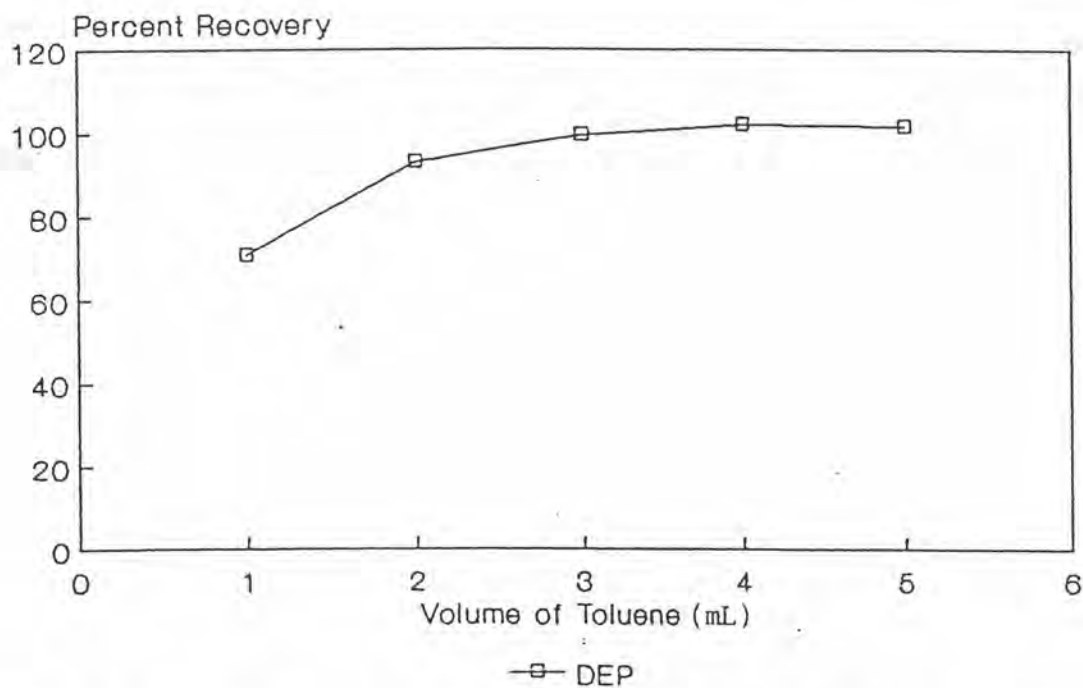


Figure 4.48 The effect of volume of toluene on the percent recovery of DEP in mixture solution with concentration of aqueous standard solution in higher level of ppm

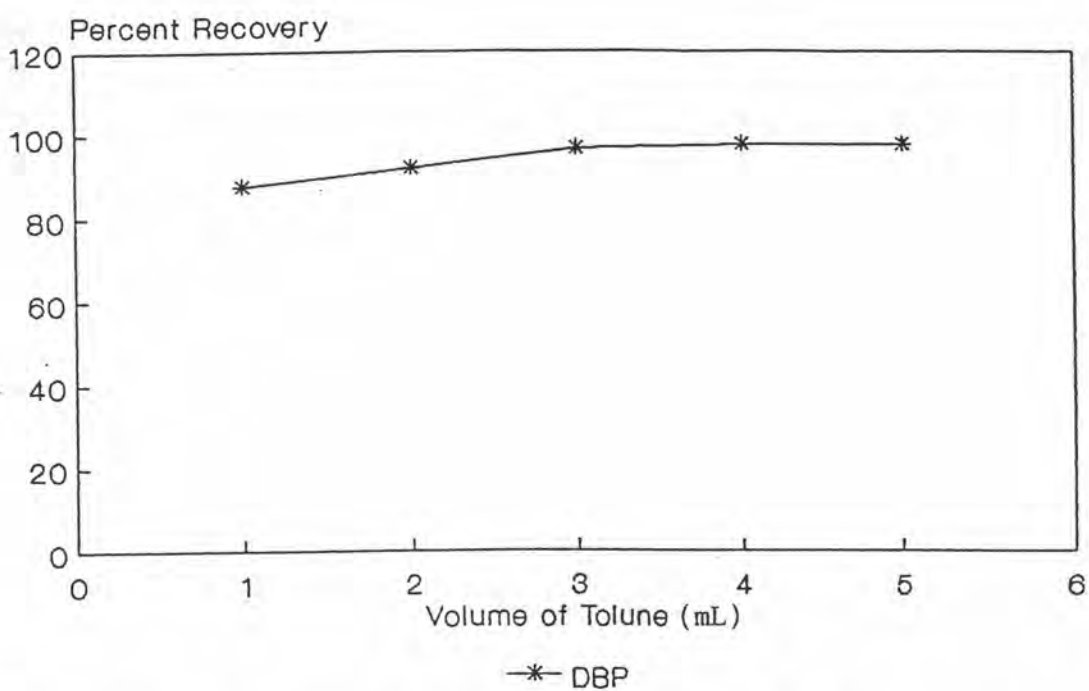


Figure 4.49 The effect of volume of toluene on the percent recovery of DBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

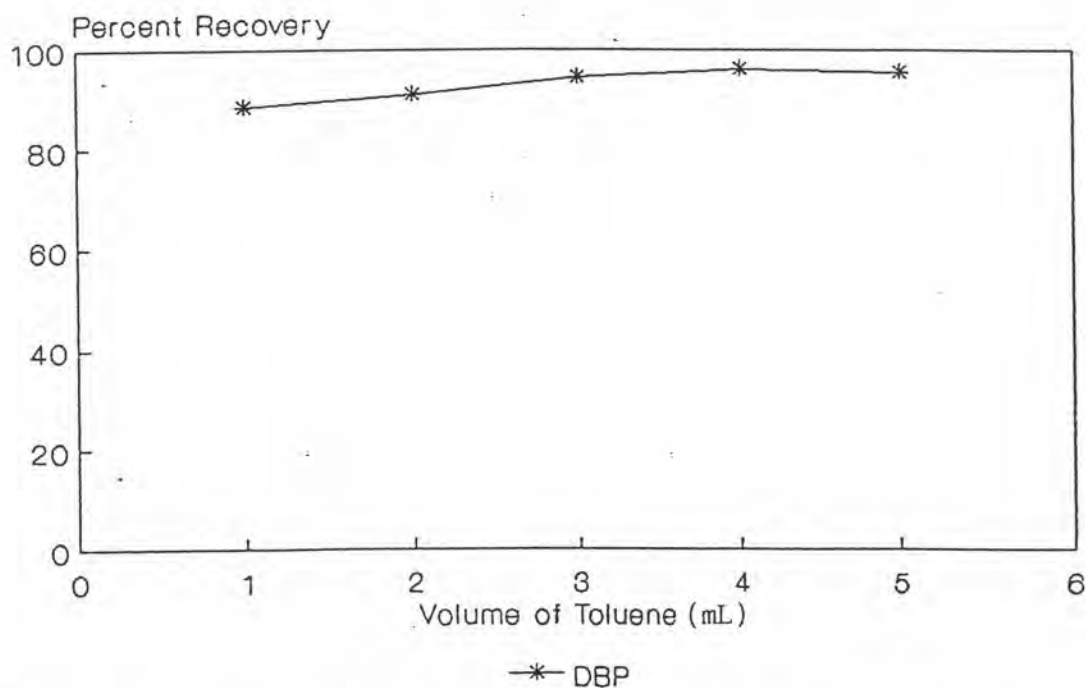


Figure 4.50 The effect of volume of toluene on the percent recovery of DBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

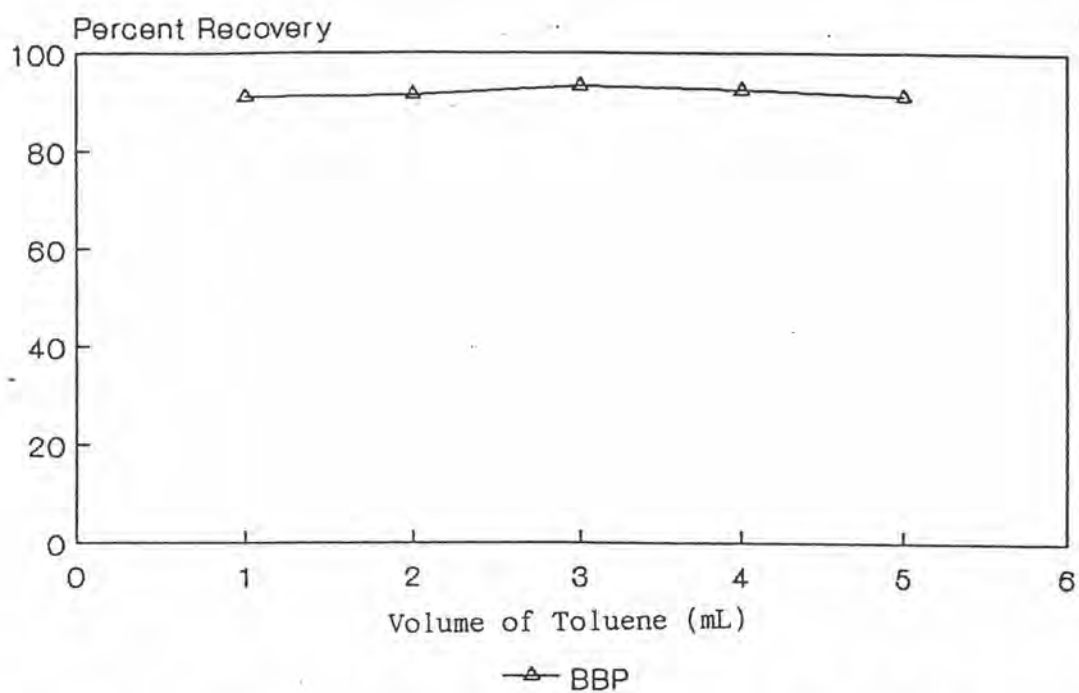


Figure 4.51 The effect of volume of toluene on the percent recovery of BBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

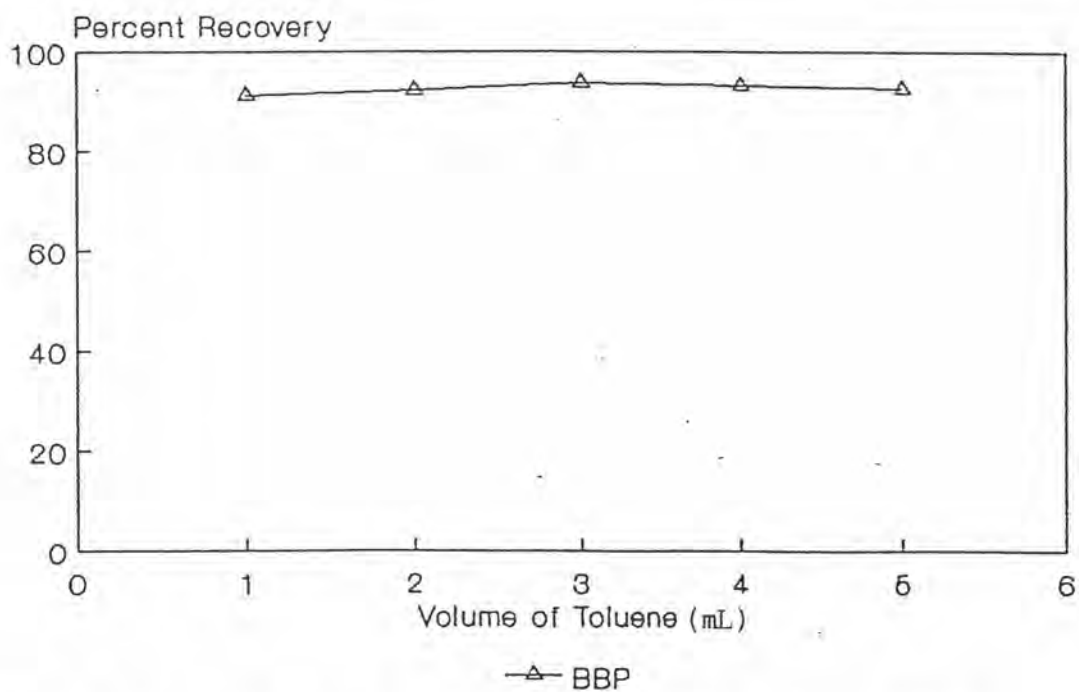


Figure 4.52 The effect of volume of toluene on the percent recovery of BBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

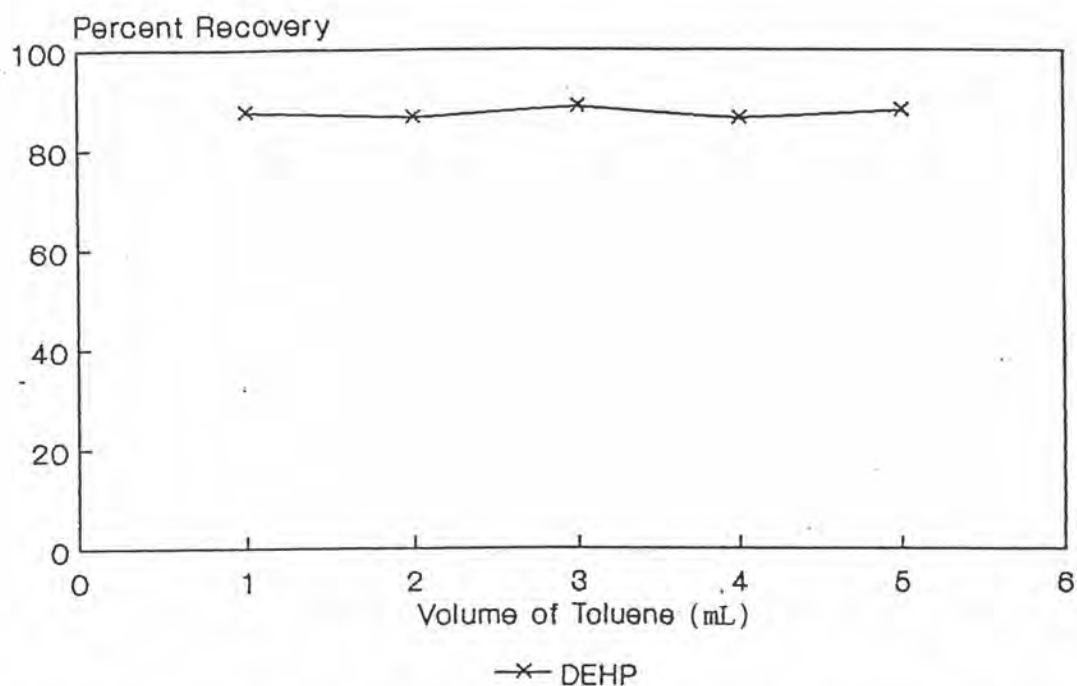


Figure 4.53 The effect of volume of toluene on the percent recovery of DEHP in mixture solution with concentration of aqueous standard solution in lower level of ppm

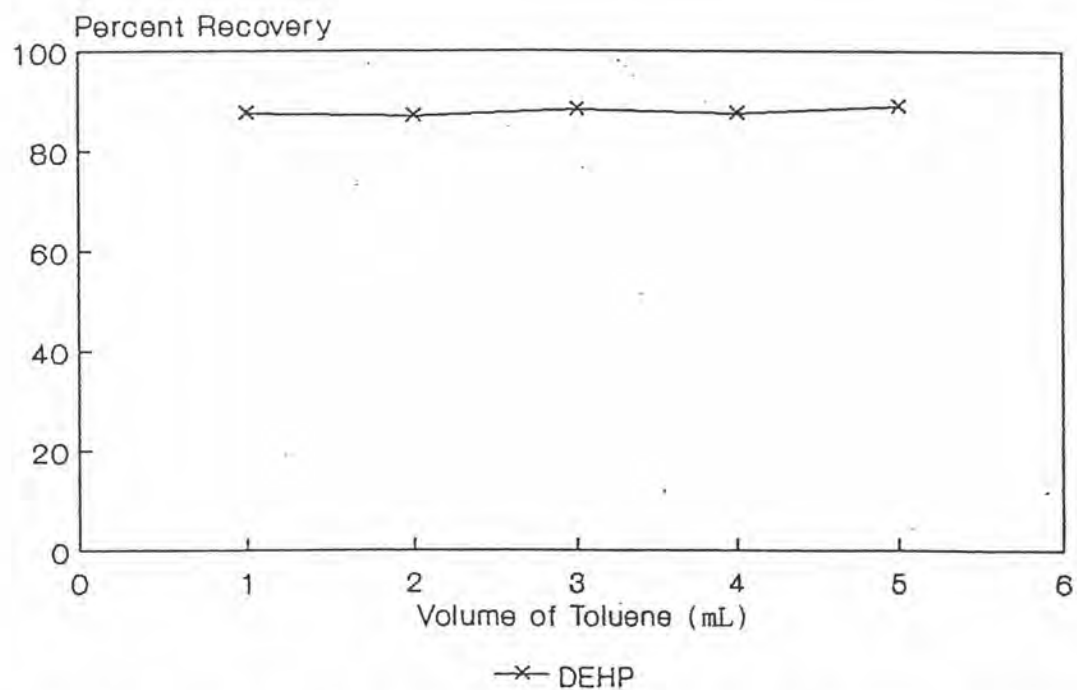


Figure 4.54 The effect of volume of toluene on the percent recovery of DEHP in mixture solution with concentration of aqueous standard solution in higher level of ppm

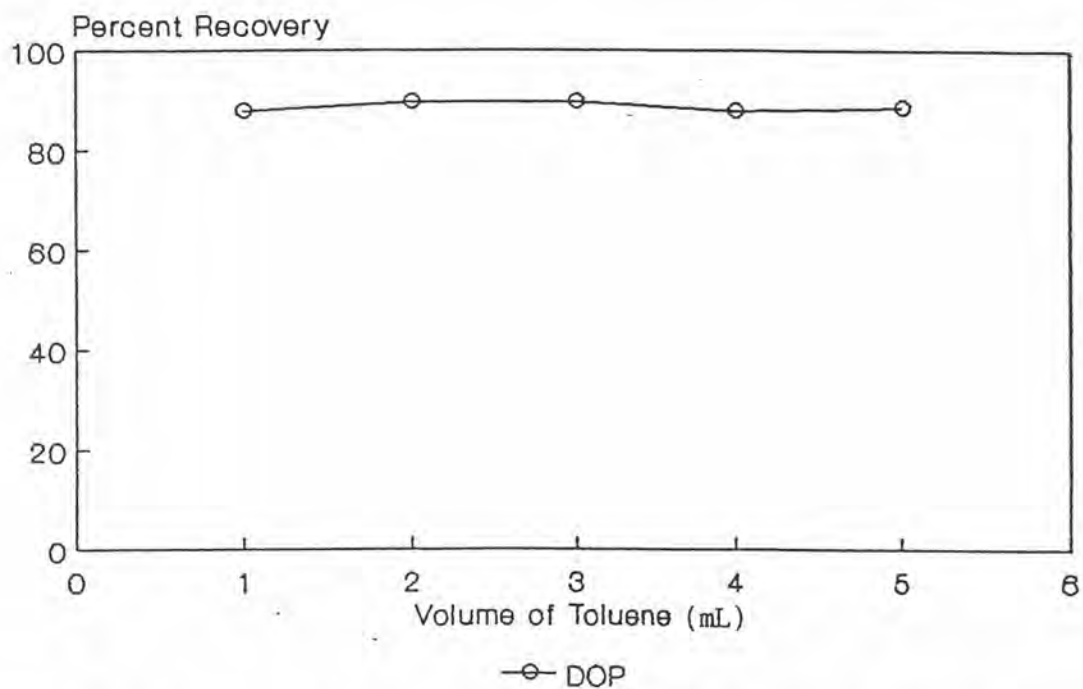


Figure 4.55 The effect of volume of toluene on the percent recovery of DOP in mixture solution with concentration of aqueous standard solution in lower level of ppm

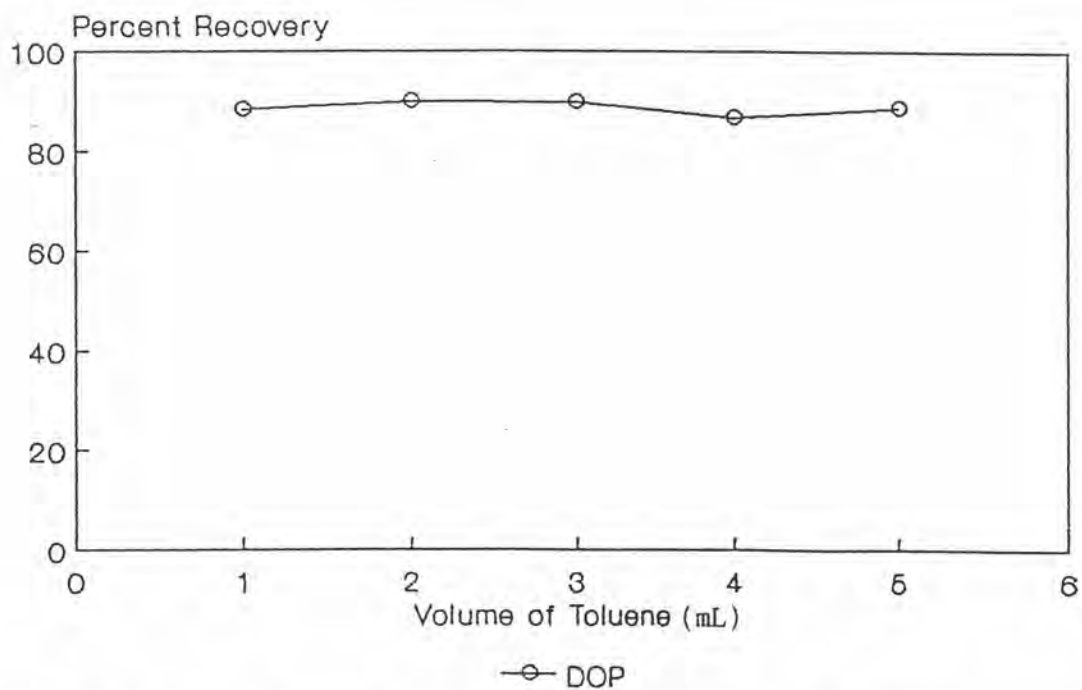


Figure 4.56 The effect of volume of toluene on the percent recovery of DOP in mixture solution with concentration of aqueous standard solution in higher level of ppm

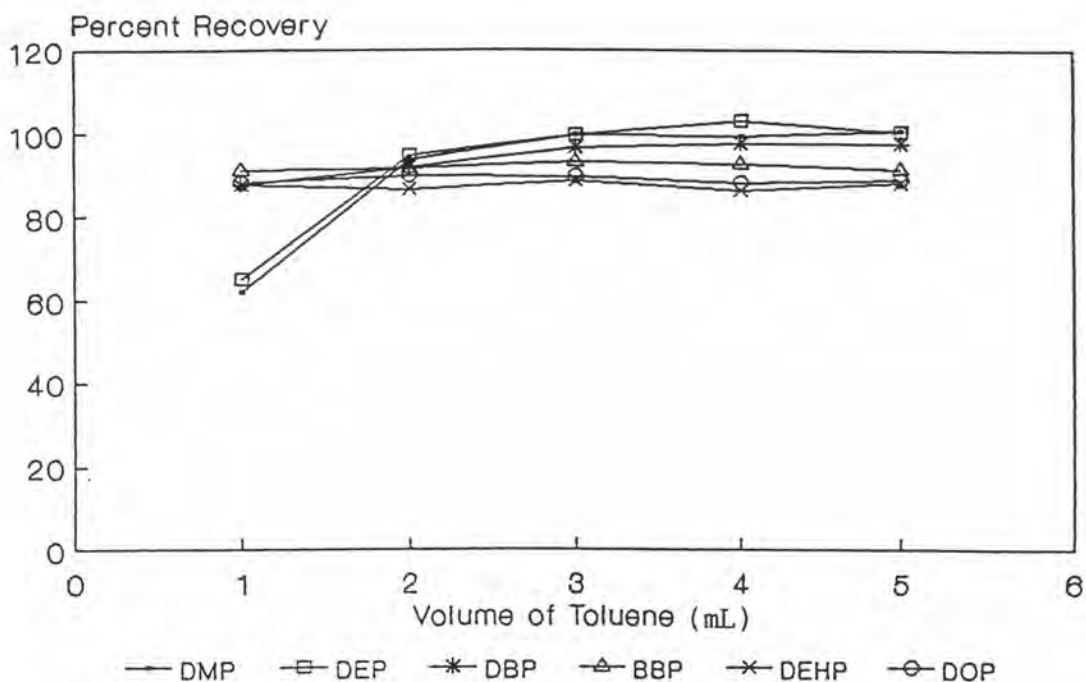


Figure 4.57 The effect of volume of toluene on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

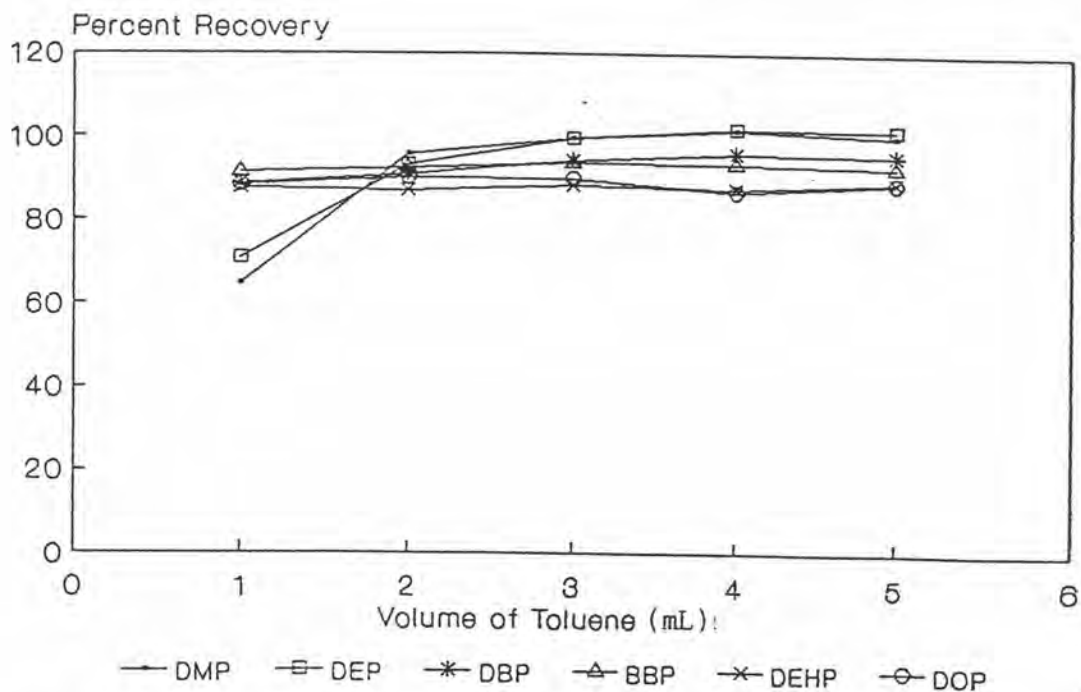


Figure 4.58 The effect of volume of toluene on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher level of ppm

4.3.6.2 The Study of Volume of Elution Solvent by Using Ethyl Acetate as Elution Solvent.

The results of the effect of volume of elution solvent by using ethyl acetate as elution solvent on the percent recovery of each phthalate ester in mixture solution at two concentrations are presented in Tables 4.20-4.21. The graphs plotted the percent recovery of each phthalate ester against volume of ethyl acetate are shown in Figures 4.59-4.72. It is demonstrated that the minimal volume of ethyl acetate employed in this study to obtain the maximal value of percent recovery is 1.0 mL for all six of the phthalate esters (DMP, DEP, DBP, BBP, DEHP, DOP). Hence, the volume of ethyl acetate at 1.0 mL is chosen as the optimum volume for the SPE study of phthalate esters.

Table 4.20 The results of the effect of volume of ethyl acetate on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

Compounds	Volume of ethyl acetate extraction (ml)	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	1	0.248	11.77	94.75	±1.89
	2	0.248	11.86	95.53	±1.19
	3	0.248	11.75	94.64	±0.84
	4	0.248	11.65	93.81	±2.54
	5	0.248	11.68	94.04	±2.35
DEP	1	0.239	11.27	94.11	±2.37
	2	0.239	11.34	94.64	±1.89
	3	0.239	11.29	94.24	±1.12
	4	0.239	11.42	95.36	±2.67
	5	0.239	11.28	94.19	±0.92
DBP	1	0.196	9.01	92.13	±1.62
	2	0.196	8.99	91.92	±2.12
	3	0.196	9.01	92.17	±2.23
	4	0.196	9.12	93.27	±2.89
	5	0.196	8.97	91.68	±0.68
BBP	1	0.201	9.12	90.61	±2.31
	2	0.201	9.19	91.43	±1.05
	3	0.201	9.30	92.47	±3.33
	4	0.201	9.29	92.38	±3.26
	5	0.201	9.24	91.84	±2.76
DEHP	1	0.203	8.76	86.25	±0.46
	2	0.203	8.99	88.49	±0.64
	3	0.203	8.91	87.65	±0.61
	4	0.203	8.91	87.71	±1.22
	5	0.203	8.96	88.17	±1.91
DOP	1	0.256	11.00	85.83	±0.52
	2	0.256	11.19	87.31	±1.53
	3	0.256	11.30	88.18	±1.62
	4	0.256	11.15	86.95	±2.48
	5	0.256	11.21	87.41	±2.75

Duplicate analyzes

Table 4.21 The results of the effect of volume of ethylacetate on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher lever of ppm

Compounds	Volume of ethyl acetate extraction (ml)	Conc. before extraction (ppm)	Conc. after extraction (ppm)	Recovery (%)	RSD (%)
DMP	1	1.24	58.72	94.55	±2.07
	2	1.24	58.69	94.51	±3.54
	3	1.24	57.98	93.37	±1.00
	4	1.24	59.29	95.47	±3.59
	5	1.24	57.77	93.02	±0.69
DEP	1	1.19	56.65	94.58	±0.80
	2	1.19	57.16	95.42	±2.88
	3	1.19	56.05	93.57	±2.67
	4	1.19	57.09	95.31	±2.17
	5	1.19	56.16	93.75	±0.66
DBP	1	0.978	44.39	90.77	±2.08
	2	0.978	44.60	91.21	±2.43
	3	0.978	45.03	92.09	±2.91
	4	0.978	44.58	91.16	±2.03
	5	0.978	44.94	91.91	±2.89
BBP	1	1.01	45.61	90.68	±2.24
	2	1.01	45.83	91.12	±3.11
	3	1.01	45.99	91.44	±3.65
	4	1.01	45.35	90.15	±1.75
	5	1.01	46.21	91.86	±1.78
DEHP	1	1.02	44.42	87.44	±2.87
	2	1.02	44.84	88.27	±0.76
	3	1.02	45.13	88.83	±1.51
	4	1.02	45.41	89.39	±2.95
	5	1.02	44.99	88.58	±3.56
DOP	1	1.28	55.98	87.33	±1.91
	2	1.28	56.58	88.27	±1.04
	3	1.28	57.34	89.46	±3.02
	4	1.28	56.95	88.84	±4.36
	5	1.28	56.26	87.77	±4.69

Duplicate analyzes

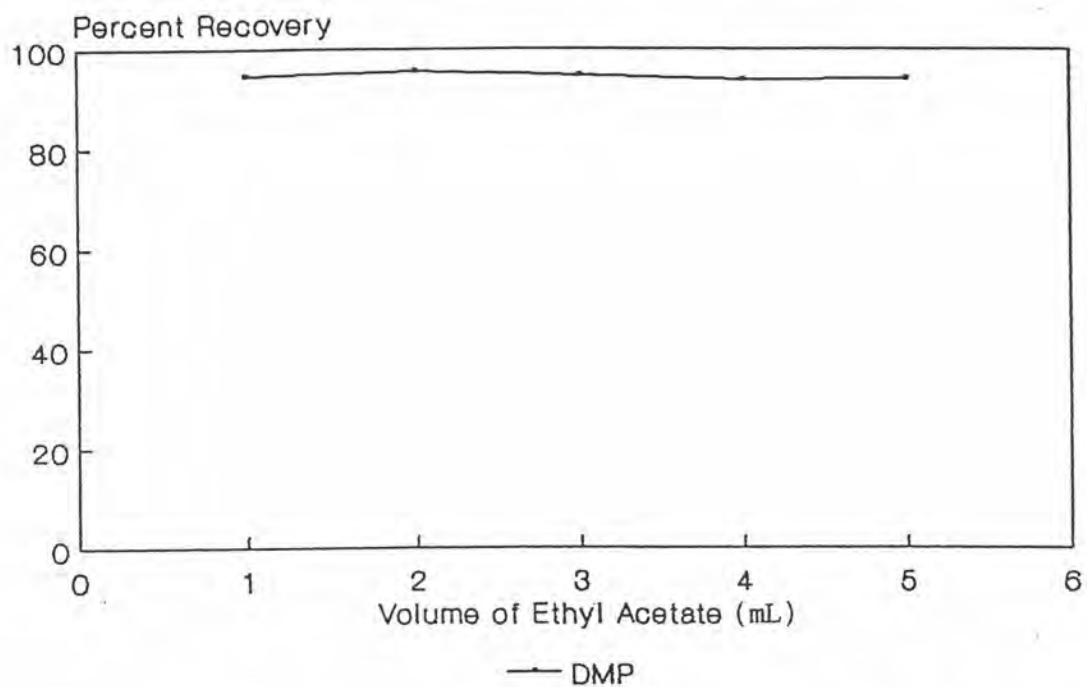


Figure 4.59 The effect of volume of ethyl acetate on the percent recovery of DMP in mixture solution with concentration of aqueous standard solution in lower level of ppm

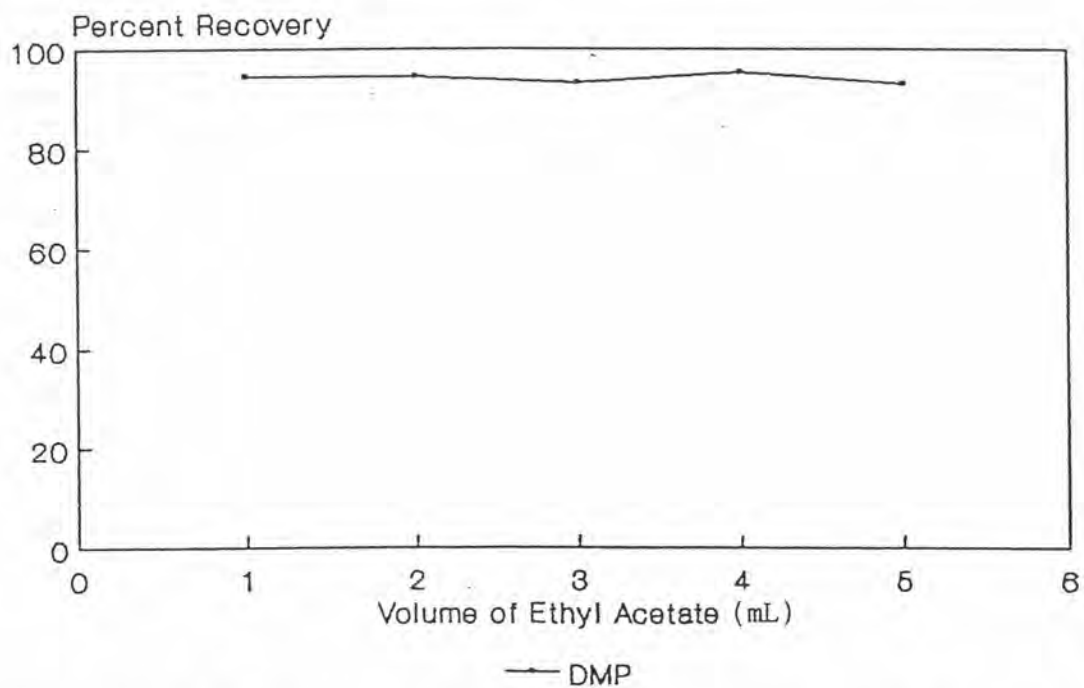


Figure 4.60 The effect of volume of ethyl acetate on the percent recovery of DMP in mixture solution with concentration of aqueous standard solution in higher level of ppm

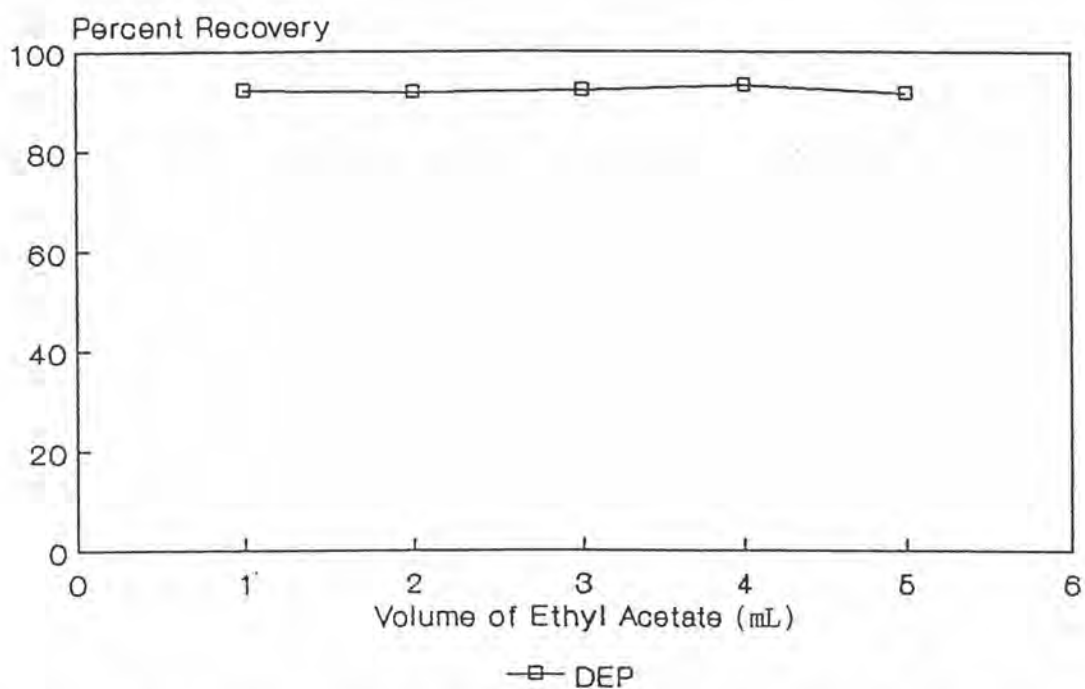


Figure 4.61 The effect of volume of ethyl acetate on the percent recovery of DEP in mixture solution with concentration of aqueous standard solution in lower level of ppm

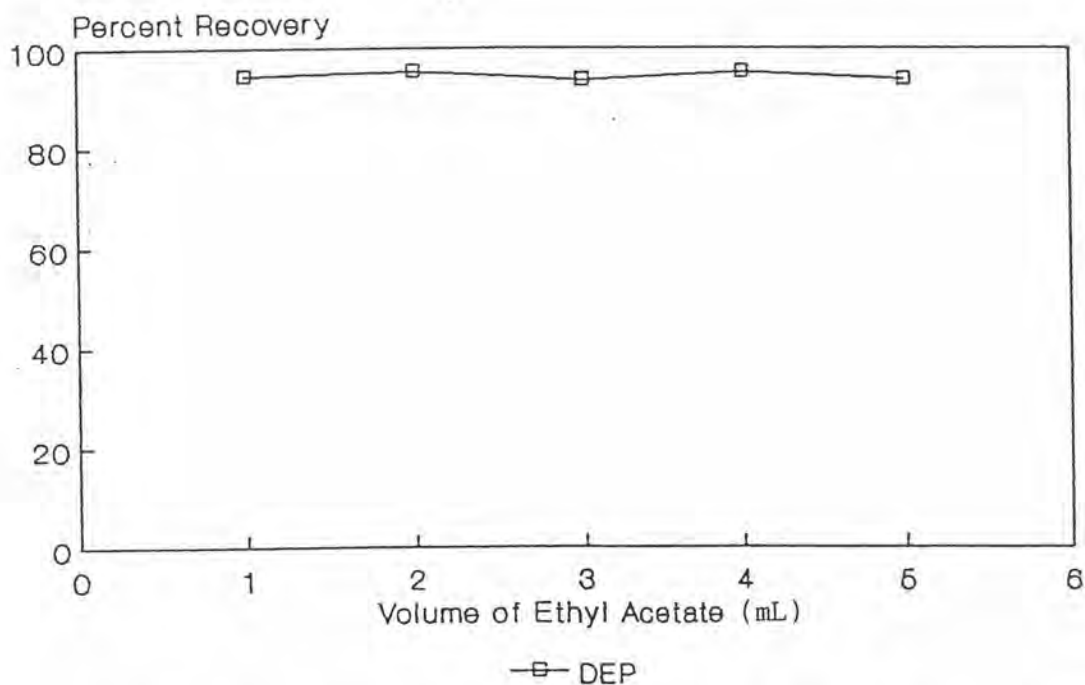


Figure 4.62 The effect of volume of ethyl acetate on the percent recovery of DEP in mixture solution with concentration of aqueous standard solution in higher level of ppm

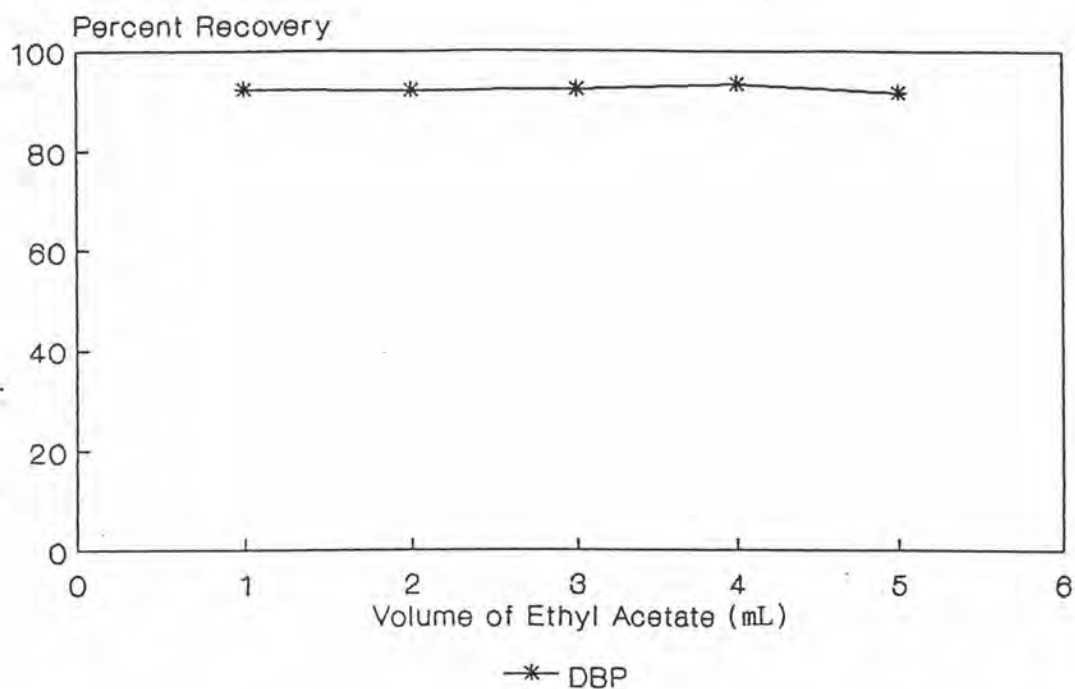


Figure 4.63 The effect of volume of ethyl acetate on the percent recovery of DBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

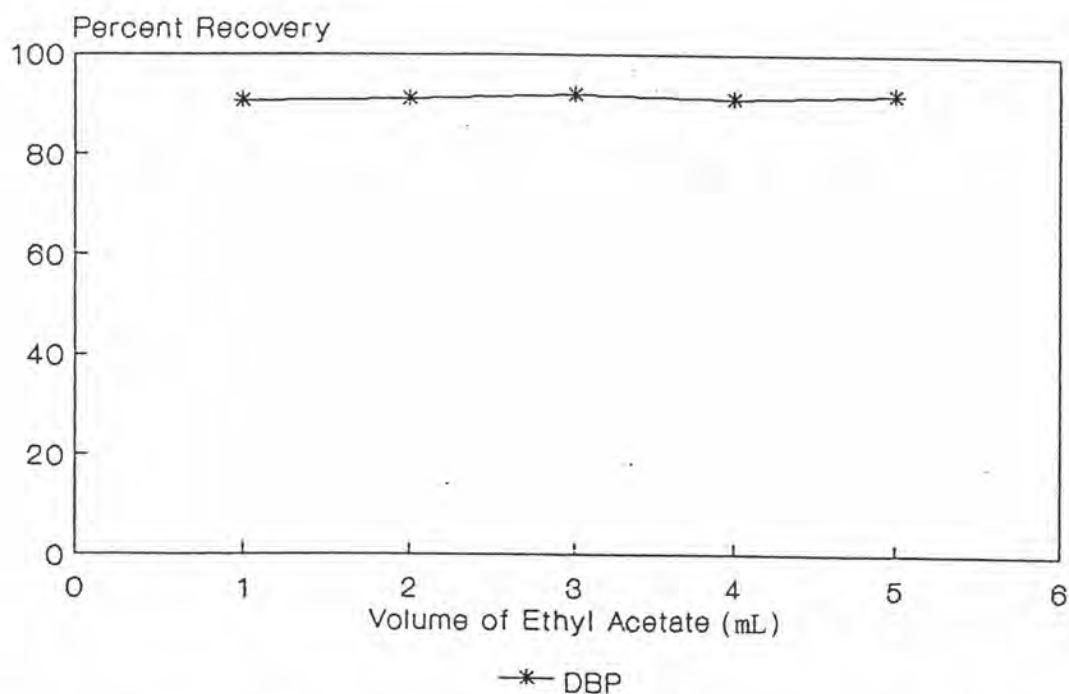


Figure 4.64 The effect of volume of ethyl acetate on the percent recovery of DBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

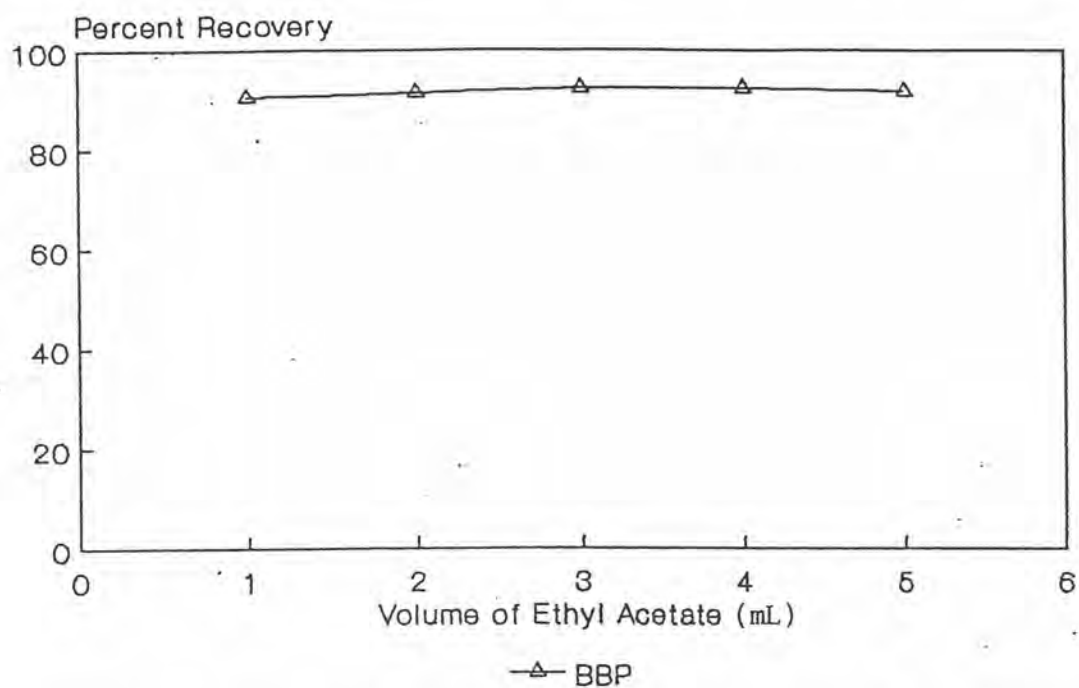


Figure 4.65 The effect of volume of ethyl acetate on the percent recovery of BBP in mixture solution with concentration of aqueous standard solution in lower level of ppm

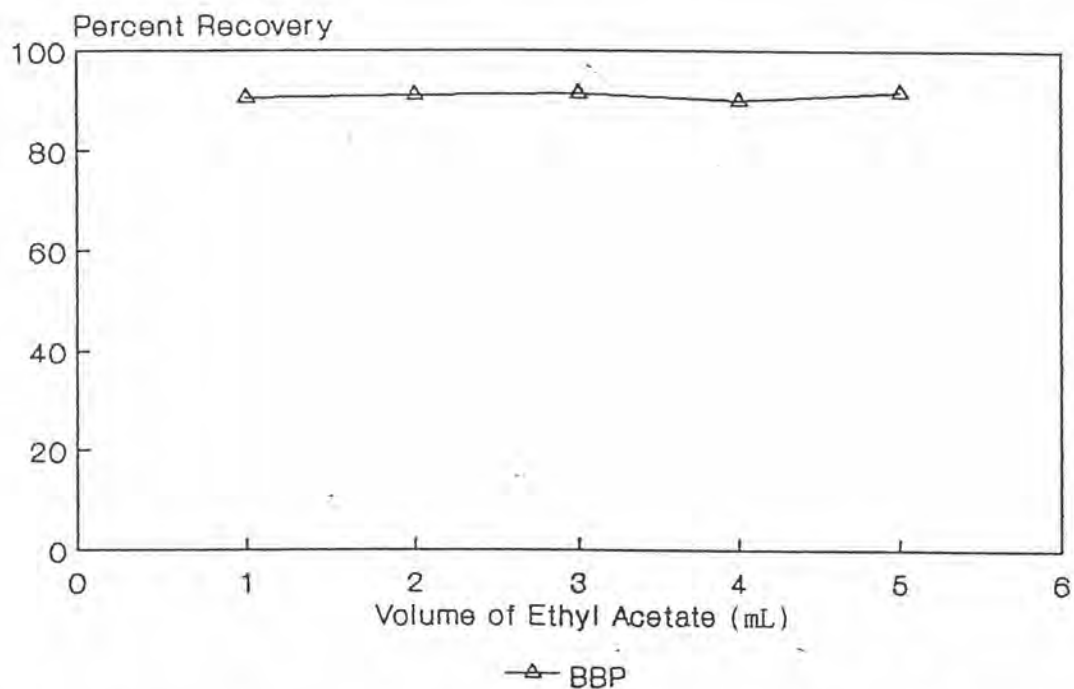


Figure 4.66 The effect of volume of ethyl acetate on the percent recovery of BBP in mixture solution with concentration of aqueous standard solution in higher level of ppm

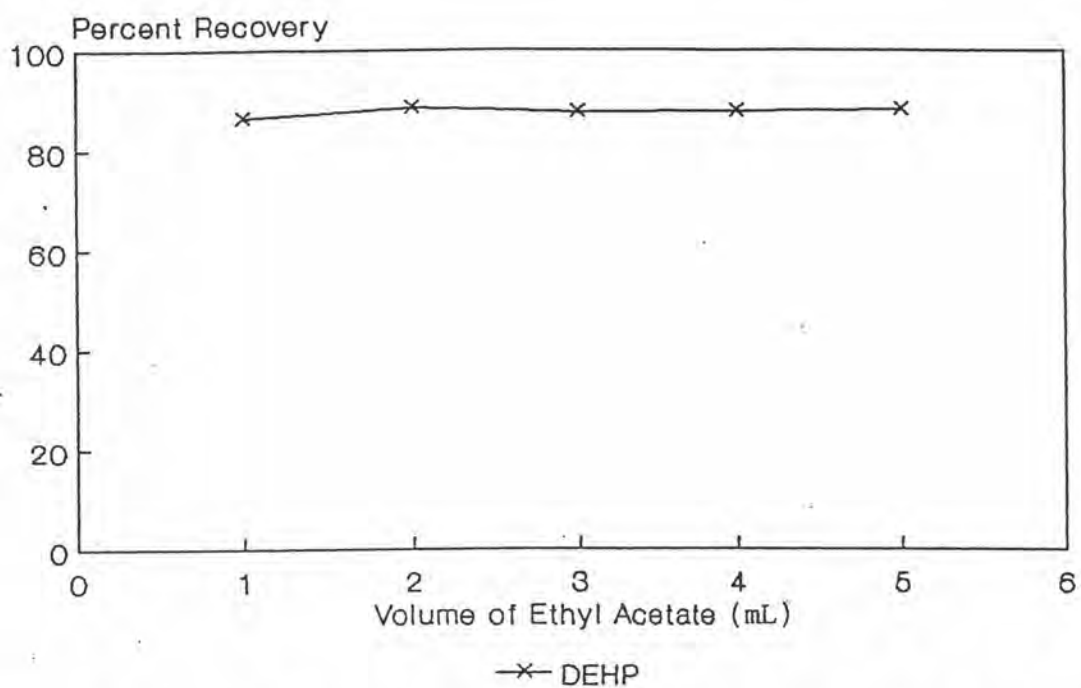


Figure 4.67 The effect of volume of ethyl acetate on the percent recovery of DEHP in mixture solution with concentration of aqueous standard solution in lower level of ppm

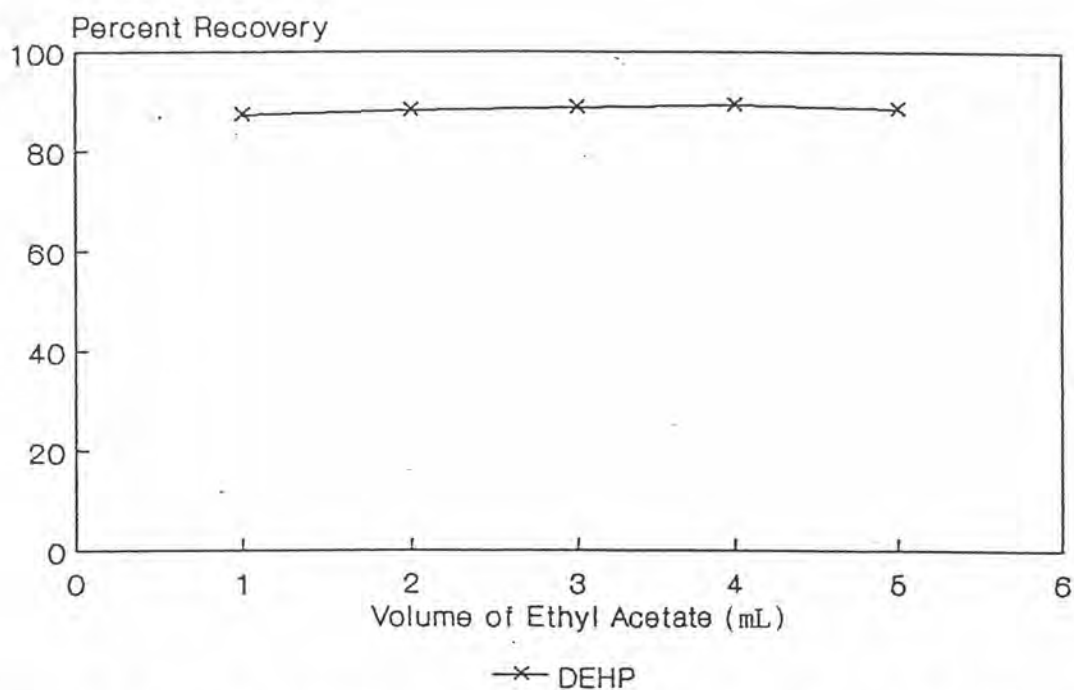


Figure 4.68 The effect of volume of ethyl acetate on the percent recovery of DEHP in mixture solution with concentration of aqueous standard solution in higher level of ppm

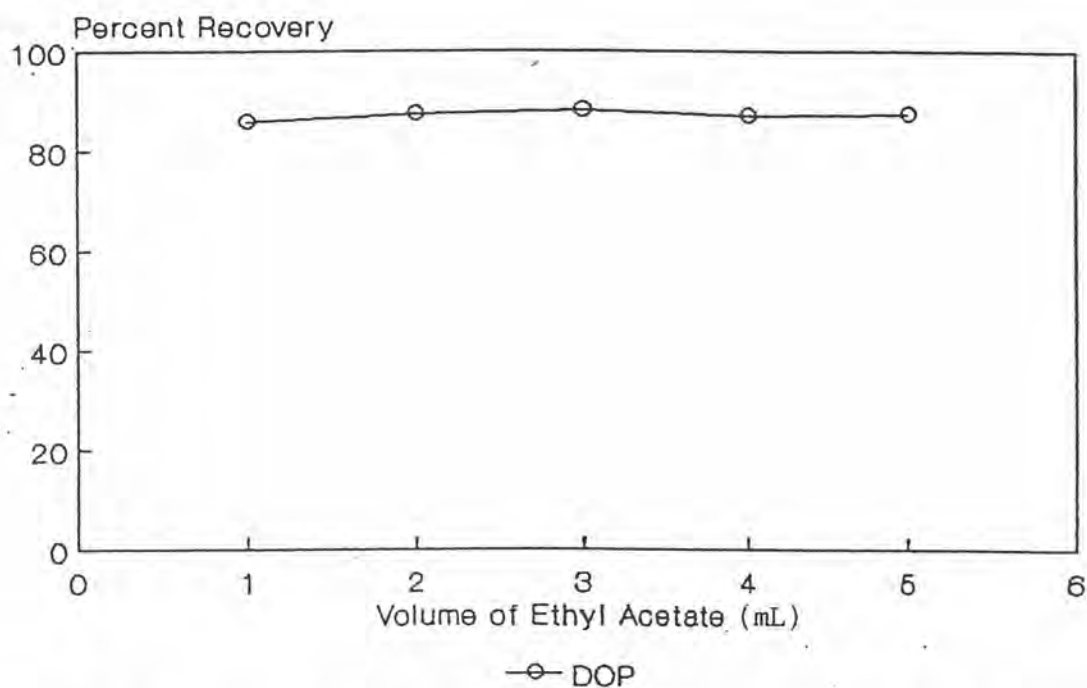


Figure 4.69 The effect of volume of ethyl acetate on the percent recovery of DOP in mixture solution with concentration of aqueous standard solution in lower level of ppm

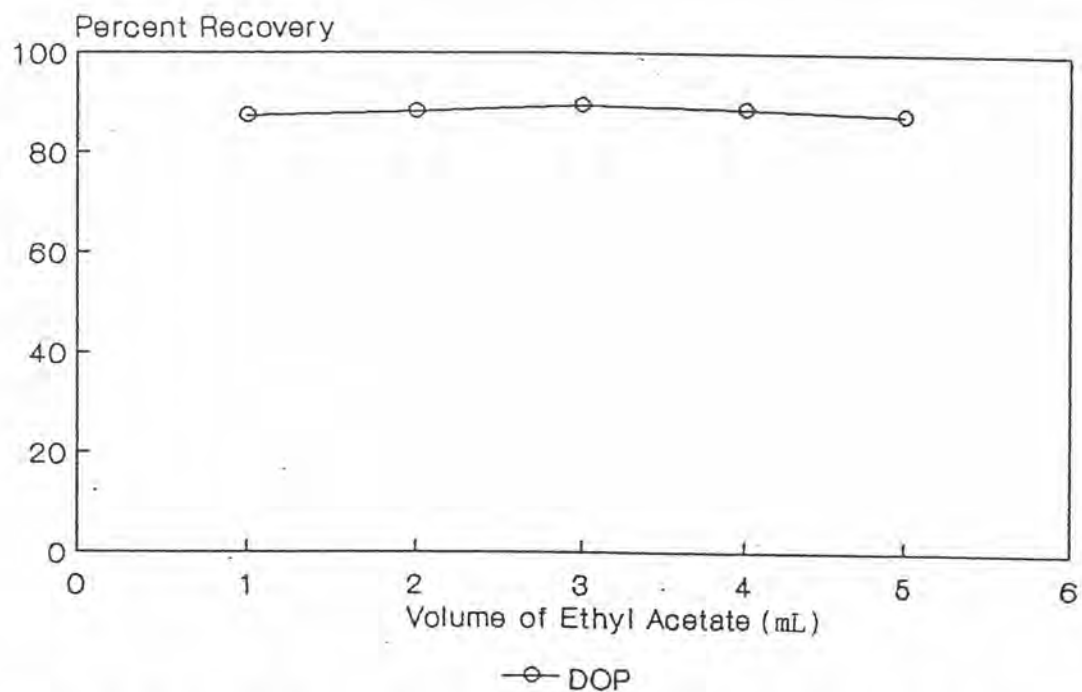


Figure 4.70 The effect of volume of ethyl acetate on the percent recovery of DOP in mixture solution with concentration of aqueous standard solution in higher level of ppm

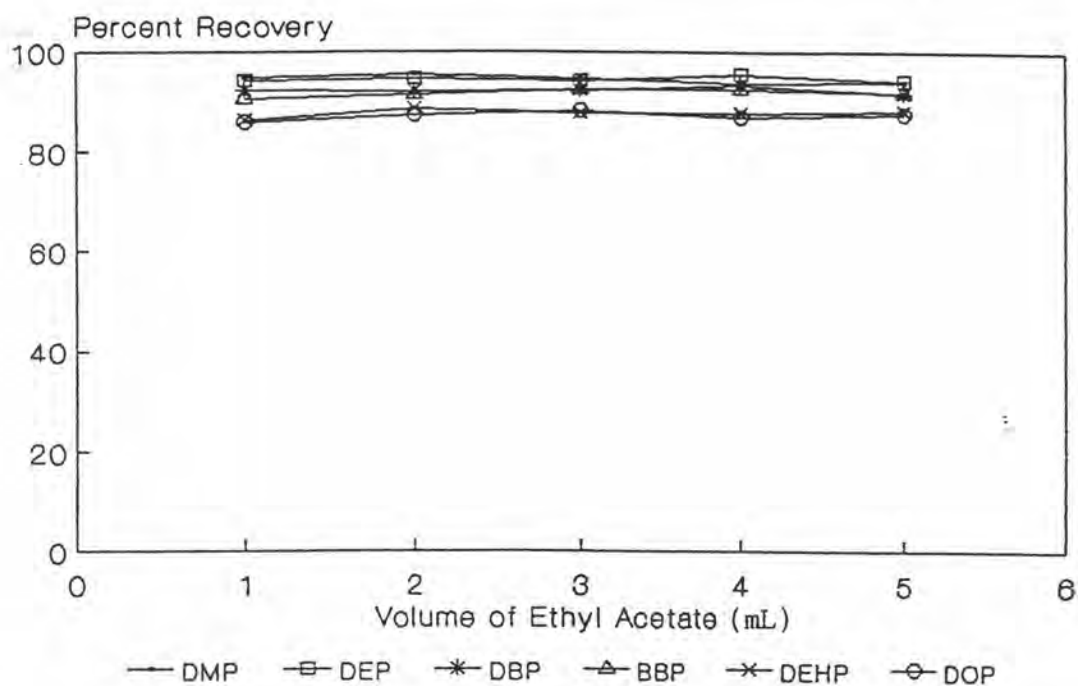


Figure 4.71 The effect of volume of ethyl acetate on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in lower level of ppm

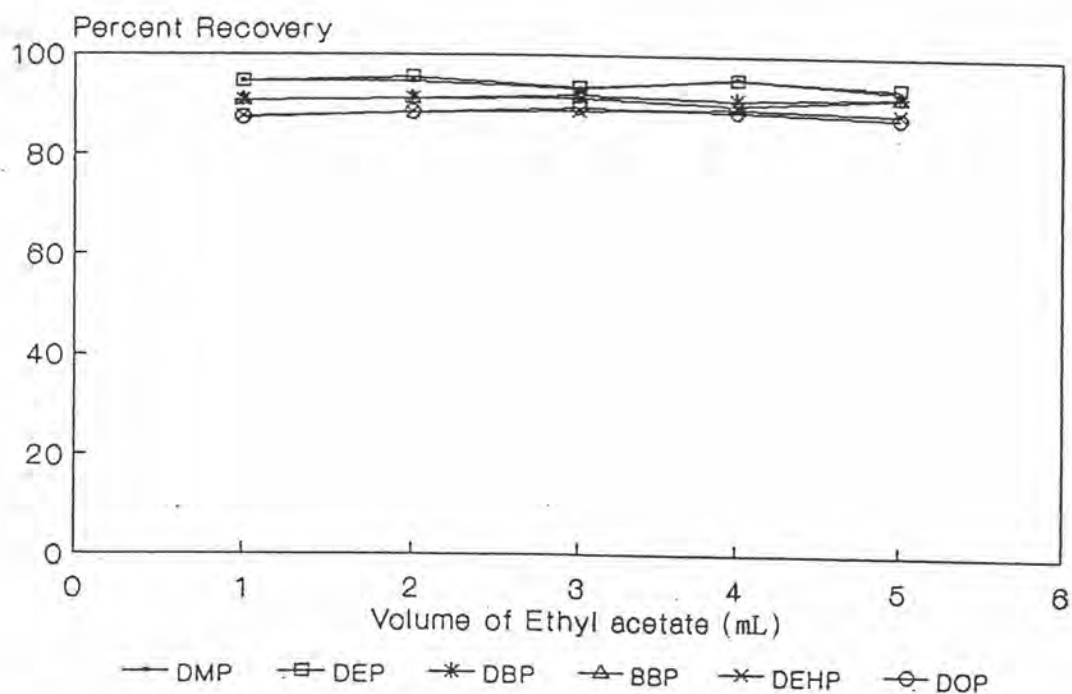


Figure 4.72 The effect of volume of ethyl acetate on the percent recovery of each phthalate ester in mixture solution with concentration of aqueous standard solution in higher level of ppm

4.3.7 The Study of Concentration

The results of the effect of two concentrations of each phthalate ester on the percent recovery in single component and mixture solution for the pH value of 2.0 to 8.0, for the elution solvent, i.e., toluene, ethyl acetate, methylene chloride, isooctane, and hexane, and for the volume of elution solvent of 1.0 to 5.0 mL are shown in Tables 4.5-4.12 and Tables 4.14-4.21, respectively. The graphs correlated to these results are depicted in Figures 4.6-4.33 and Figures 4.41-4.72.

It can be seen that the percent recovery of each phthalate ester in single component and mixture solution at the two different concentrations is insignificantly different. In addition, the percent recovery of each phthalate ester in single component solution is slightly different from the percent recovery of each phthalate ester in mixture solution. This indicates that the percent recovery of each phthalate ester is independent of the concentration of the compound and it is not affected by the presence of the other compounds in water samples.

The optimum conditions for the SPE study of each phthalate ester in aqueous solution are summarized in table 4.22.

Table 4.22 The optimum SPE analysis conditions for determination each phthalate ester in aqueous solution.

Studied Conditions	Optimum value
pH value of extracted solution	2.0
Sorbent mass	500 mg
Elution solvent	Toluene
Volume of elution solvent	≥ 3.0 mL

The optimum SPE analysis conditions are used in the investigation of the method detection limit, the precision, the accuracy and analysis of the real water samples.

4.4 Method Detection Limit (MDL)

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyzes of a sample of a given matrix containing analyte (9,56). The method detection limit of each phthalate ester in aqueous solution was determined by using the optimum SPE analysis conditions in Table 4.22 and the GC condition in Table 4.4. The results of this study are presented in Table 4.23.

Table 4.23 The method detection limit of each phthalate ester in aqueous solution

Phthalate esters	Method detection limit (MDL) (ppb)
Dimethylphthalate (DMP)	1.24
Diethylphthalate (DEP)	1.26
Di-n-butylphthalate (DBP)	0.69
Butylbenzylphthalate (BBP)	0.52
Di(2-ethylhexyl)phthalate (DEHP)	0.51
Di-n-octylphthalate (DOP)	0.68

4.5 The Study of Precision of Solid Phase Extraction Technique for Determination Some Phthalate Esters in Water

Although toluene is the elution solvent to give the highest percent recovery, it is toxic (37,101). Ethyl acetate is less toxic and also gives the high percent recovery. Hence, both of toluene and ethyl acetate are used as elution solvents in this SPE study of precision.

The results of the SPE study of precision of each phthalate ester in water by using toluene as elution solvent are shown in Table 4.24. The average recoveries of DMP, DEP, DBP, BBP, DEHP and DOP are 102.83, 105.24, 96.39, 93.11, 88.22 and 88.01, respectively. The percent relative standard deviation of DMP, DEP, DBP, BBP, DEHP and DOP are 2.19, 1.83, 1.37, 2.66, 2.28 and 2.61, respectively.

The results of the SPE study of precision of each phthalate ester in water by using ethyl acetate as elution solvent are shown in Tables 4.25. The average recoveries of DMP, DEP, DBP, BBP, DEHP and DOP are 95.27, 95.75, 92.03, 91.61, 87.74, and 87.42, respectively. The percent relative standard deviation of DMP, DEP, DBP, BBP, DEHP and DOP are 2.81, 2.64, 1.80, 1.98, 1.59 and 1.97, respectively.

The results of the SPE study of precision of each phthalate ester by using toluene or ethyl acetate as elution solvent can give the good precision. This indicates that ethyl acetate which is less toxic than toluene and also give the high percent recovery can be used as another elution solvent for determination phthalate esters in water.

Table 4.24 The results of precision of SPE technique for determining some phthalate esters in water by using toluene as elution solvent

Compounds		1	2	3	4	5	6	7	8	9	10	Average % recovery	RSD (%)
DMP	Conc. before(ppm)	0.248	0.248	0.248	0.248	0.248	0.248	0.248	0.248	0.248	0.248	102.83	±2.19
	Conc. after(ppm)	12.85	12.72	12.53	12.63	13.08	12.45	13.02	12.70	12.45	13.28		
	% Recovery	103.47	102.38	100.92	101.66	105.28	100.27	104.84	102.29	100.28	106.90		
DEP	Conc. before(ppm)	0.252	0.252	0.252	0.252	0.252	0.252	0.252	0.252	0.252	0.252	105.24	±1.83
	Conc. after(ppm)	13.55	13.42	12.72	13.17	13.45	13.21	13.25	13.01	13.09	13.48		
	% Recovery	107.69	106.69	101.52	104.69	106.88	104.99	105.35	103.44	104.05	107.14		
DBP	Conc. before(ppm)	0.196	0.196	0.196	0.196	0.196	0.196	0.196	0.196	0.196	0.196	96.39	±1.37
	Conc. after(ppm)	9.58	9.39	9.46	9.41	9.22	9.50	9.57	9.31	9.38	9.64		
	% Recovery	97.76	95.91	96.54	95.99	94.06	96.97	97.66	95.03	95.69	98.32		
BBP	Conc. before(ppm)	0.206	0.206	0.206	0.206	0.206	0.206	0.206	0.206	0.206	0.206	93.11	±2.66
	Conc. after(ppm)	9.95	9.89	9.67	9.53	9.43	9.72	9.27	9.87	9.35	9.39		
	% Recovery	96.38	95.79	93.74	92.38	91.37	94.20	89.83	95.66	90.63	91.08		
DEHP	Conc. before(ppm)	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	88.22	±2.28
	Conc. after(ppm)	9.06	9.05	9.09	8.85	8.72	9.19	9.22	8.66	8.79	9.16		
	% Recovery	89.02	88.89	89.33	86.94	85.69	90.31	90.57	85.11	86.38	89.99		
DOP	Conc. before(ppm)	0.273	0.273	0.273	0.273	0.273	0.273	0.273	0.273	0.273	0.273	88.01	±2.61
	Conc. after(ppm)	12.09	11.82	11.63	12.07	11.59	12.41	12.36	11.69	12.29	12.27		
	% Recovery	88.47	86.53	85.15	88.34	84.89	90.83	90.46	85.60	90.02	89.79		

Table 4.25 The results of precision SPE technique for determining some phthalate esters in water by using ethyl acetate as elution solvent

Compounds		1	2	3	4	5	6	7	8	9	10	Average % recovery	RSD (%)
DMP	Conc. before(ppm)	0.248	0.248	0.248	0.248	0.248	0.248	0.248	0.248	0.248	0.248	95.27	±2.81
	Conc. after(ppm)	11.29	11.94	11.82	11.84	11.20	12.07	11.89	12.20	11.93	12.14		
	% Recovery	90.95	96.14	95.14	95.31	90.20	97.16	95.75	98.25	96.07	97.74		
DEP	Conc. before(ppm)	0.252	0.252	0.252	0.252	0.252	0.252	0.252	0.252	0.252	0.252	95.75	±2.64
	Conc. after(ppm)	11.54	11.97	12.17	12.04	11.44	12.28	12.09	12.35	12.21	12.34		
	% Recovery	91.75	95.18	96.74	95.74	90.93	97.63	96.09	98.17	97.09	98.13		
DBP	Conc. before(ppm)	0.196	0.196	0.196	0.196	0.196	0.196	0.196	0.196	0.196	0.196	92.03	±1.80
	Conc. after(ppm)	8.70	8.99	9.02	9.03	9.00	9.10	9.25	8.81	9.16	9.13		
	% Recovery	88.80	91.75	92.05	92.14	91.87	92.85	94.39	89.88	93.48	93.12		
BBP	Conc. before(ppm)	0.206	0.206	0.206	0.206	0.206	0.206	0.206	0.206	0.206	0.206	91.61	±1.98
	Conc. after(ppm)	9.35	9.25	9.50	9.68	9.31	9.17	9.60	9.35	9.22	9.65		
	% Recovery	90.58	89.59	92.07	93.79	90.22	88.87	93.07	90.61	89.32	93.49		
DEHP	Conc. before(ppm)	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	87.74	±1.59
	Conc. after(ppm)	8.77	8.90	8.95	8.75	8.93	9.04	9.14	9.11	8.96	8.76		
	% Recovery	86.13	87.43	87.93	85.92	87.74	88.85	89.80	89.53	88.01	86.09		
DOP	Conc. before(ppm)	0.273	0.273	0.273	0.273	0.273	0.273	0.273	0.273	0.273	0.273	87.42	±1.97
	Conc. after(ppm)	11.61	12.11	11.73	12.25	11.98	11.64	12.07	12.26	11.90	11.86		
	% Recovery	84.96	88.64	85.90	89.69	87.69	85.22	88.36	89.77	87.14	86.84		

4.6 The Accuracy of Solid Phase Extraction Technique

The accuracy of SPE technique is investigated by comparing the concentration of each phthalate ester obtained from the analysis of synthetic unknown mixture solution with their true concentrations. The results obtained from the study are presented in Table 4.26. The percent error for determination of DMP, DEP, DBP, BBP, DEHP and DOP in synthetic unknown mixture solution are 1.71, 2.55, 1.79, 1.90, 1.51 and 1.01, respectively.

The results obtained from the above studies indicated that the SPE technique gives the good precision and good accuracy and the method detection limit is found to be lower in the ppb level. Therefore, the SPE technique is the best alternative technique for determination of phthalate esters in water samples.

Table 4.26 The results of the checked accuracy for SPE technique

Phthalate esters	Concentration (ppm)		% Error	% RSD
	True	Experiment		
DMP	0.2981	0.3018	1.24	± 1.38
DEP	0.3019	0.3018	0.03	± 1.52
DBP	0.2352	0.2355	0.12	± 0.96
BBP	0.2889	0.2877	0.41	± 3.79
DEHP	0.2443	0.2492	2.00	± 3.56
DOP	0.4371	0.4339	0.73	± 2.26

Triplicate analyzes

4.7 The Determination of Phthalate Esters in Real Water Samples

Fifteen collected water samples (see section 3.13) are concentrated by the SPE technique developed in this study and analyzed by the optimum conditions of SPE shown in Table 4.22 and gas chromatographic condition presented in Table 4.4 for determination of phthalate esters in real water samples. The gas chromatograms of the unknown water samples with dibutylsebacate as internal standard are shown in Figures 4.74(A)-4.88(A).

The retention times (t_r) of the unknown peaks obtained from the gas chromatograms of unknown water samples are compared with the retention times of the standard mixture of the phthalate ester peaks as shown in the chromatogram in Figure 4.73. It is found that sample 3 and sample 15 seem to have a peak with the same retention times of DEP, DBP and BBP. Sample 8 to sample 14 seem to have a peak with the same retention time of DEP and DBP. Sample 4 and sample 7 seem to have a peak with the same retention times of DEP. Sample 5 and sample 6 seem to have a peak with the same retention times of DBP. Sample 1 and sample 2 do not have any interested phthalate esters. To confirm this result, the samples are spiked with the standard mixture solution of the interested phthalate esters and then they are analyzed under the identical analysis condition. The gas chromatograms of the spiked samples are shown in Figures 4.74(B)-4.88(B). It can be seen that the samples having the suspected peaks appeared at the same time as the peaks of phthalate ester standard.

The phthalate esters found in collected water samples are then determined by means of internal standardization methods as mentioned in section 3.9 and the concentrations of the component are listed in Table 4.27.

To confirm the structure of phthalate esters found in collected water samples, the extracts of Samparn coconut water and the river Chao Phya (at Prapadang Pier) using C₁₈ SPE cartridges are selected to inject in GC/MSD under GC/MSD conditions in Table 3.3. The total ion chromatograms of these samples are shown in Figure 4.89 and 4.93 and the mass spectrums of the suspected peak in total ion chromatograms are shown in Figures 4.90-4.92 and Figures 4.94-4.96. It can be seen that the suspected peaks of DEP, DBP and BBP in these samples are found as indicated by the mass spectrum of these samples having the same pattern as of DEP, DBP and BBP by means of library search. The suspected peak with retention time of 7.79 min. in total ion chromatogram of a Samparn coconut water sample (Figure 4.89) is scanned and the mass spectrum is displayed in Figure 4.90(A). This mass spectrum has the same pattern as DEP from the library search as displays in Figure 4.90(B). Therefore, the suspected peak with retentime of 7.79 min. is DEP. The other suspected peaks can be identified by means of library search. It can be concluded that the peaks in total ion chromatogram of the Samparn coconut water sample in Figure 4.89 with retetion time of 7.79, 9.61 and 12.03 min. are DEP, DBP and BBP, respectively. The peaks in total ion chromatogram of the Chao Phya River in Figure 4.93 with retention time of 7.79, 9.60 and 12.02 min. are DEP, DBP and BBP, respectively.

Table 4.27 The concentration of phthalate esters in fifteen water samples collected from several places.

No	Sample	Concentration of phthalate esters (ppm)					
		DMP	DEP	DBP	BBP	DEHP	IXOP
1	Prasobchok - drinking water	ND	ND	ND	ND	ND	ND
2	Springkle - drinking water	ND	ND	ND	ND	ND	ND
3	Samparn coconut water in plastic bag	ND	0.024 ±4.23	0.151 ±3.95	0.024 ±4.19	ND	ND
4	Tap water from chemistry building 3 of Chulalongkorn University	ND	0.316 ±2.79	ND	ND	ND	ND
5	Tap water from Municipal Water Authorithies (Samsen)	ND	ND	0.012 ±2.68	ND	ND	ND
6	Tap water from Bangsue residence area	ND	ND	0.018 ±2.71	ND	ND	ND

Table 4.27 (Cont.)

No	Sample	Concentration of phthalate esters (ppm)					
		DMP	DEP	DBP	BBP	DEHP	DOP
7	Tap water from Thonburi residence area	ND	0.667 ±1.71	ND	ND	ND	ND
8	Water from Chulalongkorn University pool (near Phyathai Road)	ND	1.92 ±2.58	0.028 ±2.35	ND	ND	ND
9	Water from Chulalongkorn University Pool (near Botany building)	ND	0.256 ±2.64	0.043 ±2.33	ND	ND	ND
10	Water from Suan Lum pool	ND	0.474 ±1.91	0.028 ±2.03	ND	ND	ND
11	Water from Klong Prapa Samsen	ND	0.027 ±2.48	0.084 ±1.50	ND	ND	ND

Table 4.27 (Cont.)

No	Sample	Concentration of phthalate esters (ppm)					
		DMP	DEP	DBP	BBP	DEHP	DOP
12	Water from Klong Premprachakorn	ND	0.334 ±2.84	0.050 ±2.51	ND	ND	ND
13	Water from Klong Phadungkrunkasem	ND	0.299 ±2.24	0.036 ±1.74	ND	ND	ND
14	Water from Chao Phya River (Siphya Pier)	ND	0.392 ±2.91	0.051 ±2.55	ND	ND	ND
15	water from Chao Phya River (Prapadang Pier)	ND	0.028 ±3.06	0.071 ±2.63	0.023 ±2.84	ND	ND

Remark : DMP = Dimethylphthalate

DEP = Diethylphthalate

DBP = Dibutylphthalate

ND = Not detectable

BBP = Butylbenzylphthalate

DEHP = Di(2-ethylhexyl)phthalate

DOP = Di-n-octylphthalate

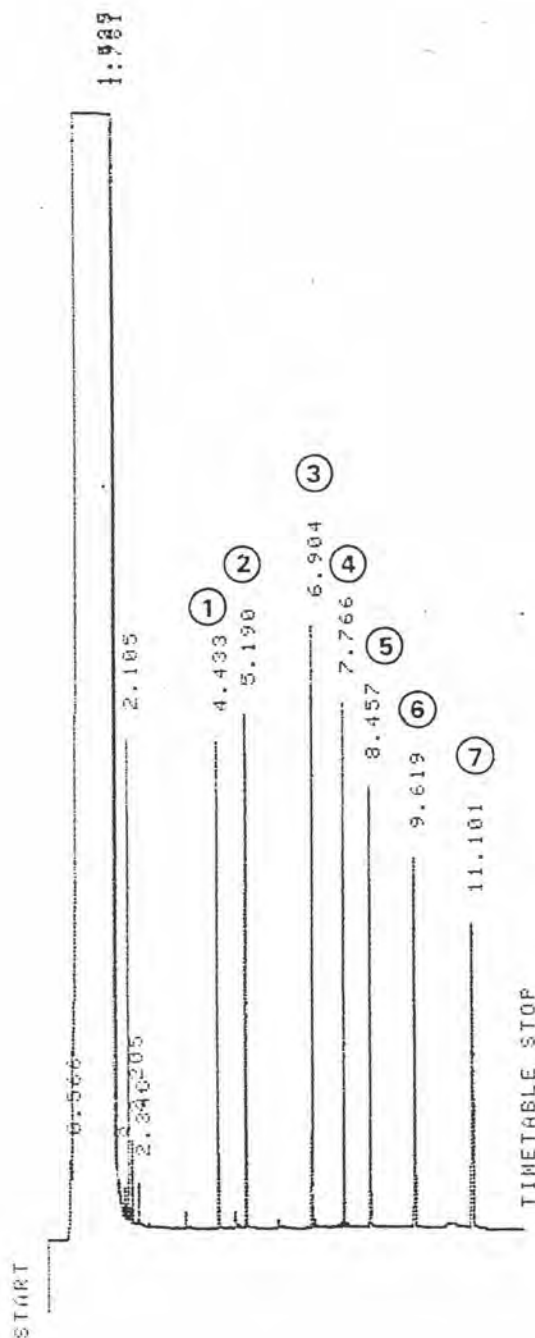


Figure 4.73 The gas chromatogram of standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

Concentration of the Component :

(1) Dimethylphthalate (DMP)	7.62	ppm
(2) Diethylphthalate (DEP)	7.67	ppm
(3) Di-n-butylphthalate (DBP)	6.04	ppm
(4) Dibutylsebacate (DBS)	4.88	ppm
(5) Butylbenzylphthalate (BBP)	6.30	ppm
(6) Di(2-ethylhexyl)phthalate (DEHP)	6.08	ppm
(7) Di-n-octylphthalate (DOP)	8.22	ppm

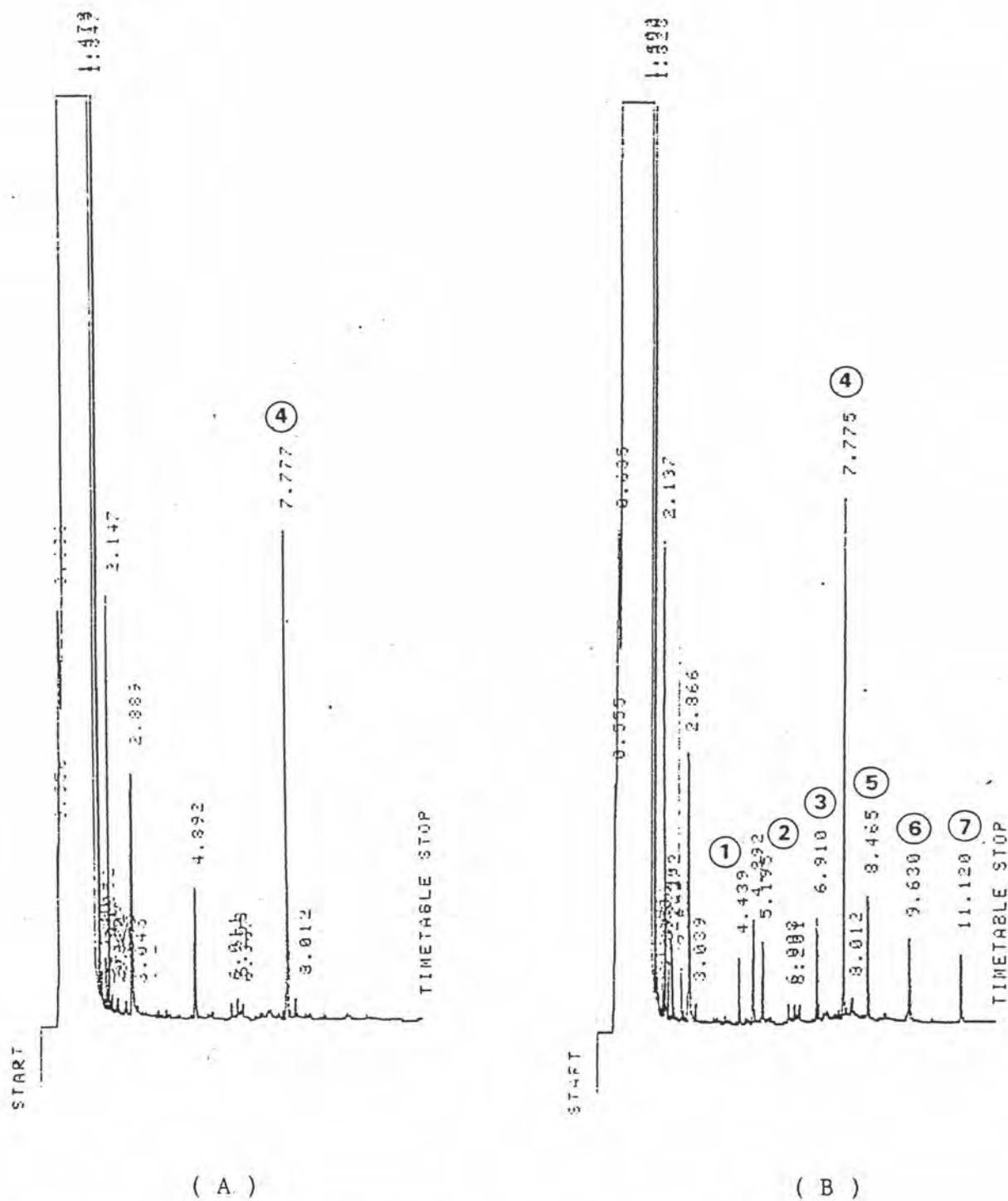


Figure 4.74 The gas chromatogram of

(A) sample 1

(B) sample 1 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

sample 1 = Prasobchok - drinking water

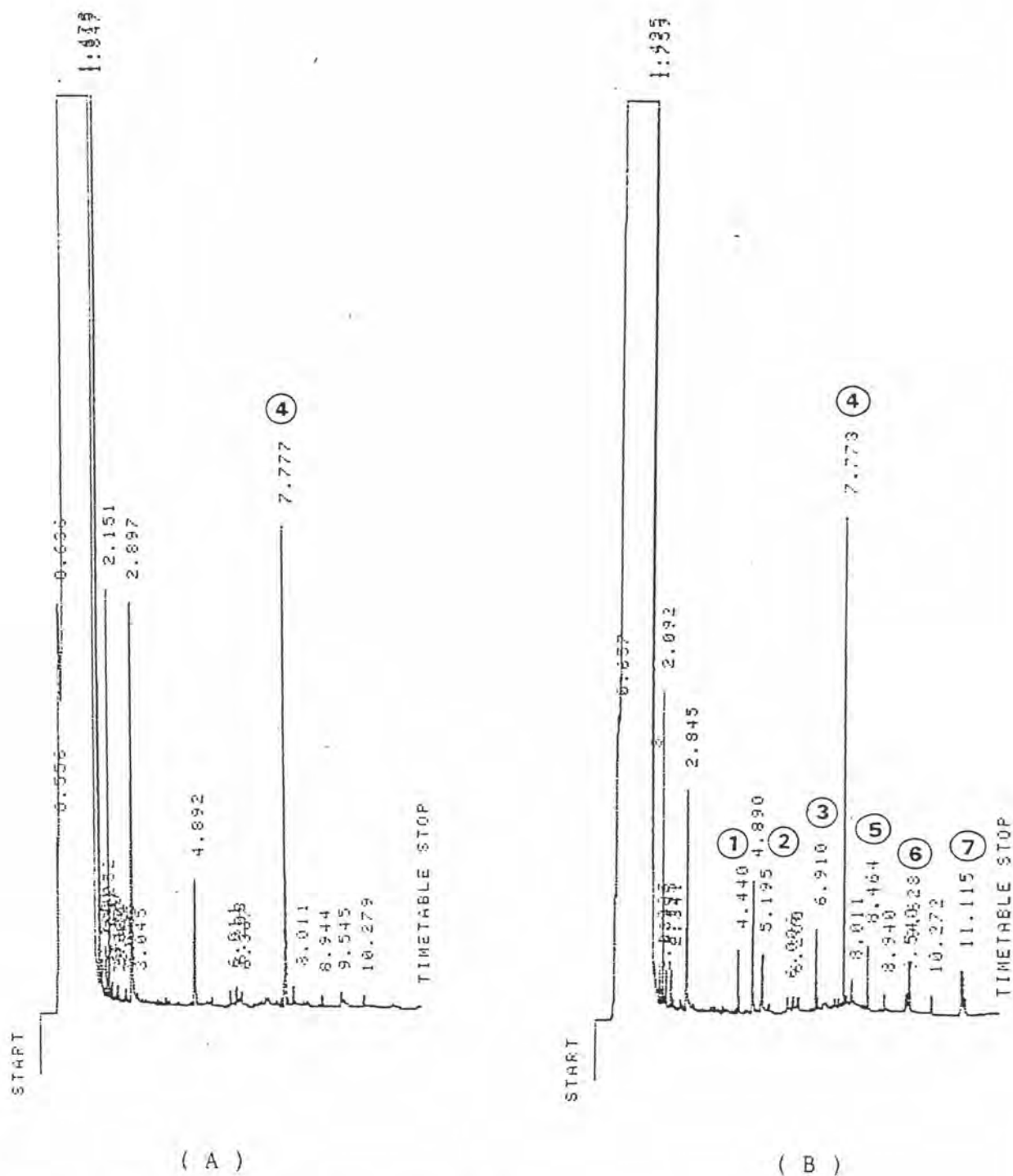


Figure 4.75 The gas chromatogram of

(A) sample 2

(B) sample 2 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

sample 2 = Sprinkle - drinking water

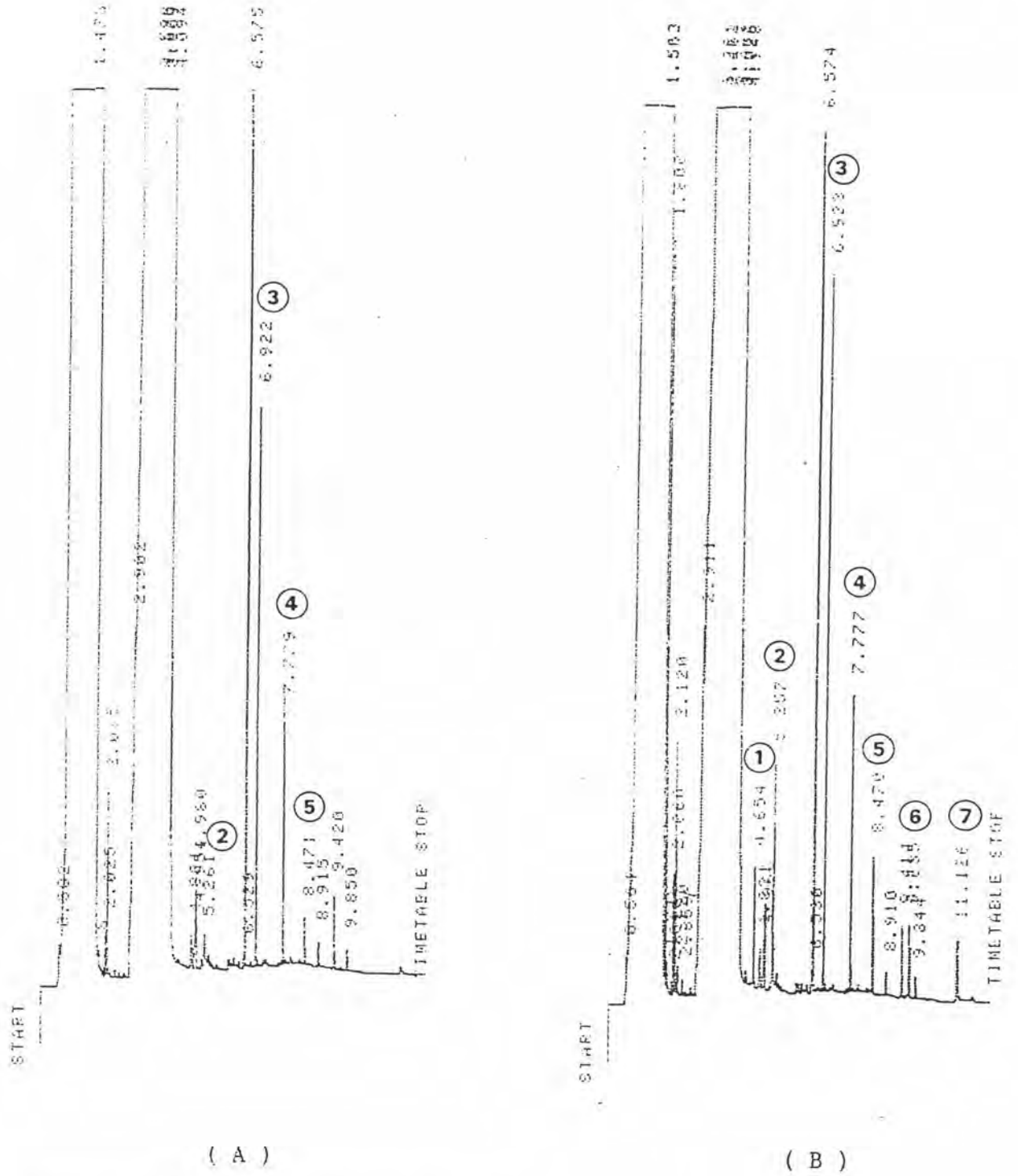


Figure 4.76 The gas chromatogram of

(A) sample 3

(B) sample 3 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample 3 = Sampran coconut water in plastic bag

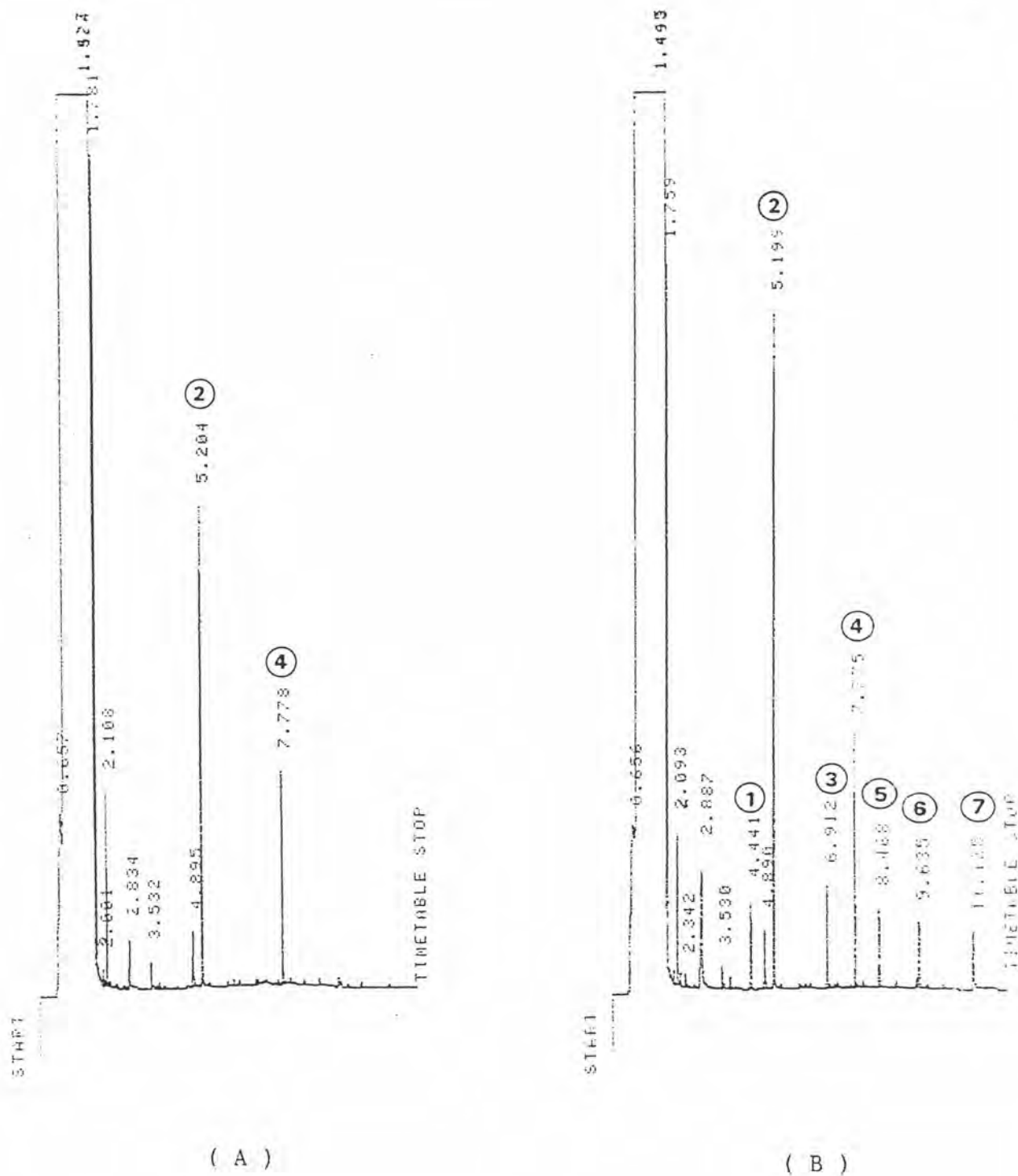


Figure 4.77 The gas chromatogram of

(A) sample 4

(B) sample 4 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample = Tap water from chemistry building 3 of
Chulalongkorn University

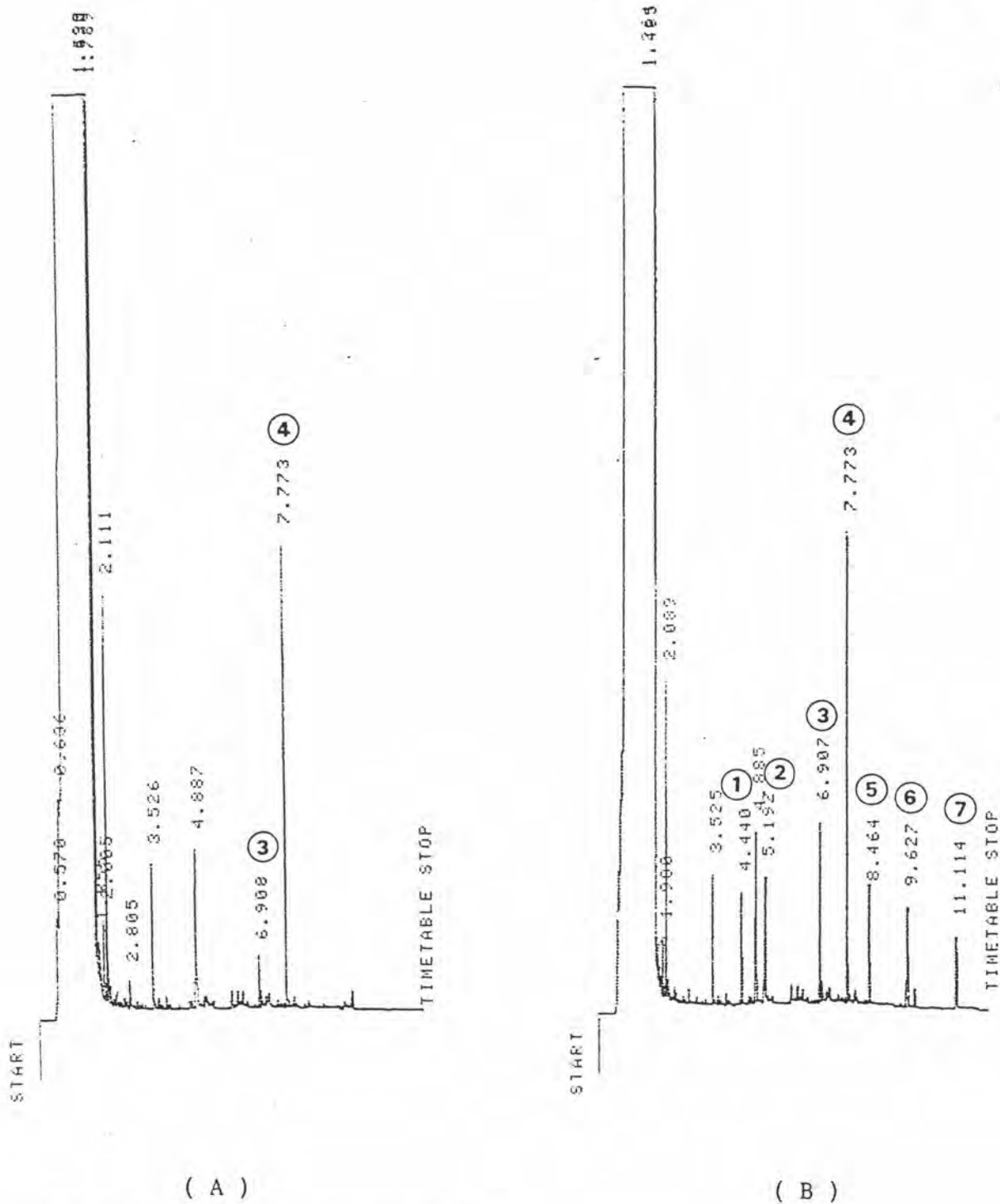


Figure 4.78 The gas chromatogram of

(A) sample 5

(B) sample 5 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

sample 5 = Tap water from Municipal water
Authorities (Samsen)

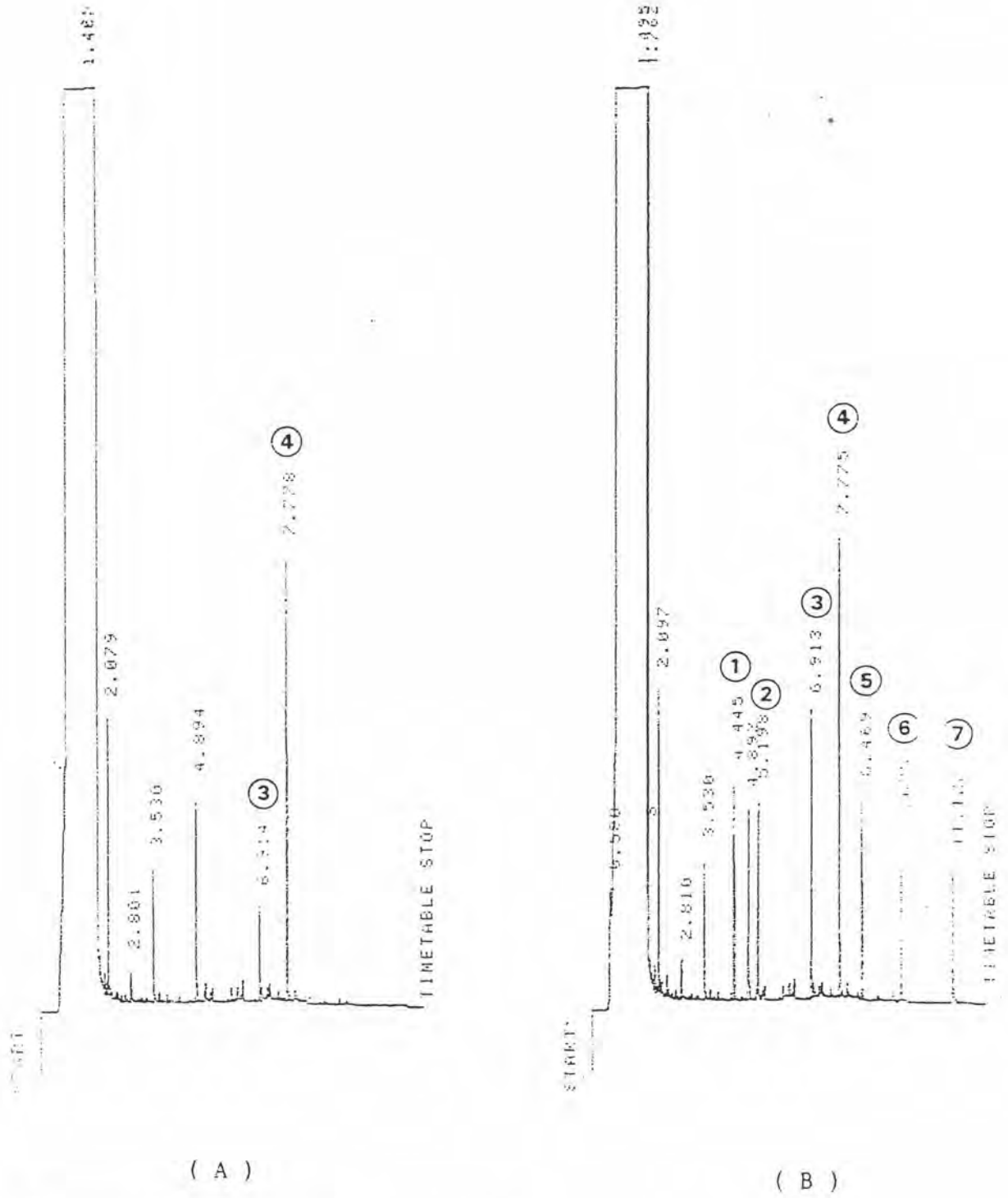


Figure 4.79 The gas chromatogram of

(A) sample 6

(B) sample 6 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

sample 6 = Tap water from Bangsue residence area

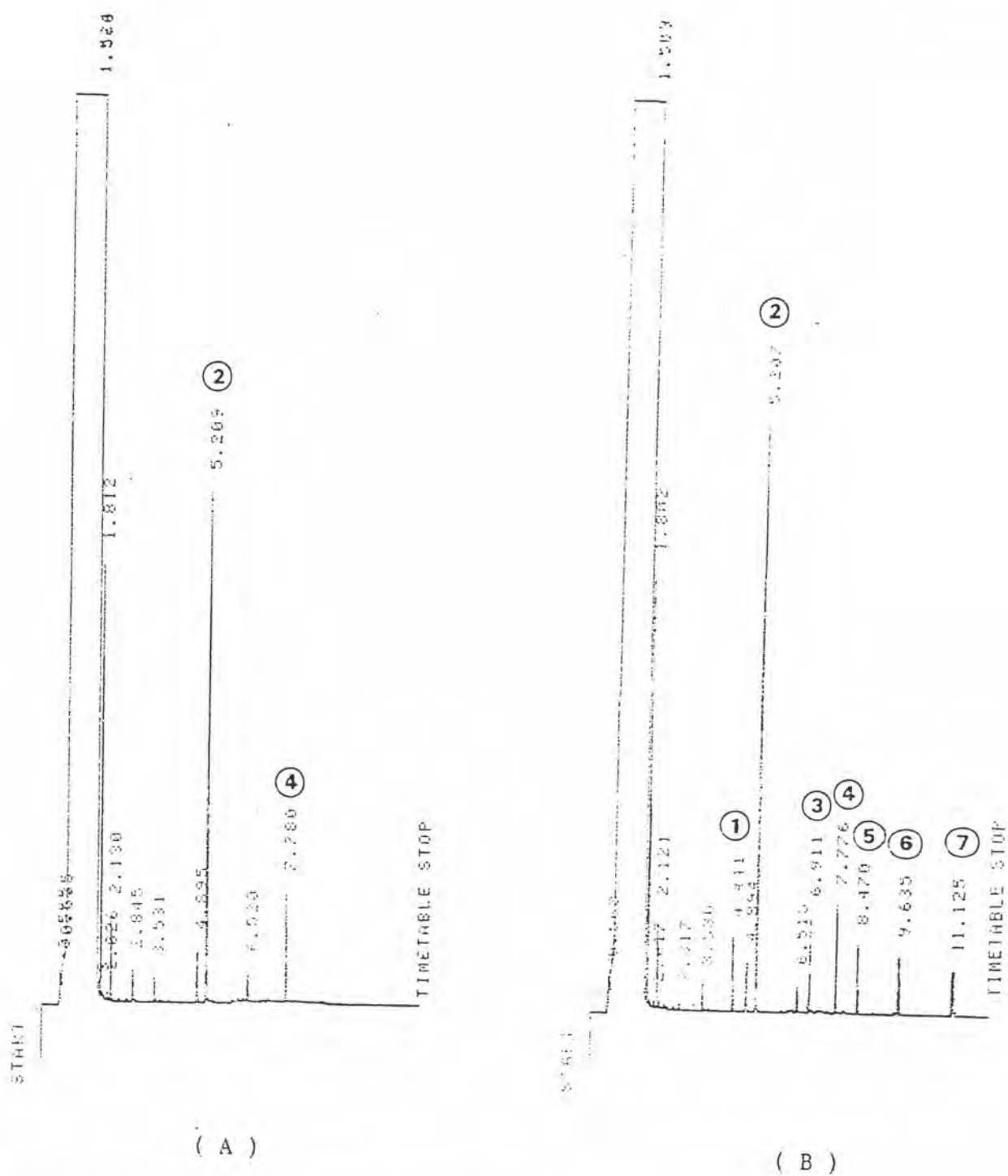


Figure 4.80 The gas chromatogram of

(A) sample 7

(B) sample 7 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 4

sample 7 = Tap water from Thonburi residence area

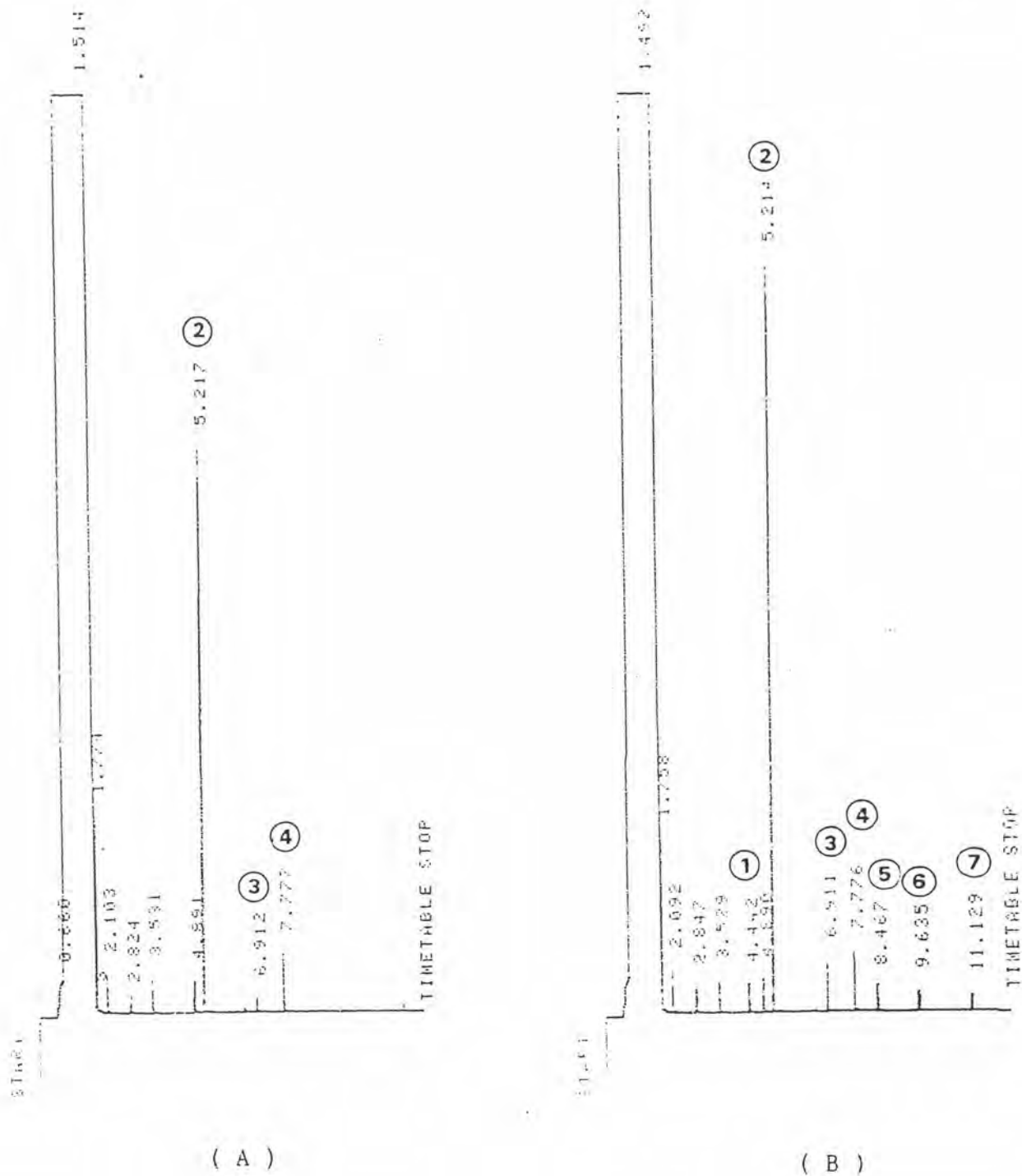


Figure 4.81 The gas chromatogram of

(A) sample 8

(B) sample 8 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 5

sample 8 = Water from Chulalongkorn University pool
near Phayathai Road

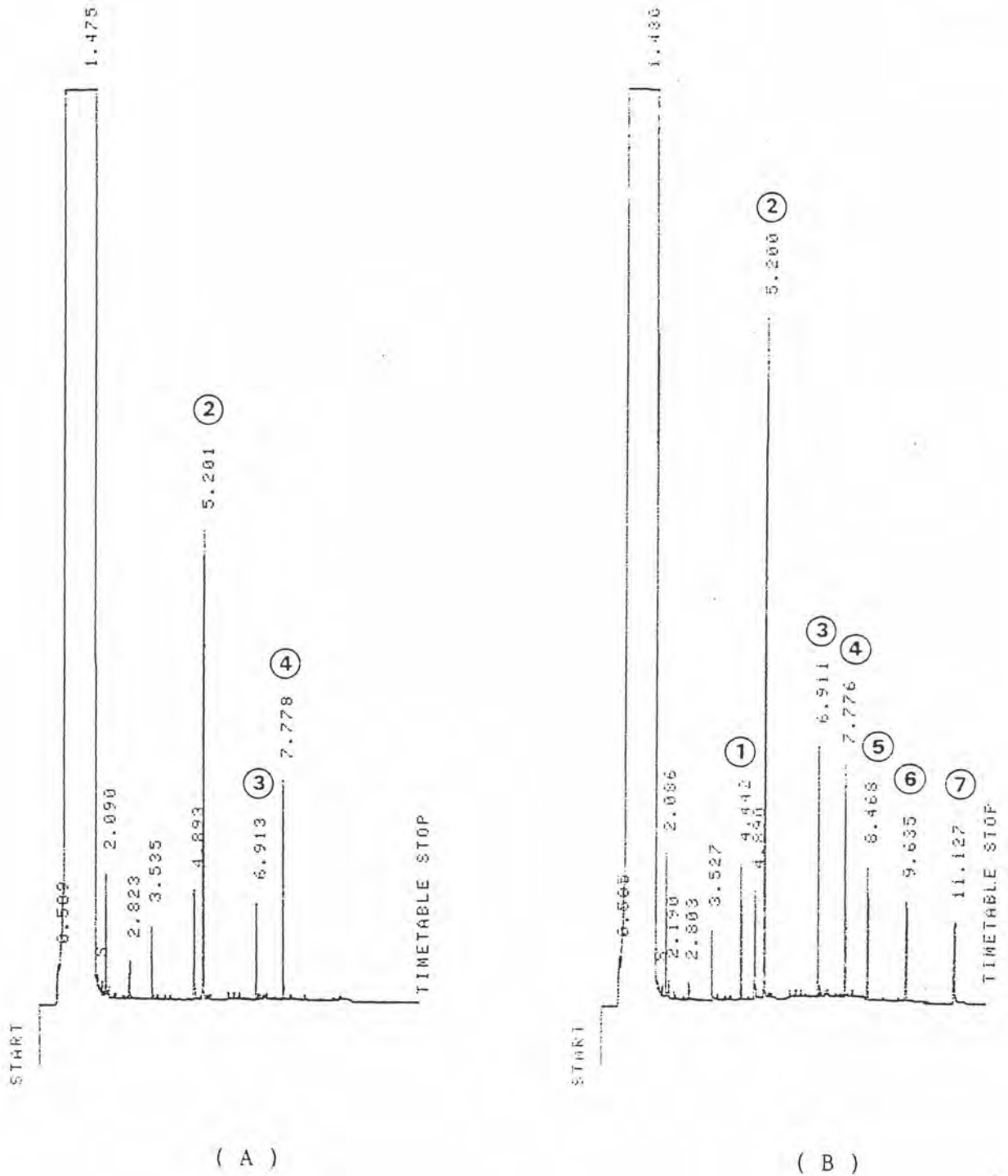


Figure 4.82 The gas chromatogram of

(A) sample 9

(B) sample 9 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample 9 = Water from Chulalongkorn University pool
near Botany building

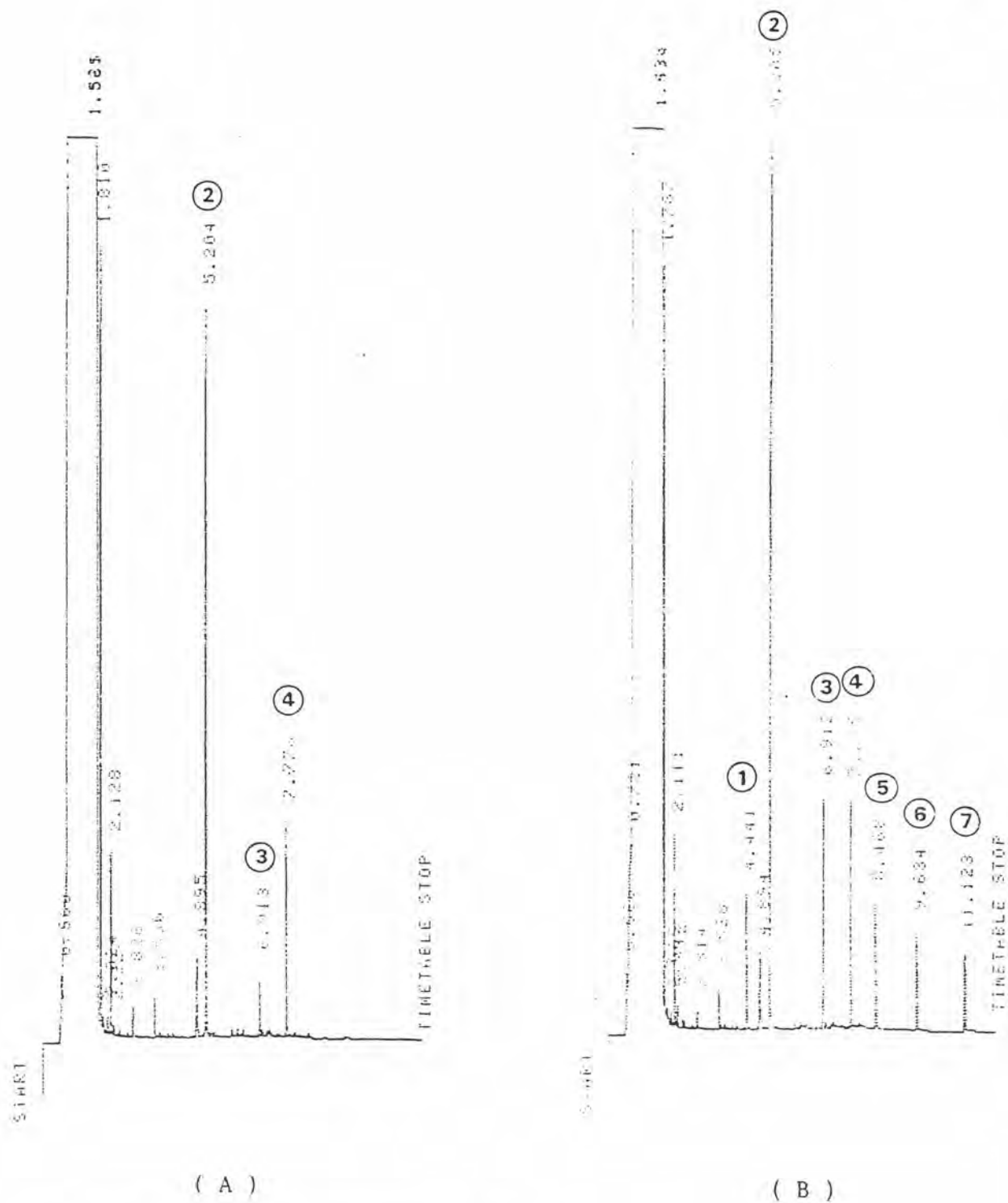


Figure 4.83 The gas chromatogram of

(A) sample 10

(B) sample 10 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample 10 = Water from Suan Lum pool

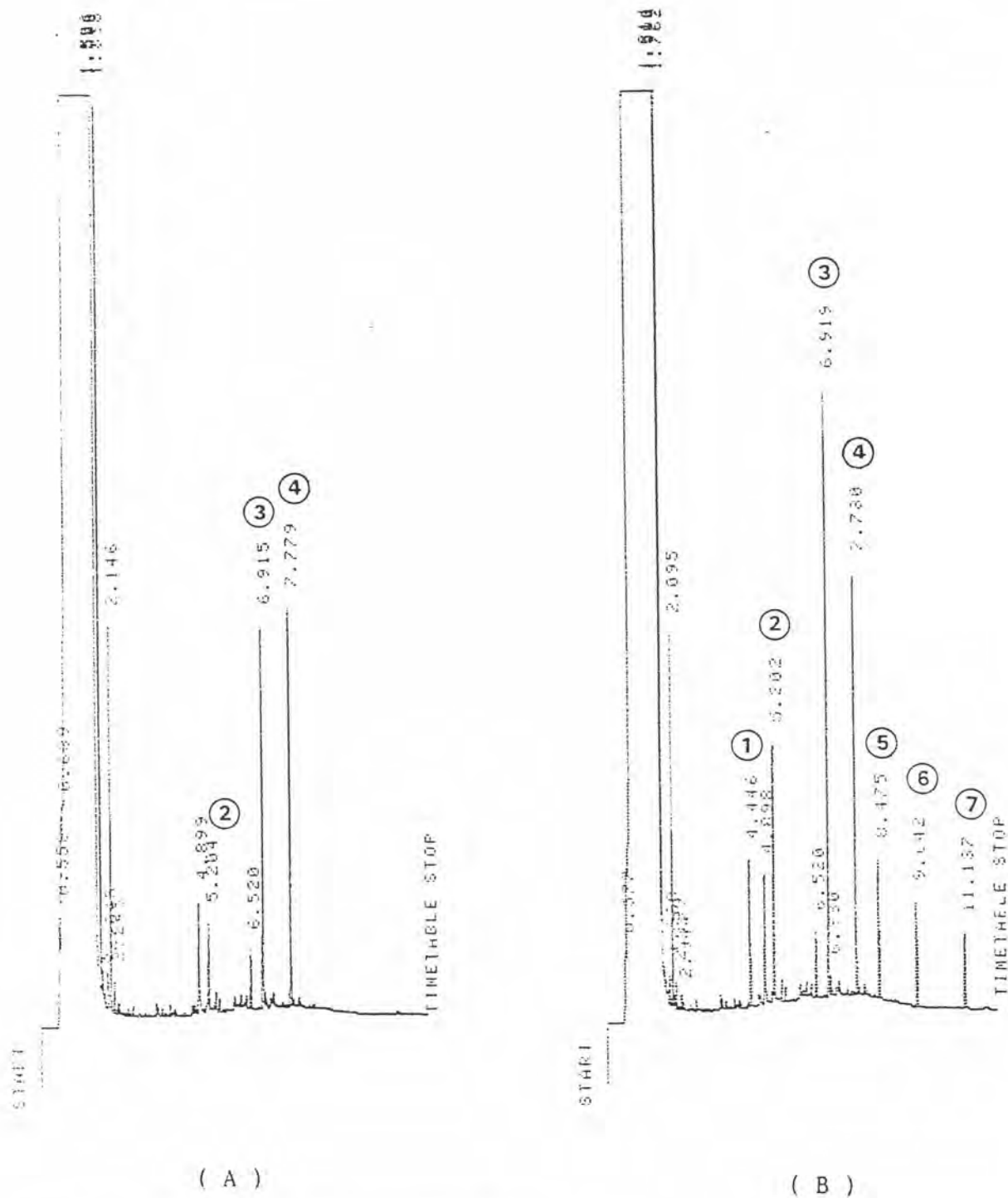


Figure 4.84 The gas chromatogram of

(A) sample 11

(B) sample 11 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

sample 11 = Water from Klong Prapa Samsen

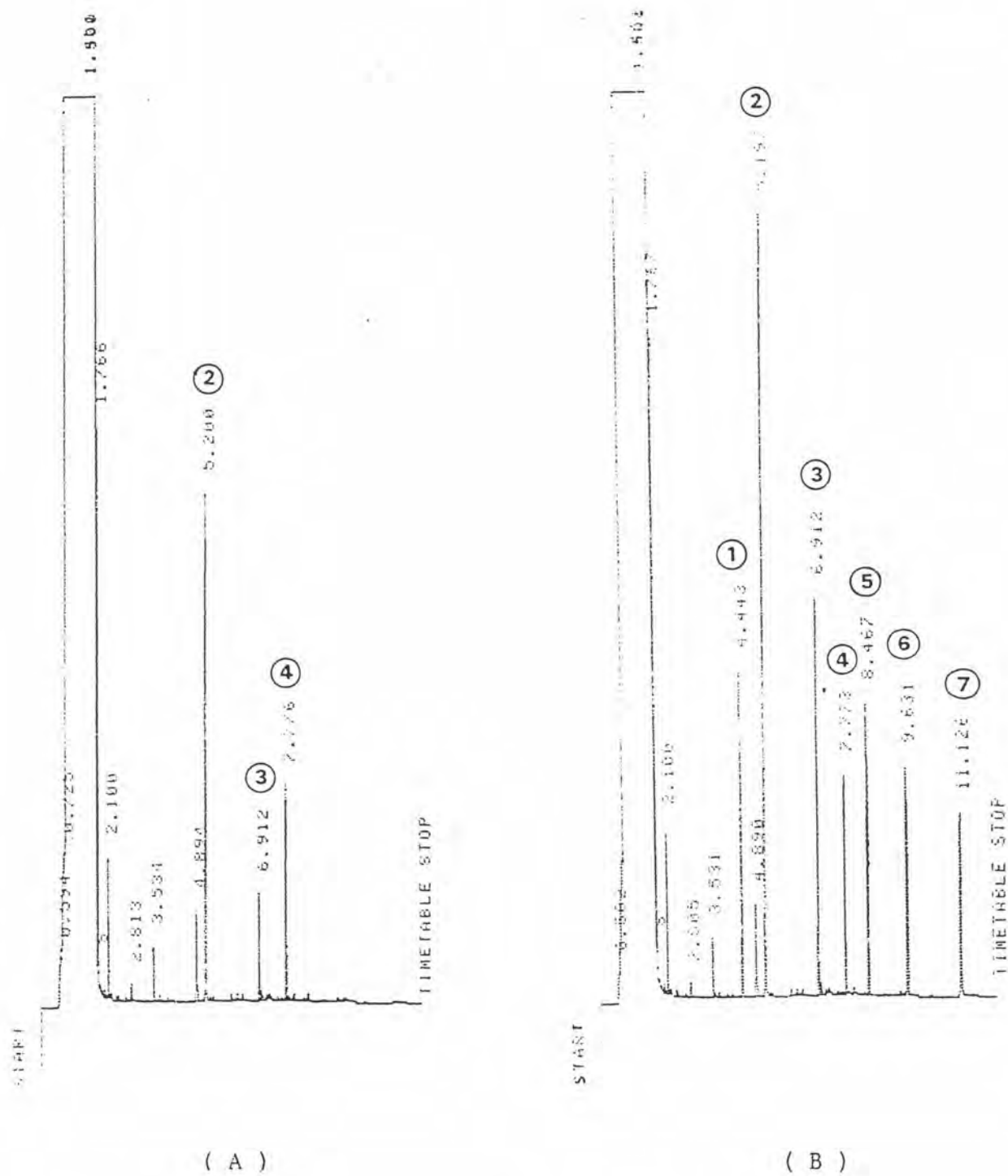


Figure 4.85 The gas chromatogram of

(A) sample 12

(B) sample 12 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample 12 = Water from Klong Premprachakorn

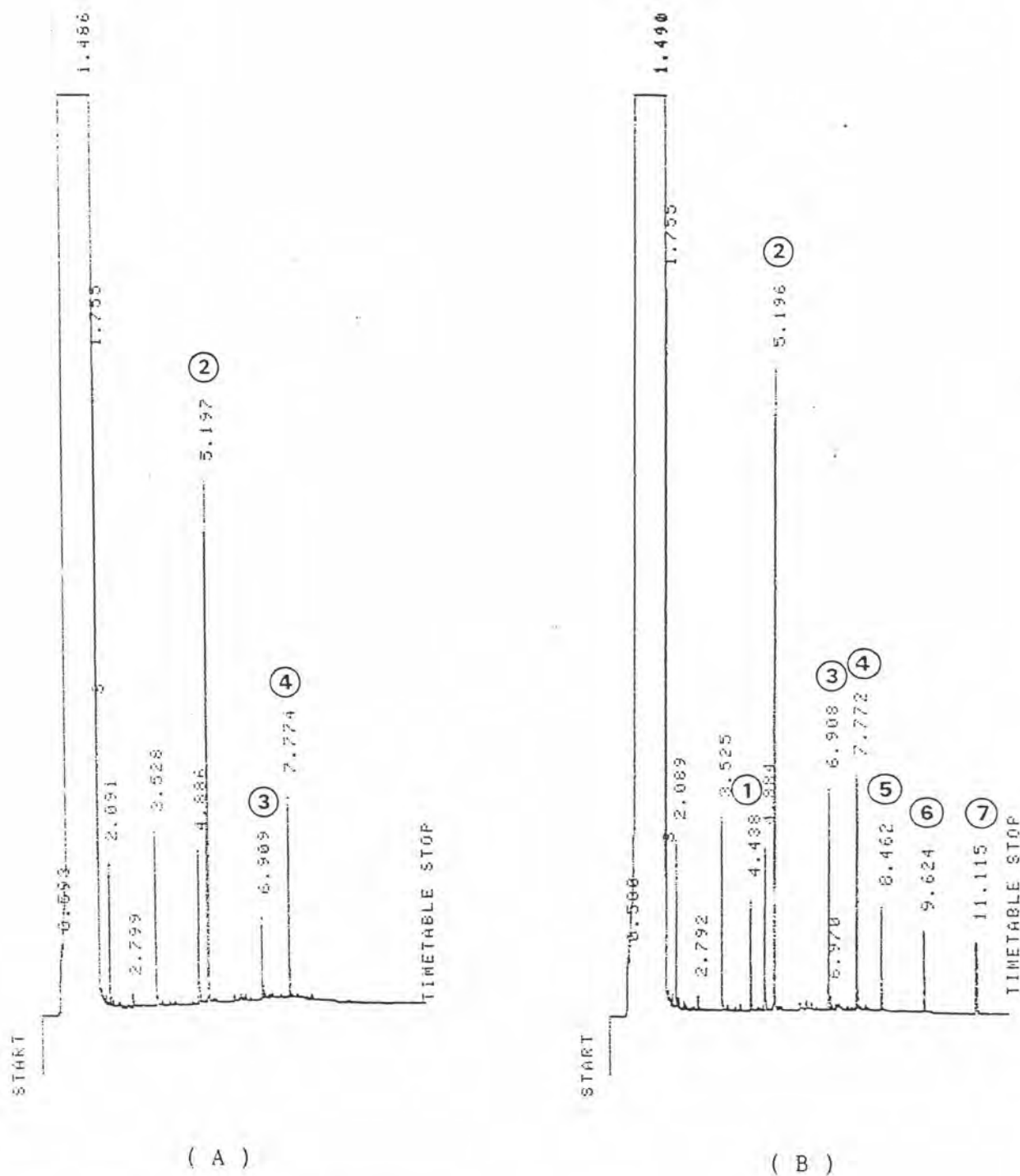


Figure 4.86 The gas chromatogram of

(A) sample 13

(B) sample 13 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample 13 = Water from Klong Phadungkrunkasem

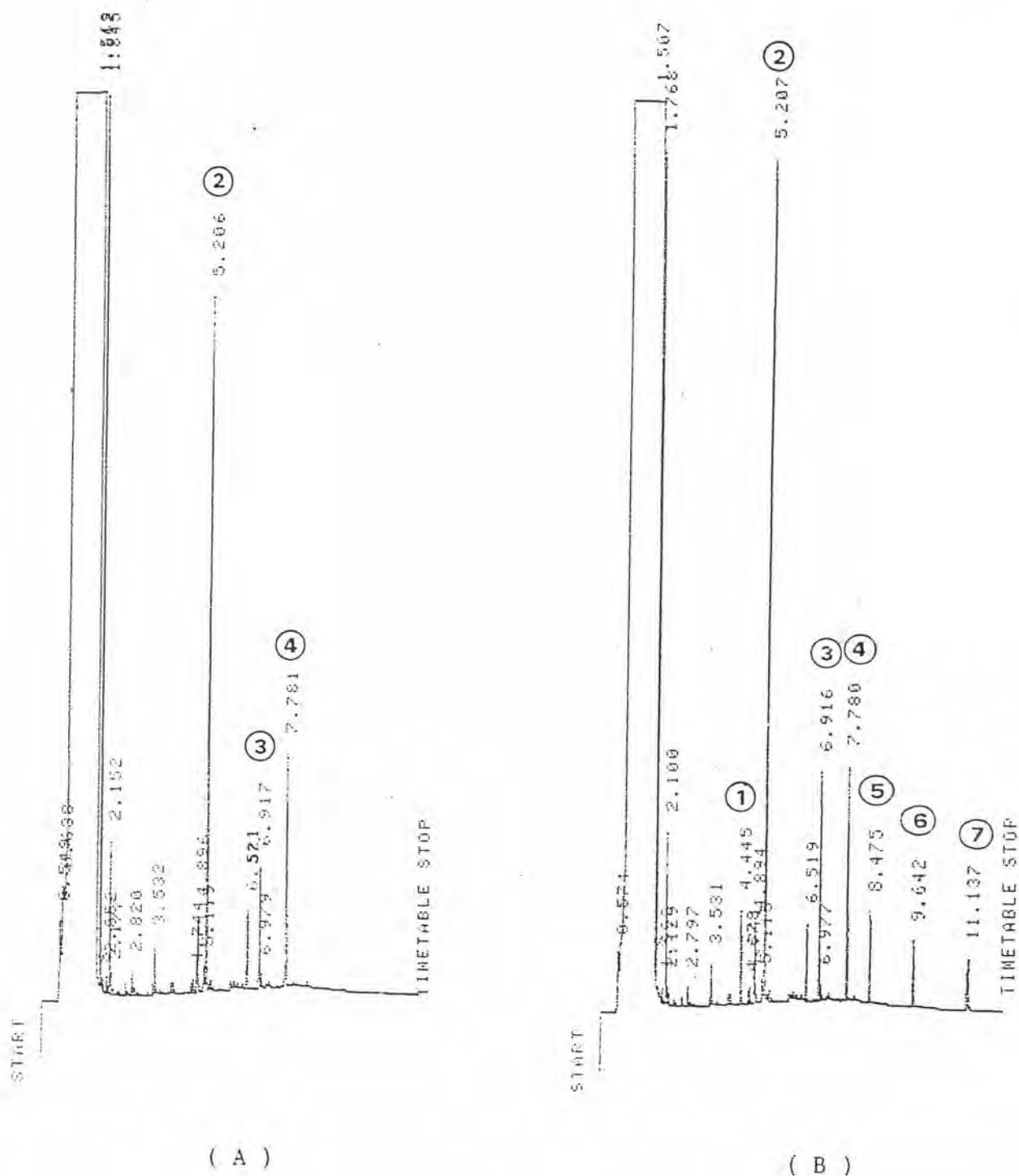


Figure 4.87 The gas chromatogram of

(A) sample 14

(B) sample 14 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 3

sample 14 = Water from Chao Phya River
(Siphya Pier)

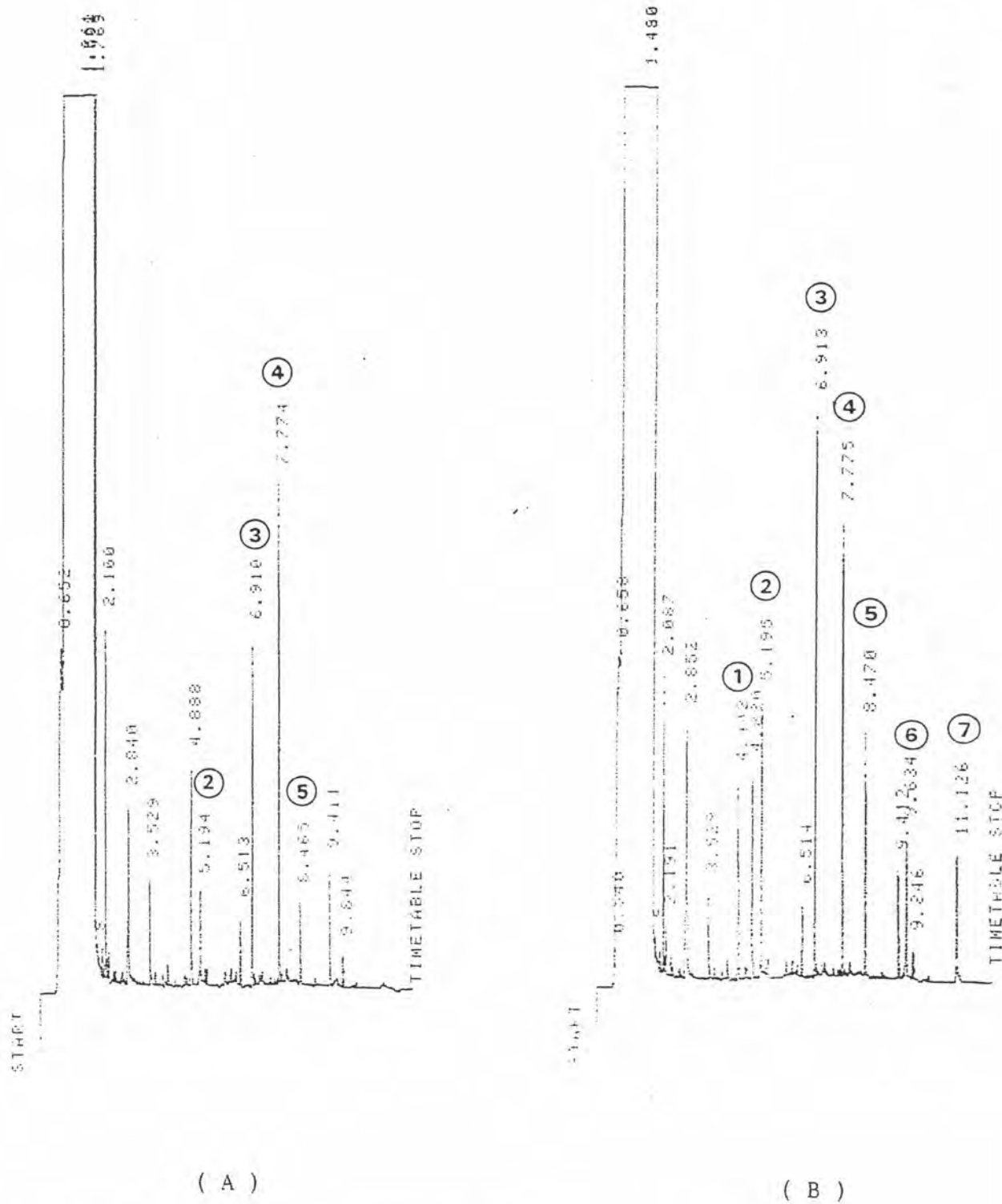


Figure 4.88 The gas chromatogram of
 (A) sample 15
 (B) sample 15 + standard mixture in toluene

GC Condition : described in Table 4.4

Integrator : atten 2

sample 15 = Water from Chao Phya River(Prapadang Pier)

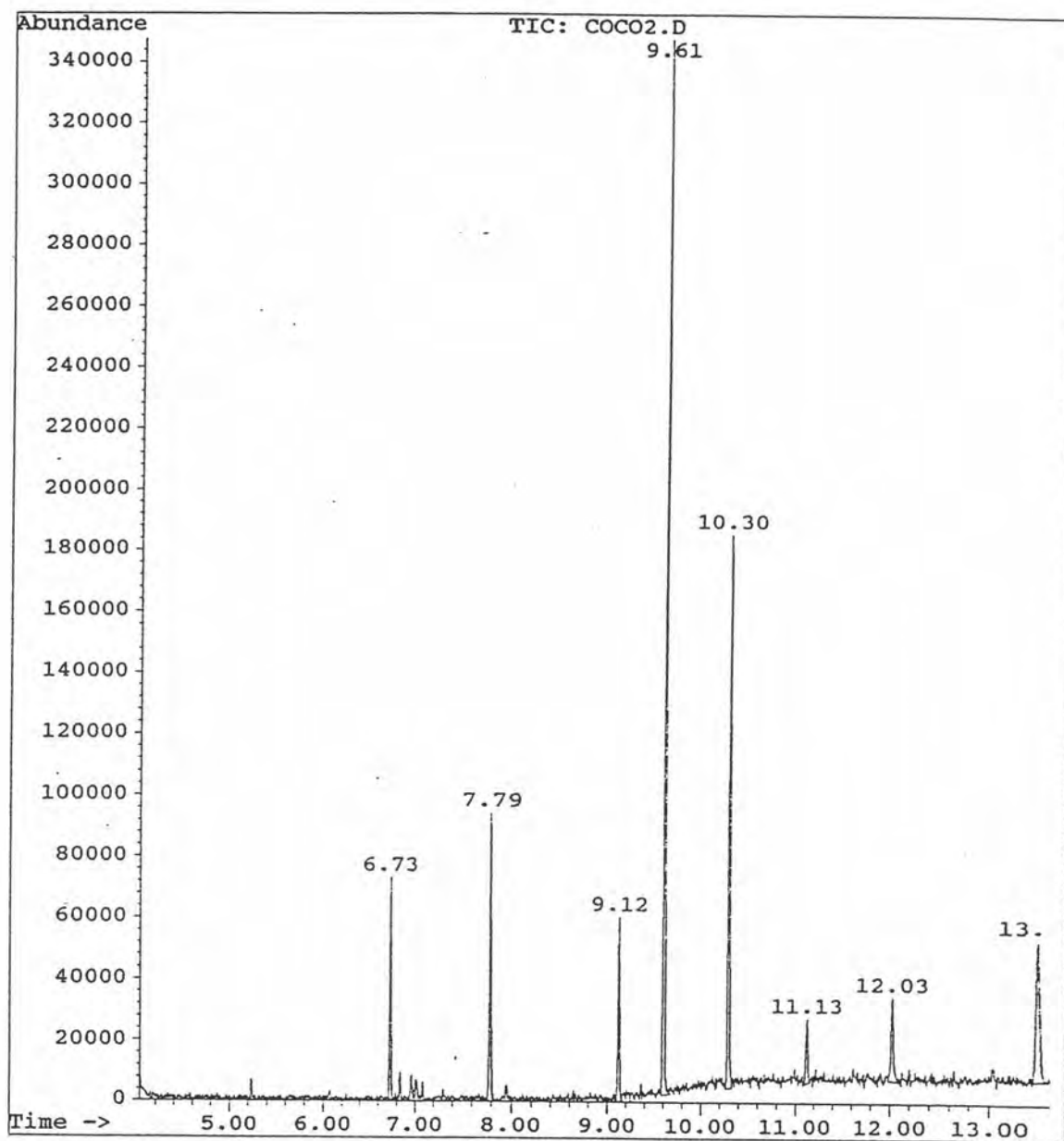


Figure 4.89 The gas chromatogram with MSD detection for an extract of a Samparn coconut water sample

GC/MSD Condition : described in Table 3.3

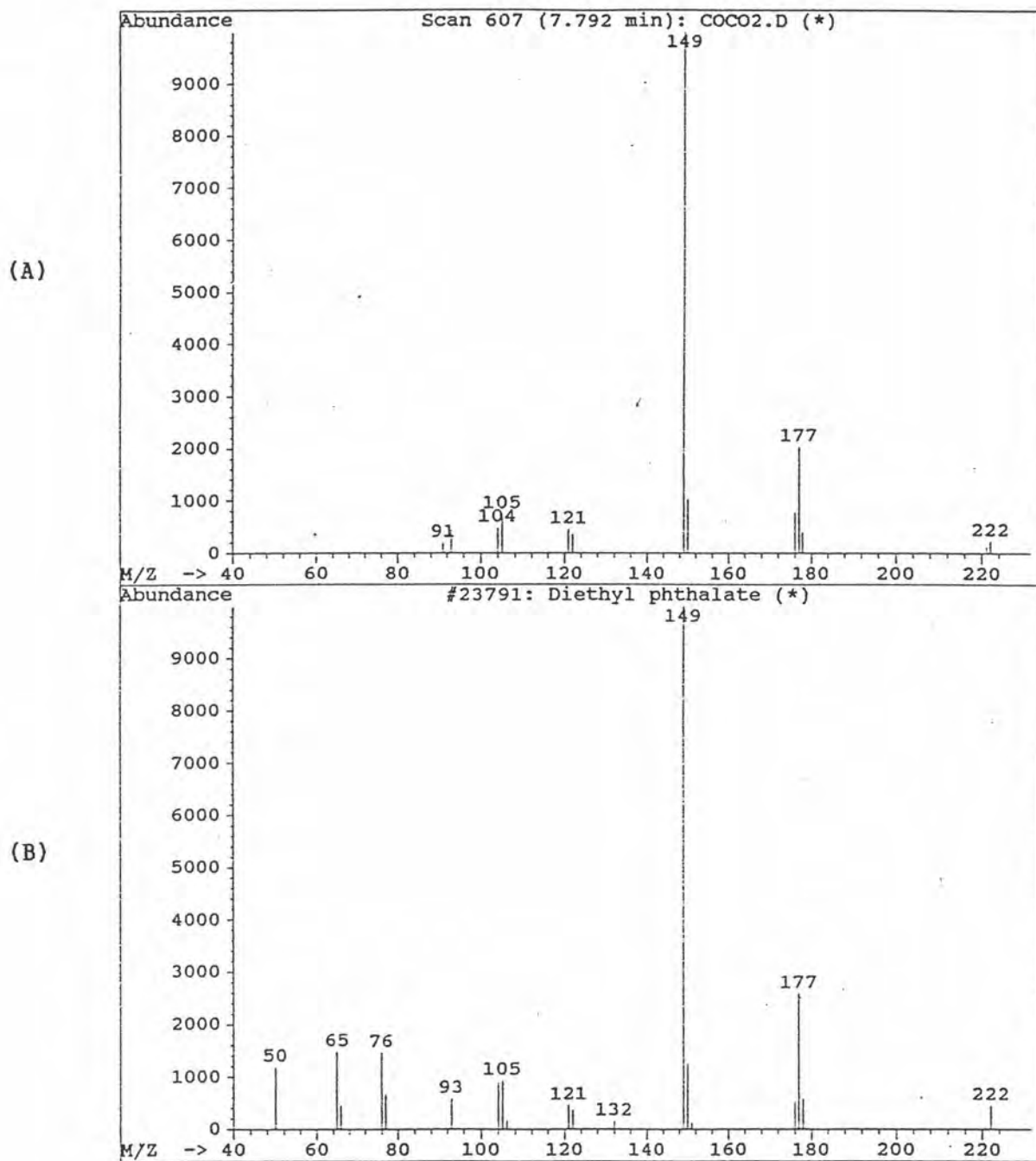


Figure 4.90 The mass spectrum for an extract of a Samparn coconut water sample with the retention time of 7.79 min. from the gas chromatogram in Figure 4.89.

(A) Scan

(B) Library searched

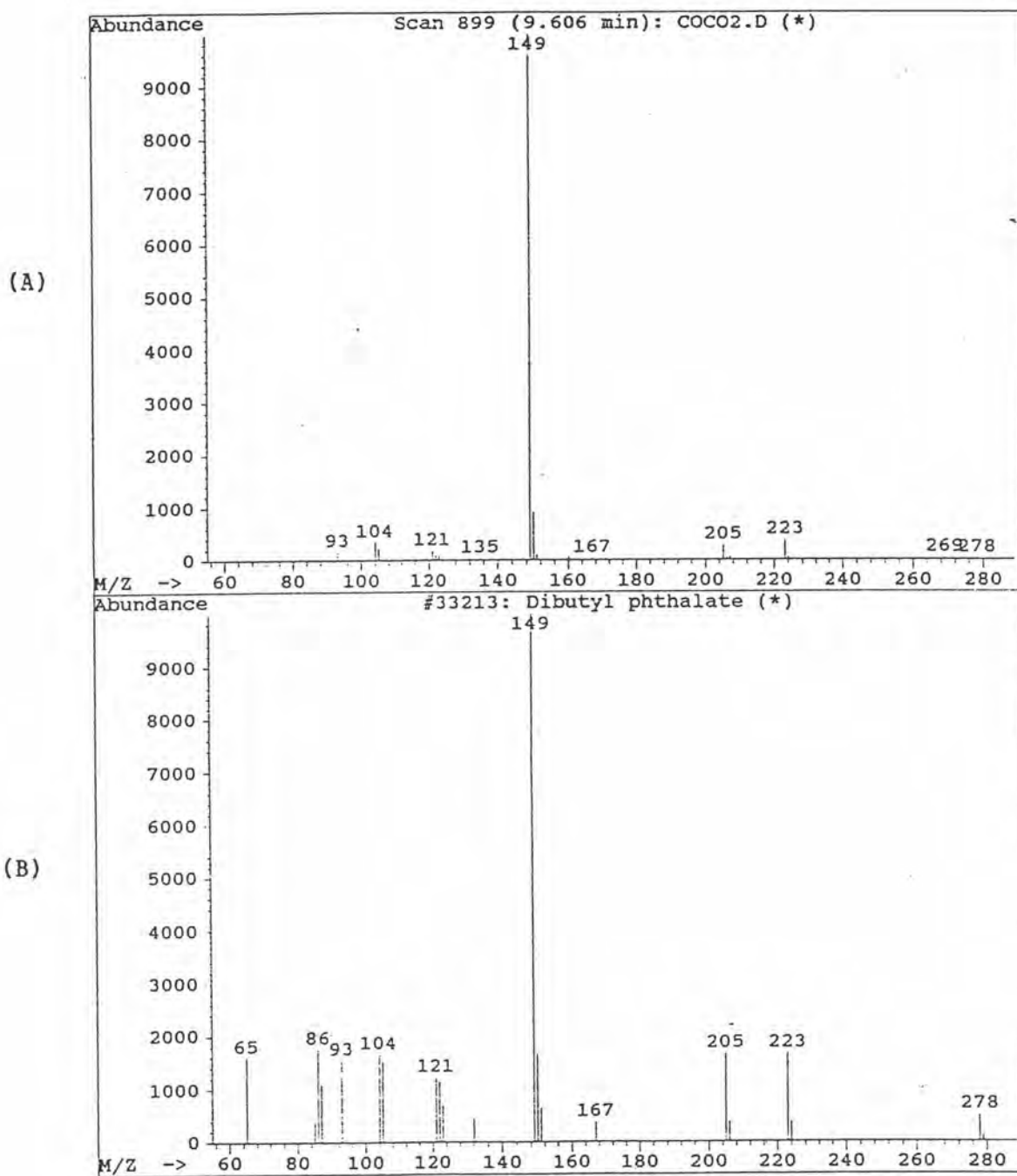


Figure 4.91 The mass spectrum for an extract of a Samparn coconut water sample with the retention time of 9.61 min. from the gas chromatogram in Figure 4.89.

(A) Scan

(B) Library searched

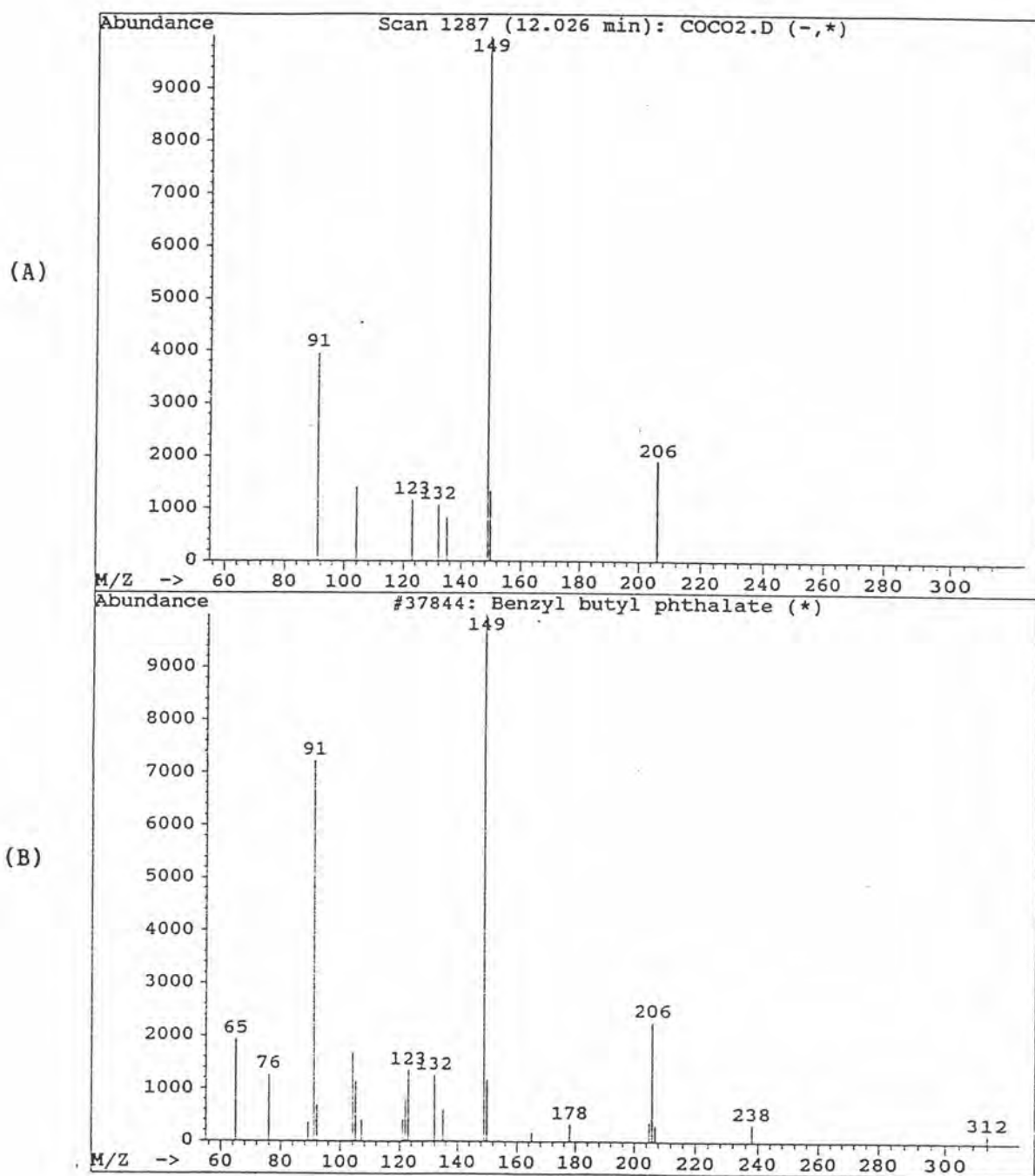


Figure 4.92 The mass spectrum for an extract of a Samparn coconut water sample with the retention time of 12.03 min. from gas chromatogram in Figure 4.89.

(A) Scan

(B) Library searched

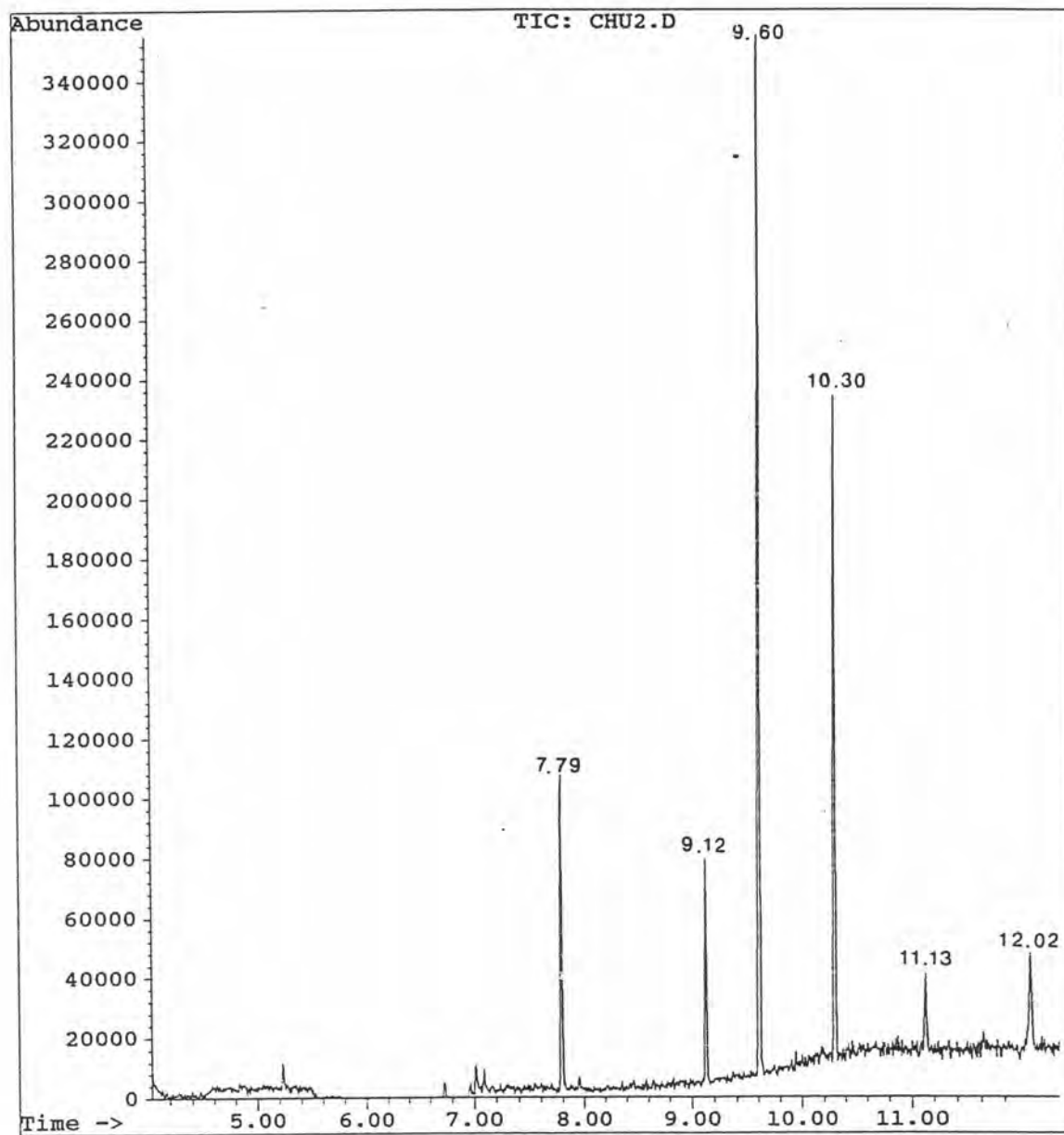


Figure 4.93 The gas chromatogram with MSD detection for an extract of a water sample from the Chao Phya River (Prapadang Pier)

GC/MSD Condition : described in Table 3.3

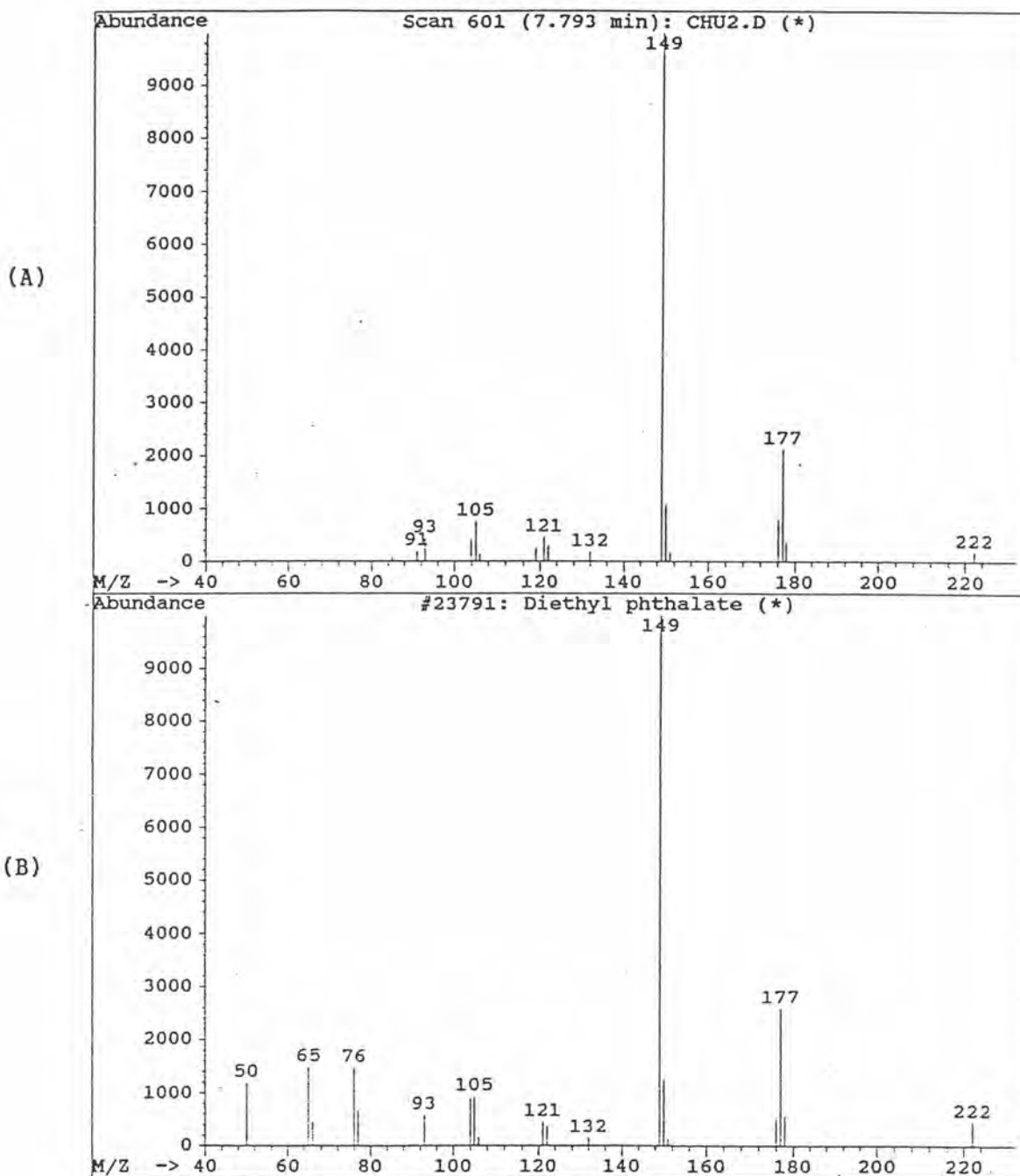


Figure 4.94 The mass spectrum for an extract of a water sample from the Chao Phya River (Prapadang Pier) with the retention time of 7.79 min. from the gas chromatogram in Figure 4.93.

(A) Scan

(B) Library searched

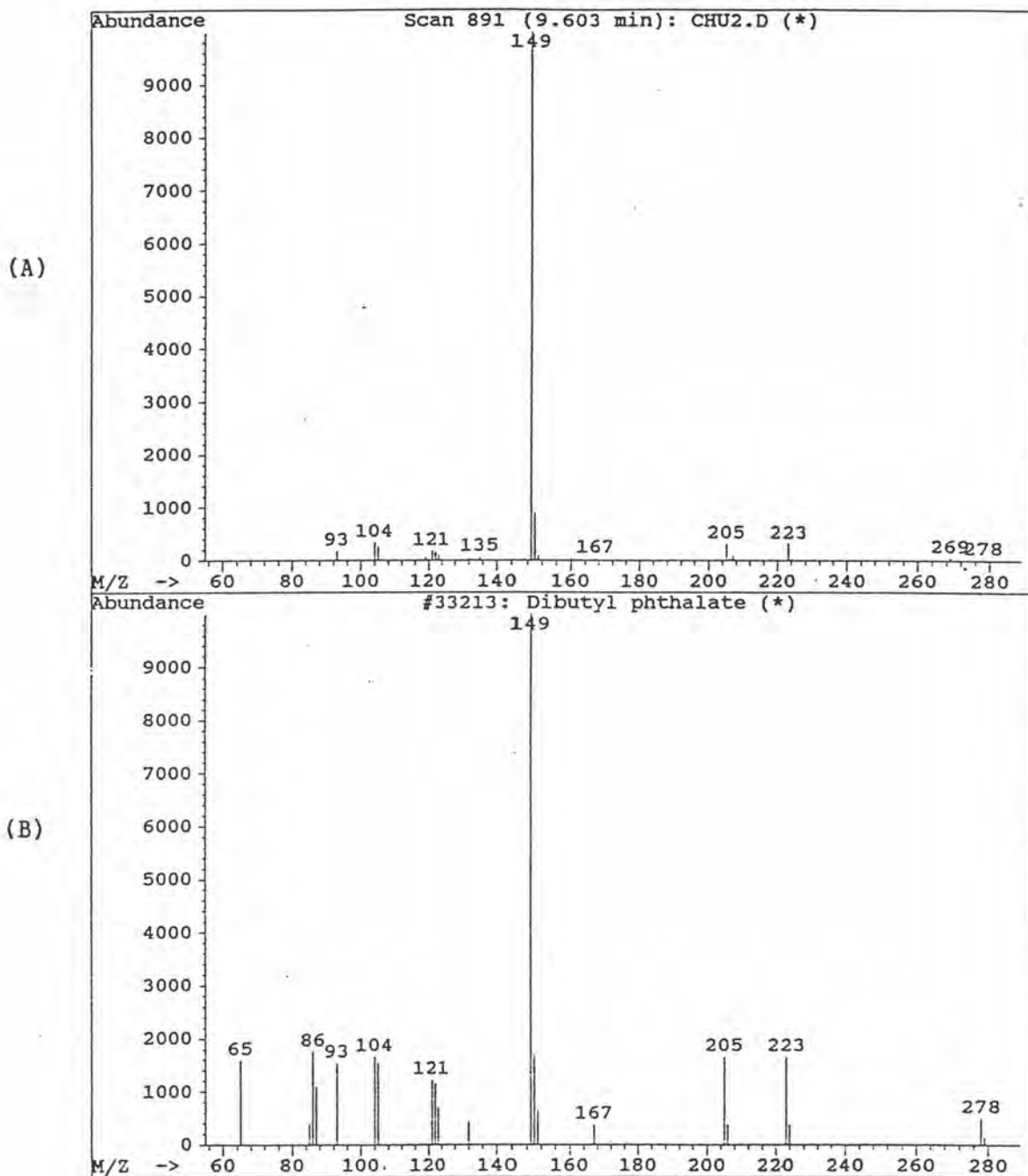


Figure 4.95 The mass spectrum for an extract of a water sample from the Chao Phya River (Prapadang Pier) with the retention time of 9.60 min. from the gas chromatogram in Figure 4.93.

(A) Scan

(B) Library searched

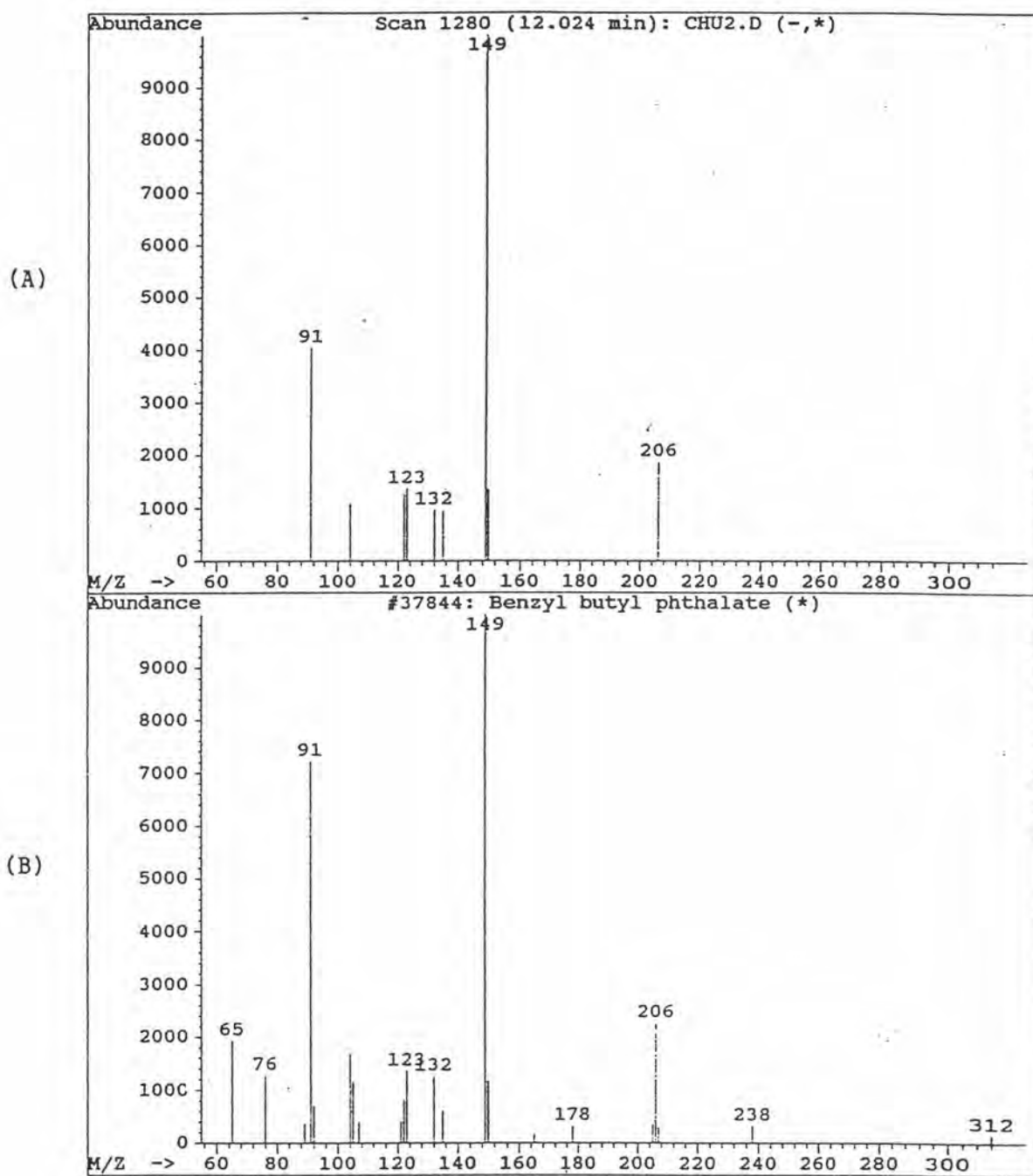


Figure 4.96 The mass spectrum for an extract of a water sample from the Chao Phya River (Prapadang Pier) with the retention time of 12.02 min. from the gas chromatogram in Figure 4.93.

- (A) Scan
(B) Library searched

4.8 Recommended SPE Technique

From all of the studies above, the author can proposed the recommended SPE technique for the determination of phthalate esters as follows:

1. The C₁₈ SPE cartridge is conditioned before usage. This is done by passing 5 mL of methanol through the column followed by 1 mL of double distilled water.
2. The 250 mL of sample solution is adjusted pH to 2.
3. The sample solution is passed through the C₁₈ SPE cartridge. The vacuum pump is used to suck the solution downward at 15 mm Hg pressure. The C₁₈ SPE cartridge is washed once more with 1 mL double distilled water and the vacuum is left for 15 min. to dry the sorbent.
4. The C₁₈ SPE cartridge is eluted with 5 mL of toluene at 5 mm Hg vacuum pressure. The internal standard dibutyl sebacate is then added and the eluate is injected into gas chromatograph equipped with flame ionization detector.
5. The blank solution is prepared the same as step 1 to 4 but the double distilled water is used instead of the sample solution. The internal standard solution is not added in step 4.
6. The concentrations of each phthalate ester is calculated by using the internal standardization method.

Because it can perform three samples in the same time, analysis time for one sample is 15 min.

The method detection limit of this technique is in the range of 0.51-1.26 ppb. The percent recoveries of the phthalate esters are in the range of 105.24-88.01 % with \pm 1.37-2.66 % RSD and the percent