CHAPTER III

EXPERIMENTAL

3.1 Apparatus

A Hewlett Packard HP 5890 gas chromatograph equipped with Flame Ionization Detector (FID) and Hewlett Packard HP3396A Integrator.

A Hewlett Packard HP 5890 Series II gas chromatograph equipped with FID, Hewlett Packard HP 5971 Mass Selective Detector (MSD), Computer Chem Station HP Vectra 386s and Printer Desk Jet 500.

A Hewlett Packard 12 m x 0.2 mm ID. x 0.33 μm flim thickness HP-1 (Crosslinked Methyl Silicone Gum) capillary column.

A Hewlett Packard 25 m x 0.32 mm ID. x 0.25 mm flim thickness PAS 1701 capillary column

An Orion Research Digital Ionanalyzer model 710A pH/ISE meter, U.S.A.

A RC-2 magnetic bar and a magnetic stirrer, Japan.

A Baker-12 Extraction System, J.T. Baker, U.S.A.

Reservoir 75 mL, J.T. Baker, U.S.A.

Disposable column 3 mL, J.T. Baker, U.S.A.

Glass fiber prefilter dimension 10 mm, Millipore, U.S.A.

Membrane type HA 0.2 μm Millipore, U.S.A.

Microsyringes 10.00, 50.00 and 250.00 μL (Hamilton Company, Switzerland)

Graduated pipettes 1.00, 2.00, and 5.00 mL

Volumetric pipettes 1.0, 5.0, 10.0, and 25.0 mL

Volumetric flasks 5.0, 10.0, 25.0, 50.0, 100.0, 250.0 and 1,000.0 mL

Beakers 50, 250, 500, and 1,000 mL

A Gast Model 0522 V4B G21D x general electric AC motor to use as a vacuum pump, U.S.A.

All glass apparatus was washed in detergent, thoroughly rinsed with double distilled water and then soaked in dilute HNO_3 (1:1) overnight. The glass apparatus was then rinsed with double distilled water and baked in an oven at 150°C for at least 3 hours.

3.2 Chemicals

3.2.1 The Standard of Phthalate esters (PEs)

Dimethylphthalate (DMP), Diethylphthalate (DEP), Di-n-butylphthalate (DBP), Butylbenzylphthalate (BBP), Di(2-ethylhexyl) phthalate (DEHP), and Di-n-octylphthalate (DOP) which had percent purity of 99.0, 99.0, 99.0, 98.5, 99.5 and 95.5 respectively were purchased from Chem Service, Inc., West Chester, PA., U.S.A.

Dibutylsebacate (DBS) with percent purity > 97 was purchased from Fluka Chemie AG, Switzerland.

3.2.2 Organic Solvents

Absolute methanol, hexane, ethyl acetate, toluene, isooctane and methylene chloride were purchased from J.T. Baker Chemical Company, Deventer, Holland. All solvents were analytical

reagent grade (AR Grade) and they were purified by fractional distillation in all-glass apparatus and the distillate was checked for the purity by gas chromatograph prior to use.

3.2.3 Reagents

Nitric acid and hydrochloric acid were analytical reagent grade and were purchased from E.Merck, Darmstadt, Germany.

Sodium hydroxide pellet was laboratory reagent grade and was purchased from EKA Nobel, SWEDEN.

3.3 Preparation of the Standard Solutions

3.3.1 The Stock Standard Solutions of PEs in organic solvents

The 2,000.00 ppm stock standard solutions of each PE, i.e., DMP, DEP, DBP, BBP, DEHP and DOP in each organic solvent including methanol, ethyl acetate, methylene chloride, toluene, isooctane and hexane were prepared by dissolving 0.1000 g of each standard and diluting it to the mark with the organic solvent in 50.00 mL volumetric flasks. The 200.00 ppm of standard solution of each PE were prepared by pipetting 10.00 mL of 2,000.00 ppm stock standard solution into 100.00 mL volumetric flasks and then diluting it to the mark with the organic solvent. The 200.00 ppm of standard mixture solution of PEs were prepared in the same as the single component standard solution.

All standard solutions of PEs for preparation of sample

and standard calibration curve were prepared from 200.00 ppm of the standard solution of PE_S. The desire concentrations were prepared by further dilution of these 200.00 ppm standard solutions.

3.3.2 The Internal Standard Solution of Dibutylsebacate (DBS) in organic solvents

A 2,000.00 ppm internal standard solution of DBS in each organic solvent, i.e. ethyl acetate, methylene chloride, toluene, isooctane and hexane were prepared by dissolving 0.0500 g of internal standard DBS and diluting it to the mark with the organic solvent in 25.00 mL volumetric flasks.

3.3.3 The pH Adjustment Solutions

A 1.0×10^{-2} M hydrochloric acid, and (or) a 1.0×10^{-2} M sodium hydroxide solution were employed for pH adjustment of the solution

3.4 The Study of Resolution of PEs on Two GC Columns

The procedure for the study of resolution of PEs on two GC columns, i.e., HP-17 and HP-1 can be described as follows:

1. A 10mL of 100.00 ppm standard mixture solution of PEs in hexane was prepared from 2000.00 ppm stock single component standard solution of PEs in hexane. A 1 μL of prepared standard mixture solution in step 1 was injected into GC at each GC column under the GC

condition in Table 3.1 and 3.2.

2. The chromatogram of standard mixture solution of PEs on two GC columns were shown in figure 4.1 and 4.2.

Table 3.1 The gas chromatographic conditions for the study of resolution of PEs on HP-17 (Crosslinked 50% Phenyl Methyl Silicone) capillary column

GC Parameter	GC Condition
Analytical Column	10 m x 0.53 mm x 2.0 μm film thickness HP-17 (Crosslinked 50% Phenyl Methyl Silicone) Capillary column
Temperature Program	A. 60°C (1 min) to 160°C at 30°C/min B. 160°C (1 min) to 220°C at 7°C/min C. 220°C (1 min) to 250°C at 2°C/min
Splitless Time	1.0 min
Split Ratio	50:1
Flow Rate of Carrier Gas(He)	25.00 mL/min
H_2	45.00 mL/min
Air	320.00 mL/min
N_2	30.00 mL/min
Detector	Flame Ionization Detector (FID)
Detector Temperature	300°C
Inlet Temperature	280°C

Table 3.2 The gas chromatographic conditions for the study of resolution of PEs on HP-1 (Crosslinked Methyl Silicone Gum) capillary column

GC Parameter	GC Condition
Analytical Column	12 m x 0.2 mm ID.x 0.33 μm film thickness HP-1 (Crosslinked Methyl Silicone Gum) Capillary column
Temperature Program	60°C (1 min) to 260°C (5 min) at 25°C/min
Splitless Time	1.0 min
Split Ratio	50:1
Flow Rate of Carrier Gas (He)	1.12 mL/min
H_2	45.00 mL/min
Air	320.00 mL/min
N_2	40.00 mL/min
Detector	Flame Ionization Detector (FID)
Detector Temperature	300°C
Inlet Temperature	280°C

3.5 The Study of Various Parameters on Sensitivity of GC

The parameters such as purge time, split ratio, and make-up flow rate were studied for increasing sensitivity of GC and obtaining reproducible, accurate and representative quantitative results. In this study, DEHP was one of the PEs and was used as a model compound.

3.5.1 The Purge Time

The procedure for the study of effect of purge time at 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0 and 4.0 minute on the sensitivity of GC can be described as follows:

1. A 10 mL of 100.00 ppm DEHP in hexane was prepared from 2000.00 ppm stock standard solution of DEHP in hexane. Eight sequential 1 μL injections were made at each purge time (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0 and 4.0 min) under the GC condition in Table 3.2

2. The relationships between the purge time and peak area were shown in Table 4.1 and Figure 4.3.

3.5.2 The Split Ratio (S3)

The procedure for the study of effect of split ratio (inlet flow/column flow) at 15:1, 25:1, 30:1, 40:1, 45:1, 60:1 and 70:1 on the sensitivity of GC can be described as follows:

1. A 10 mL of 100.00 ppm DEHP in hexane was prepared from 2000.00 ppm stock standard solution of DEHP in hexane. Seven sequential 1 μL injections were made at each split ratio under the GC

condition in table 3.2.

2. The relationships between the split ratio and peak area were shown in Table 4.2 and Figure 4.4

3.5.3 The Make-up Gas(N_2) Flow Rate

The procedure for the study of effect of make-up gas(N_2) flow rate at 0.0, 20.0, 30.0, 40.0, 50.0, 55.0, 60.0, 65.0 and 70.0 mL/min on the sensitivity of GC can be described as follows:

1. A 10 mL of 100.00 ppm DEHP in hexane was prepared from 2000.00 ppm stock standard solution of DEHP in hexane. Nine sequential 1 uL injections were made at each flow rate of make up gas (N_2) under the GC condition in table 3.2 except that the purge time and split ratio were 1.0 min and 25:1 respectively.

2. The relationships between the split ratio and peak area were shown in Table 4.3 and Figure 4.5.

3.6 The Procedure of Packing C_{18} into Cartridge

A C_{18} SPE cartridges for the study of all in this work was prepared as follows:

1. One piece of 10 mm glassfiber prefilter was put into 3 mL polypropylene column.

2. 500 mg of C_{18} bulk packing were carefully poured into the cartridge as prepared in step 1.

3. The another piece of 10 mm glassfiber prefilter was

placed over C_{18} as described in step 2.

3.7 The Procedure of Activated C_{18} SPE Cartridge on the Conditioning Step

An inevitable condition for effective retention is perfect mutual contact between the solid and the liquid phases. The C_{18} SPE cartridge must be activated before usage. Activating of chemically bonded silicas causes opening of the hydrocarbon chains of the stationary phase, thus increasing its surface area. The C_{18} SPE cartridge which was prepared in section 3.6 was activated by the addition of 3 mL of methanol which was allowed to set for 5 min prior to being drawn off (remained over the top of packing about 2 mm). The cartridge was then flushed with 3 mL of double distilled water. The solution was pulled through the sorbent with vacuum at 5 mm Hg pressure. The materials used in this SPE technique were shown in Appendix B.

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

The various effects on the percent recovery of solid phase extraction method including the pH of extracted sample, C_{18} bulk packing mass, the elution solvent and the volumes of elution solvent were studied in order to be able to determine the optimum condition of this method. Both of the concentrations of each standard solution, i.e., 0.20 and 1.00 ppm were studied. The procedures can be described

as follows:

3.8.1 The Effect of pH

The procedure for the study of the effect of pH at 2.0, 3.0, 4.0, 5.0, 6.0 7.0 and 8.0 of two concentrations, i.e., 0.20 and 1.00 ppm on the percent recovery of PEs can be described as follows:

1. Seven 0.25 mL and seven 1.25 mL of 200.00 ppm standard solution in methanol were pipetted into a series of 250 mL beakers and suitable amount of water was then added. The pH adjustment solution was added into the solution while it was measured by pH-meter until it was the desired pH (2.0 to 8.0 with the interval of 1.0). The pH probe was washed throughly with double distilled water into the solution until it reached to the mark in the volumetric flask. The pH value of the solution was checked again. The 0.20 and 1.00 ppm standard in aqueous solutions were already prepared.

2. Each solution which was prepared in step 1 was passed through each C_{18} SPE cartridge which was activated before usage (see section 3.7). The vacuum pump was used to suck the solution downward at 15 mm Hg pressure. Finally, each of C_{18} SPE cartridge was washed once more with 1 mL double distilled water and the vacuum was left on for 15 min to dry the sorbent.

3. Each of C_{18} SPE cartridge was eluted with 5 mL of ethyl acetate into 5.0 mL volumetric flask at 5 mm Hg vacuum pressure. The 25 µL and 120 µL of 2000.00 ppm internal standard DBS were then added in 5.0 mL volumetric flasks which were prepared from the 0.20 and 1.00 ppm standard in aqueous solution respectively and the solutions

were injected into gas chromatograph under GC condition as described in Table 4.4.

4. The blank solutions were prepared the same as step 1 to step 3 but the standard and internal standard solution were not added in step 1 and step 3.

5. The concentration of each PE was calculated by using the internal standardization method. The concentrations of standard calibration curve were 2.00, 5.00, 10.00, 15.00 and 20.00 ppm for extracting 0.20 ppm standard in aqueous solution and were 10.00, 30.00, 50.00, 70.00 and 80.00 ppm for extracting 1.00 ppm standard in aqueous solution.

6. The relationships between the percent recovery of each PEs and the pH value were shown in Tables 4.5-4.12 and Figures 4.6-4.33.

The optimum pH of PEs found in this section would be used in the next study.

3.8.2 The Effect of Sorbent Mass

The procedure of the study of the effect of sorbent mass at 100, 200, 300, 400 and 500 mg on the percent recovery of PEs can be described as follows:

1. The C_{18} SPE cartridges were prepared at various mass (100,200,300,400,500 mg). The procedure of packing C_{18} into the cartridge was done as same as section 3.6 and the procedure of activated C_{18} SPE cartridge was prepared as mentioned in section 3.7.

2. Five 1.25 mL of 200.00 ppm standard solution in

methanol were pipetted into a series of 250 mL beakers and suitable amount of water was then added. The pH of the solutions were adjusted to 2.0 as same as step 1 in section 3.8.1.

3. The preparation of the solution for the study of this effect was performed as same as step 2 in section 3.8.1.

4. Each of C_{18} SPE cartridge was eluted with 5 mL of ethyl acetate into 5.0 mL volumetric flask at 5 mm Hg vacuum pressure. The 120 µL of 2000.00 ppm internal standard DBS was then added in 5.0 mL volumetric flask and the solution was injected into gas chromatograph under GC condition as described in Table 4.4.

5. The blank solutions were prepared the same as step 1 to step 4 but the standard and internal standard solution were not added in step 2 and step 4.

6. The concentration of each PE was calculated by using the internal standardization method. The concentrations of standard calibration curve were 10.00, 30.00, 50.00, 70.00 and 80.00 ppm.

7. The relationships between the percent recovery of each PE_S and the sorbent mass were shown in Table 4.13 and Figures 4.34-4.40.

3.8.3 The Effect of Elution Solvent

The procedure of the study of the effect of elution solvent including ethyl acetate, methylene chloride, toluene, isooctane and hexane on the percent recovery of PEs can be described as follows:

1. Five 0.25 mL and five 1.25 mL of 200.00 ppm standard solution in methanol were pipetted into a series of 250 mL beakers

and suitable amount of water was then added. The pH of the solutions of each concentration were adjusted to 2.0 as same as step 1 in section 3.8.1. The 0.20 and 1.00 ppm standard in aqueous solution was already prepared.

2. The preparation of the solution was performed as same as step 2 in section 3.8.1

3. Each of C_{18} SPE cartridge was eluted with 5 mL of each elution solvent including ethyl acetate, methylene chloride, toluene, isooctane and hexane into 5.0 mL volumetric flask at 5 mm Hg Vacuum pressure The 25 µL and 120 µL of 2000.00 ppm internal standard DBS were then added in 5.0 mL volumetric flasks which were prepare from the 0.20 and 1.00 ppm standard in aqueous solution respectively and the solutions were injected into gas chromatograph under GC condition as described in Table 4.4.

4. The blank solutions were prepared the same as step 1 to step 3 but the standard and internal standard solutions were not added in step 1 and step 3.

5. The concentration of each PE was calculated by using the internal standardization method. The concentrations of standard calibration curve were 2.00, 5.00, 10.00, 15.00 and 20.00 ppm for extracting 0.20 ppm standard in aqueous solution and were 10.00, 30.00, 50.00, 70.00 and 80.00 ppm for extracting 1.00 ppm standard in aqueous solution.

6. The relationships between the percent recovery of each PEs and the elution solvent were shown in Tables 4.14-4.17 and Figures 4.41-4.44.

3.8.4 The Effect of Volume of Elution Solvent

The procedure of the study of the effect of volume of elution solvent (ethyl acetate and toluene) at 1.0,2.0,3.0,4.0, and 5.0 mL on the percent recovery of PEs can be described as follows:

1. The preparation of the solution was performed as same as step 1 and 2 in section 3.8.3.

2. Five volumes of elution solvent 1.0, 2.0, 3.0, 4.0 and 5.0 mL were passed through each cartridge at 5 mm Hg vacuum pressure. Five 5.0 mL of volumetric flasks were employed as the receivers. The 25 μL and 120 μL of 2000.00 ppm internal standard DBS were then added in 5 mL volumetric flasks which were prepared from the 0.20 and 1.00 ppm standard in aqueous solutions respectively. The volume of each volumetric flask was made up to the mark with elution solvent. These solutions were injected into gas chromatograph under GC condition as described in Table 4.4.

3. The blank solutions were prepared as same as step 1 to step 2 but the standard and internal standard solutions were not added in step 1 and step 3.

4. The concentration of each PE was calculated by using the internal standardization method. The concentrations of standard calibration curve were 2.00, 5.00, 10.00, 15.00 and 20.00 ppm for extracting 0.2 ppm standard in aqueous solution and were 10.00, 30.00, 50.00, 70.00 and 80.00 ppm for extracting 1.00 ppm standard in aqueous solution.

5. The relationships between the percent recovery of each PE and volume of elution solvent were shown in Tables 4.18-4.21

3.9 Internal Standardization Method (60, 82)

A widely used technique of quantitation involves the addition of an internal standard to compensate for small variations in injection volumes by rationing all peak measurements to that of a known amount of the reference analog the compound of interest. The assumption is that the reference is affected by handling variations to the same degree as the sample. Several standard solutions containing known weights or concentrations of the compound of interest and internal standard are prepared and chromatographed. The calibration curve is generated by plotting the ratio of the peak heights or areas of the compound of interest and the internal standard against their concentration ratio and shows in Figure 3.1. This plot must be linear for the particular system. From the linear curve, the response factor (RF) can be calculated from any of the standard solutions prepared and the following equation:

$$\text{slope} = \frac{\text{peak area ratio}}{\text{concentration ratio}} = RF \qquad (3.1)$$

$$RF = \frac{A_c\, C_{is}}{A_{is}\, C_c} \qquad (3.2)$$

where A_c and C_c are the peak area and concentration of the compound of interest.

A_{is} and C_{is} are the peak area and concentration of the internal standard

To determine the amount of the compound of interest in the sample, a known concentration of the internal standard is added into the sample. This mixture is then chromatographed and the peak area ratio of components is measured. The concentration of the compound of interest in the sample can be calculated by using the following equation:

$$C_C = \frac{A_c\, C_{is}}{A_{is}\, RF} \qquad (3.3)$$

The selection of the internal standard is critical for both peak height and peak area measurements, and the requirements are summarized as follow:

1. It must have a completely resolved peak; no interferences
2. It must elute close to compounds of interest
3. It must be have equivalently to compounds of interest
4. It must not be present in original sample
5. It must be stable; unreactive with sample components
6. It is desirable for it to be commercially available in high purity.

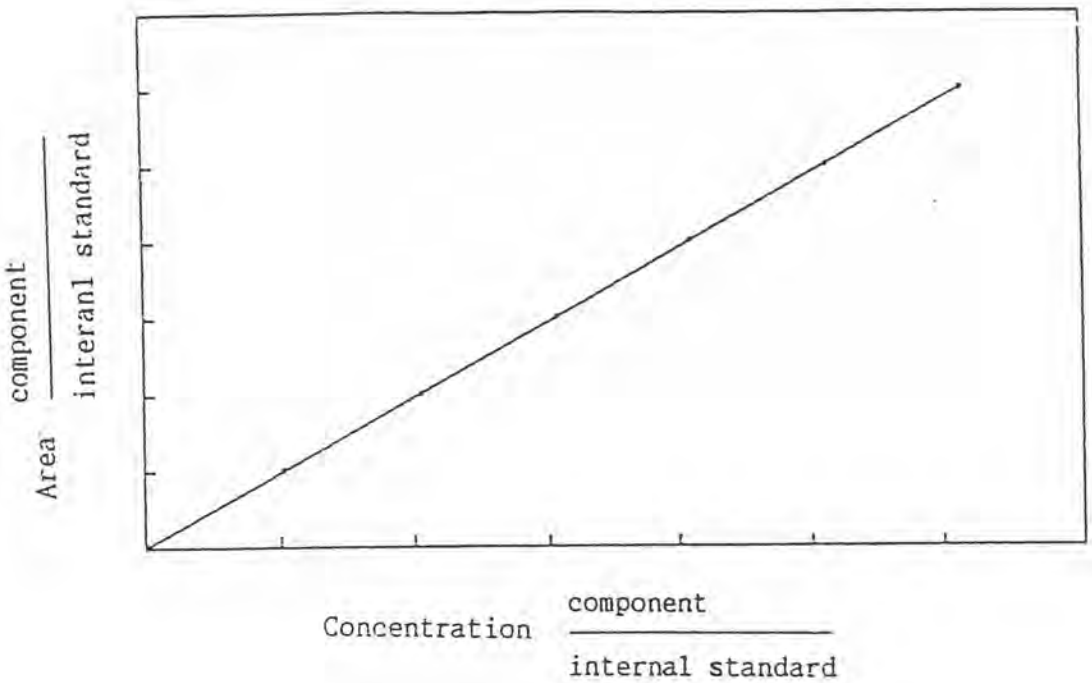

Figure 3.1 Internal standard calibration curve

The concentration of standard calibration curve are 2.00, 5.00, 10.00, 15.00, and 20.00 ppm for extracting 0.20 ppm standard in aqueous solution and are 10.00, 30.00, 50.00, 70.00, 80.00 ppm for extracting 1.00 ppm standard in aqueous solution. The concentration of internal standard DBS are 10.00 ppm for extracting 0.20 ppm standard in aqueous solution and are 48.00 ppm for extracting 1.00 ppm standard in aqueous soluton.

3.10 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 procedure for the study of method detection limit can be described as follows:

1. Three aliquot of each concentration of each PE at pH 2.0 were prepared in 250 mL aqueous solutions.

2. Each solution which was prepared in step 1 was passed through each C_{18} SPE cartridge which was activated before usage(see section 3.7). The vacuum pump was used to suck the solution downward at 15 mm Hg pressure. Finally each of C_{18} SPE cartidge was washed once more with 1 mL double distilled water and the vacuum was left for 15 min. to dry the sorbent.

3. Each of C_{18} SPE cartridge was eluted with 5 mL of toluene into 5.0 mL volumetric flask at 5 mm Hg vacuum pressure. The solution was injected into gas chromatograph under GC condition as described in Table 4.4.

4. The blank solution was prepared the same as step 1 to step 3 but the standard solution was not added in step 1.

5. The result of this study was presented in Table 4.23.

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

The study of precision has been used toluene and ethyl acetate as elution solvents. The optimum conditions from the previous studies in Table 4.22 and the GC condition in Table 4.4 have been employed for this study. The procedure for the study of precision can be described as follows:

3.11.1. The Procedure for the Study of Precision of Each Phthalate Ester by Using Toluene as Elution Solvent

1. Ten 0.25 mL of 200.00 ppm standard mixture of PEs in methanol were pipetted into a series of 250 mL beakers and suitable amount of water was then added. The pH of the solutions were adjusted to 2.0 as same as step 1 in section 3.8.1.

2. Each solution which was prepared in step 1 was passed through each C_{18} SPE cartridge which was activated before use (see section 3.7). The vacuum pump was used to suck the solution downward at 15 mm Hg pressure. Finally, each of C_{18} SPE cartridge was washed once more with 1 mL double distilled water and the vacuum was left for 15 min to dry the sorbent.

3. Each of C_{18} SPE cartridge was eluted with 5 mL of toluene into 5.0 mL volumetric flask at 5 mm Hg vacuum pressure. The 25 µL of 2000.00 ppm internal standard DBS were then added in 5.0 mL volumetric flask and the solution was injected into gas chromatograph under GC condition as described in Table 4.4.

4. The blank solution was prepared the same as step 1 to step 3 but the standard and internal standard solution were not added in step 1 and step 3.

5. The concentration of each PE was calculated by using the internal standardization method.

6. The precision result of solid phase extraction method for determination some PEs in water by using toluene as elution solvent was shown in Table 4.24.

3.11.2. The Procedure for the Study of Precision of Each Phthalate ester by Using Ethyl Acetate as Elution Solvent

The procedure can be performed the same as the procedure for the study of precision of each PE by using toluene as elution solvent which was described above.

The precision result of solid phase extraction method for determination some PEs in water by using ethyl acetate as elution solvent was shown in Table 4.25.

3.12 The Procedure for Checking the Accuracy of Solid Phase Extraction Technique

The synthetic unknown mixture solutions in methanol were prepared to evaluate the accuracy of solid phase extraction method. The concentration of each PE i.e., DMP, DEP, DBP, BBP, DEHP and DOP was determined by means of the internal standardization method as described in section 3.9 using DBS as the internal standard under the optimum condition found in the previous studies (see Table 4.22) and GC condition in Table 4.4. The procedure can be described as follows:

1. Three 200.00 mL of the synthetic unknown solution were pipetted into a series of 250 mL beakers and suitable amount of water was then added. The pH of the solutions were adjusted to 2.0 as same as step 1 in section 3.8.1.

2. Each solution which was prepared in step 1 was passed through each C_{18} SPE cartridge which was activated before usage (see section 3.7). The vacuum pump was used to suck the solution downward

at 15 mm Hg pressure. Finally, each of C_{18} SPE cartridge was washed once more with 1 mL double distilled water and the vacuum was left for 15 min. to dry the sorbent.

3. Each of C_{18} SPE cartridge was eluted with 5 mL of toluene into 5.0 mL volumetric flask at 5 mm Hg vacuum pressure. The 25 μL of 2000.00 ppm internal standard DBS was then added in 5.0 mL volumetric flask and the solution was injected into gas chromatograph under GC condition as described in Table 4.4.

4. The blank solution was prepared the same as step 1 to step 3 but the double distilled water was used instead of the synthetic unknown. The internal standard solution was not added in step 3.

5. The concentration of each PE was calculated by using the internal standardization method and the results were presented in Table 4.26. The concentrations of standard calibration curve were 1.00, 3.00, 5.00, 10.00, 15.00 and 20.00 ppm. The internal standard calibration curve was shown in Figures 3.2-3.7.

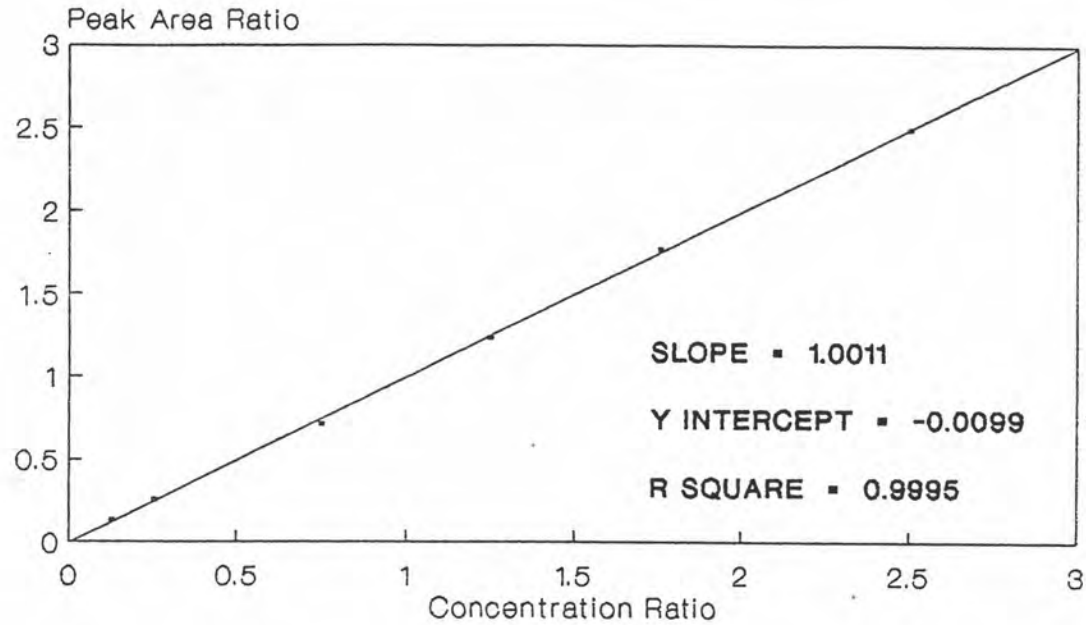

Figure 3.2 Internal standard calibration curve of DMP in toluene

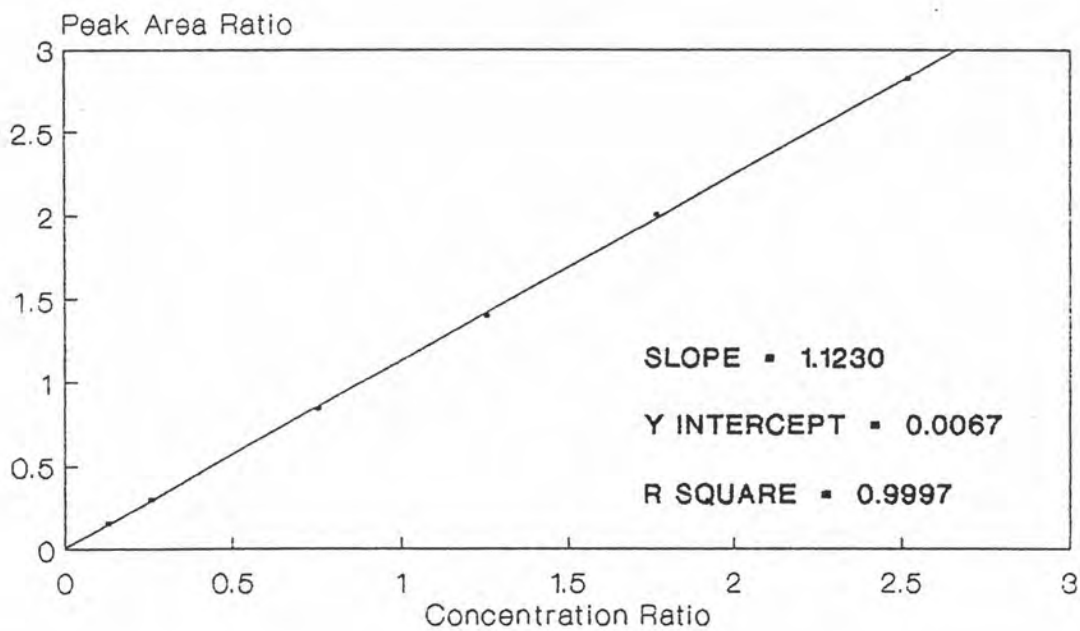

Figure 3.3 Internal standard calibration curve of DEP in toluene

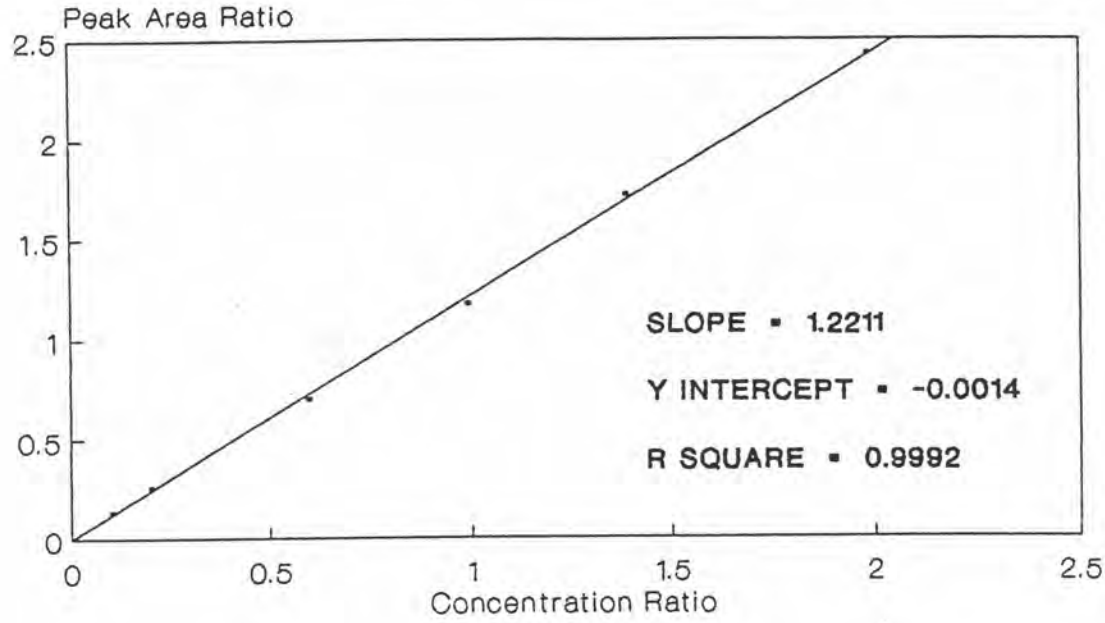

Figure 3.4 Internal standard calibration curve of DBP in toluene

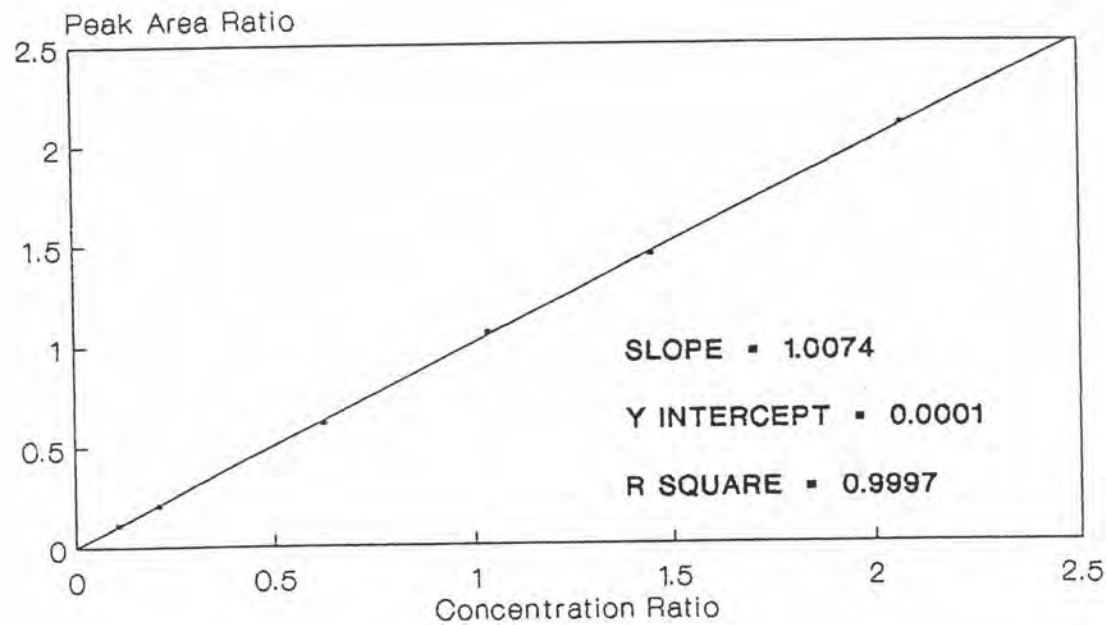

Figure 3.5 Internal standard calibration curve of BBP in toluene

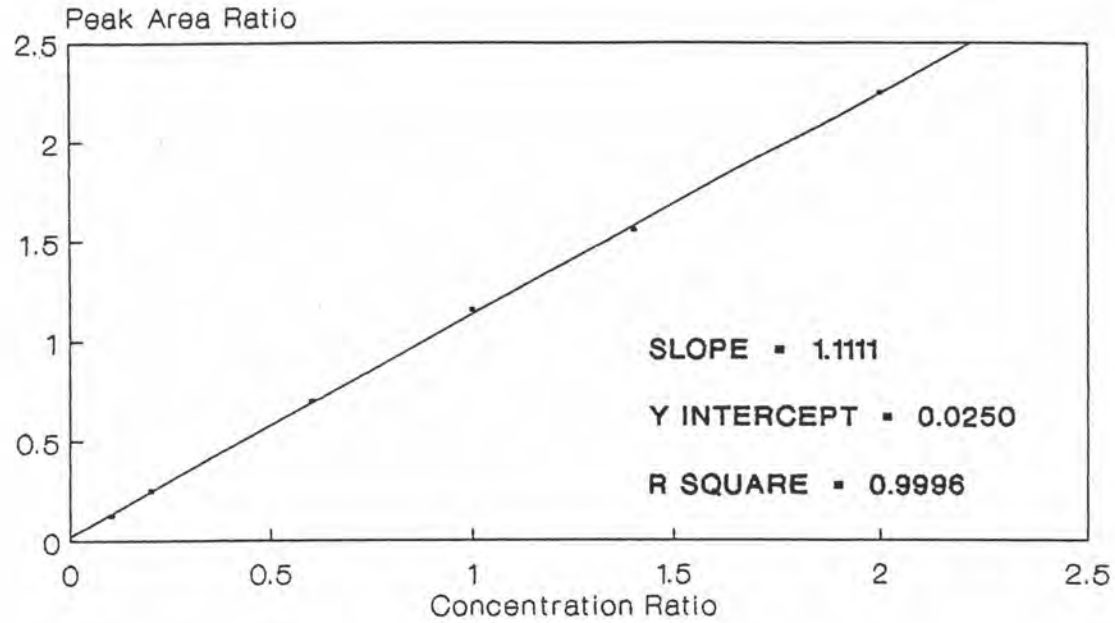

Figure 3.6 Internal standard calibration curve of DEHP in toluene

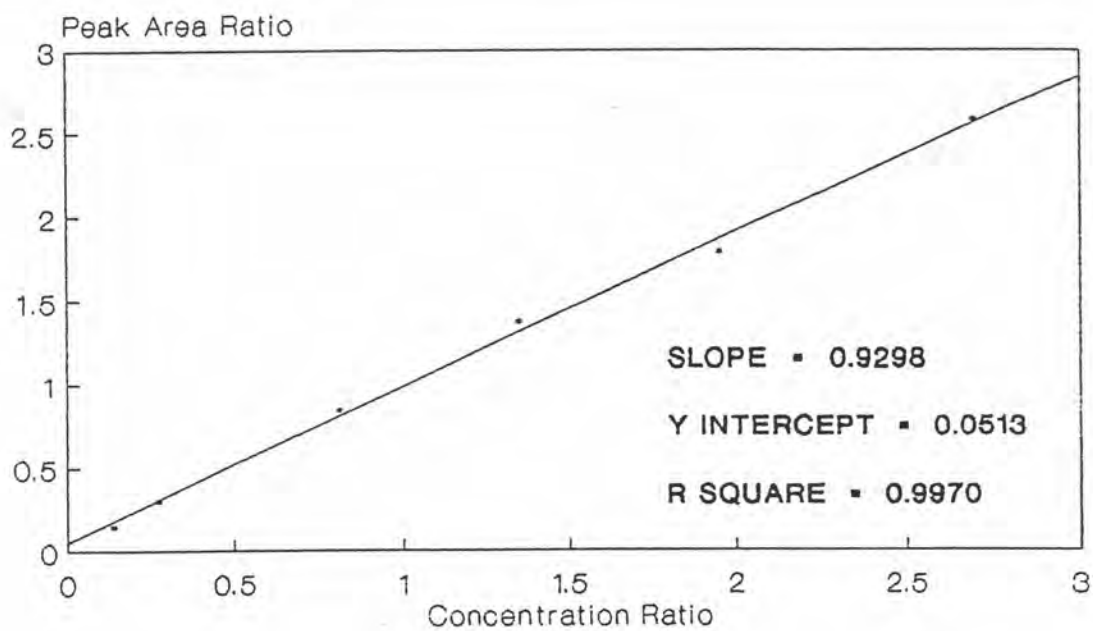

Figure 3.7 Internal standard calibration curve of DOP in toluene

3.13 The Determination of Phthalate Esters in Real Water Samples

Fifteen collected water samples from several places can be described as follows:

1. Prasobchok-drinking water collected from a store in september 18th, 1993 time 10.00 a.m.

2. Sprinkle-drinking water colleted from a store in september 18th, 1992 time 11.30 a.m.

3. Samparn coconut water in plastic bag collected from a store in september 18th, 1992 time 10.00 a.m.

4. Tap water collected from chemistry building 3 in September 18th, 1993 time 11.30 p.m.

5. Tap water collected from Bangsue residence area in September 22nd, 1993 time 7.00 a.m.

6. Tap water collected from Thonburi residence area in September 21st, 1993 time 6.00 p.m.

7. Tap water Collected from Municipal water Authorities on Samsen Area in September 15th, 1993 time 11.00 a.m.

8. Water collected from Chulalongkorn University Pool near Phyathai Road in September 18th, 1993 time 1.00 p.m.

9. Water collected from Chulalongkorn University Pool near Botany building in September 20th, 1993 time 12.05 p.m.

10. Water collected from Suan Lum Pool in September 20th, 1993 time 11.40 p.m.

11. Water collected from Klong Prapa Samsen in September 15th, 1993 time 10.40 a.m.

12. Water collected from Klong Premprachakorn in September

19th, 1993 time 09.00 a.m.

13. Water collected from Klong Phadungkrunkasem in September 22nd, 1993 time 04.30 a.m.

14. Water collected from Chao Phya River at Siphya Pier in September 15th, 1993 time 01.35 p.m.

15. Water collected from Chao Phya River at Prapadang Pier in September 18th, 1993 time 08.25 a.m.

Each collected water samples were filtered by using 0.2 μm membrane filter prior be performed by the SPE technique that was developed in this study. The procedure can be described as follows:

1. Three 200.00 mL of each water sample were pipetted into a series of 250 mL beakers and suitable amount of water was then added. The pH of the solutions were adjusted to 2.0 as same as step 1 in section 3.8.1.

2. Each solution which was prepared in step 1 was passed through each C_{18} SPE Cartridge which was activated before usage (see section 3.7). The vacuum pump was used to suck the solution downward at 15 mm Hg pressure. Finally, each of C_{18}SPE cartridge was washed once more with 1 mL double distilled water and the vacuum was left for 15 min. to dry the sorbent.

3. Each of C_{18} SPE cartridge was eluted with 5 mL of toluene into 5.0 mL volumetric flask at 5 mm Hg Vacuum pressure. The 12 μL of 2000.00 ppm internal standard DBS was then added in 5.0 mL volumetric flask and the solution was injected into gas chromatograph under GC condition as described in Table 4.4.

4. The blank solution was prepared the same as step 1 to step 3 but the water sample was replaced by the double distilled water.

The internal standard solution was not added in step 3.

5. The concentration of each PE was calculated by using the internal standardization method and the results were presented in Table 4.27.

3.14 Confirmation on the Structure of Some Phthalate Esters by GC/MSD

The extracts of two water samples from Samparn coconut water and the river Chao Phya (at Prapadang Pier) by means of SPE technique were injected into GC/MSD under GC/MSD conditions in Table 3.3.

Table 3.3 The GC/MSD conditions for the confirmation on structure of some PEs

GC Parameter	GC/MSD Condition
Analytical column	25 m x 0.32 mm.ID. x 0.25 mm film thickness PAS - 1701
Temperature Program	90 ^{o}C (1 min) to 260 ^{o}C (5.0 min) at 25 ^{o}C/min
Splitless Time	1.0 min
Split Ratio	25 : 1
Flow Rate of Carrier Gas(He)	1.5 mL/min
Detector	Mass Selective Detector (MSD)
Inlet Temperature	280 ^{o}C
Transfer line Temperature	280 ^{o}C
Ion Source	EI (Electron-Impact)
Ion Analyzer	Quadrupole