CHAPTER 3

EXPERIMENTAL

3.1 Apparatus

A Shimadzu model GC-R1A gas chromatograph (Shimadzu Corp. Kyoto, Japan.) equipped with Flame Ionization Detector (FID) and the Shimadzu model RPR-G1 integrator (Shimadzu Corp. Kyoto, Japan) were used in this study.

A Memmert model 854 constant temperature water bath (Schwabach, W-Germany)

A Pressure-Lok series A2 gas-tight syringe 2.00 milliliters. (Precision Sampling Corp.,U.S.A.). (see appendix A).

Microsyringes 1.00 and 5.00 µL (Hamilton Company, Switzerland)

BLD-pipettlers 50.00 and 200.00 µL (Becton Dickinson Labware, U.S.A.)

Pipettes 1.00, 2.00, 5.00, 10.00, 25.00 mL.

Vials 3 and 8 drams.

Volumetric flasks 5.00, 10.00, 25.00, 50.00, 250.00, and 500.00 mL.

60 mL serum vials. (see appendix A).

Black rubber septa, aluminum foils, aluminum caps. (see appendix A).

Manual Hand Operated Crimper (Supelco.Inc., Bellefonte, PA, U.S.A.). (see appendix A).

All glasswares, including vials and serum vials were cleaned with detergent, 1:1 HNO_3:H_2O, water, and rinsed with double distilled water respectively and dried in an oven at 150 ^oC for 3 hours.

The procedure for calibrating the volume of all serum vials is described in appendix B.

3.2 CHEMICALS

3.2.1 The Standard of Semivolatile Organic Compounds

Ethylbenzene was purchased from Chem Service, Inc., West Chester, PA, U.S.A.

Chlorobenzene which was analytical reagent grade was purchased from Carlo Erba, Italy.

1,2-Dichlorobenzene 1,3-Dichlorobenzene and 1,4-Dichlorobenzene which were analytical reagent grade were purchased from Fluka A.G., Switzerland.

The standard chemicals were checked for the purity by gas chromatograph prior to use in the study and the standard chemicals used as primary standards in checking for the purities of these standard chemicals were provided by EPA. The result of the purities of standard was shown in Table 3.1 .

3.2.2 Organic Solvent

All solvents including absolute methanol and carbon disulfide were analytical reagent grade and were purchased from J.T. Baker Chemical Company, Deventer, Holland and E. Merck, Darmstdt, Germany, respectively. They were purified by fractional

distillation and the distillate was checked for the purity by gas chromatograph prior to use in the study.

Table 3.1 The result of the purities of semivolatile standard chemicals used in the headspace study.

Name of compound	% purity of chemical from EPA	% purity (± %RSD) of standard compounds
Ethylbenzene	99.30	91.50 ± 0.97
Chlorobenzene	99.90	91.13 ± 1.20
1,2-Dichlorobenzene	99.17	96.34 ± 0.43
1,3-Dichlorobenzene	-*	> 99.5
1,4-Dichlorobenzene	99.98	98.37 ± 0.38

Note * There is no primary standard chemical provided by EPA for checking the purity of standard 1,3-dichlorobenzene.

3.2.3 Sodium Sulfate and Sodium Chloride

Sodium chloride (A.R. Grade) and anhydrous sodium sulfate (A.R. Grade) were obtained from E. Merck, Darmstadt, Germany and J.T. Baker Chemical Company, Deventer, Holland, respectively. They were heated in an oven at 210 ^{o}C for 6 hours and were kept in desiccator before used.

3.2.4 Double distilled Water

The double distilled water used in this study was distilled by the Yamato distillator model WA-52R (Yamato Scientific

Co; Ltd. Tokyo, Japan) and it was checked for the purity by the headspace technique before used in the study.

3.3 Preparation of the Standard Solutions

3.3.1 The 2000.00 ppm Single Component Standard Solutions of Ethylbenzene, Chlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Carbon Disulfide.

The 2000.00 ppm single component standard stock solutions of each semivolatile organic compound, i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in carbon sulfide were prepared by weighing 0.0500 g of each standard, dissolving , diluting to the mark with carbon disulfide in 25.00 mL volumetric flask and mix thoroughly.

3.3.2 The Standard Mixture Solution of Ethylbenzene, Chlorobenzene, 1.2-Dichlorobenzene, 1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Carbon Disulfide.

A standard mixture solution containing 2008.00 , 2100.00, 2028.00, 2048.00, 1992.00 ppm of ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene, respectively, in carbon disulfide was prepared by dissolving 0.0502 g ethylbenzene, 0.0525 g chlorobenzene, 0.0507 g 1,2-dichlorobenzene, 0.0512 g 1,3-dichlorobenzene and 0.0498 g 1,4-dichlorobenzene with carbon disulfide and was then diluted to the mark with carbon disulfide in 25.00 mL volumetric flask.

3.3.3 The Single Component Standard Solutions of Ethylbenzene, Chlorobenzene, 1,2-Dichlorobenzene 1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Methanol.

The 125,000.00 ppm single component standard stock solutions of each semivolatile organic compound including ethylbenzene, chlorobenzene, 1,2-dichlorobenzene,1,3-dichlorobenzene and 1,4-dichlorobenzene were prepared by weighing 6.2500 g of each semivolatile standard , dissolving and diluting it with methanol to the mark in 50.00 mL volumetric flask. The other concentrations i.e., 12,500.00 ppm and 1,250.00 ppm of each semivolatile standard in methanol were prepared by pipetting 1.00 mL of 125,000.00 ppm of each standard stock solution into 10.00 mL and 100.00 mL volumetric flasks, respectively ,and were then diluted to the mark with methanol.

3.3.4 The Standard Mixture Solution of Ethylbenzene, Chlorobenzene, 1,2-Dichlorobenzene 1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Methanol.

The standard mixture solution containing 12,500.00 ppm of each standard compound, i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in methanol was prepared by transferring 1.00 mL of 125,000.00 ppm of each standard stock solution into a 10.00 mL volumetric flask and was diluted the mixture to the mark with methanol. The 1.00 mL of the 12,500.00 ppm standard mixture solution was then transferred into 10.00 mL volumetric flask and was diluted to the mark with methanol, resulting the standard mixture solution with final

concentration of 1,250.00 ppm.

3.3.5 The 500.00 ppb Single Component Standard Solutions of Ethylbenzene, Chlorobenzene, 1,2-Dichlorobenzene,1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Water.

The 500.00 ppb single component standard solutions of each semivolatile organic compound including ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in water were prepared by transferring 20.00 µL of the 12,500.00 ppm standard solutions of each semivolatile organic compound in methanol into 500.00 mL volumetric flask and was then diluted to the mark with double distilled water and mix thoroughly.

3.3.6 The 50.00 ppb Single Component Standard Solutions of Ethylbenzene, Chlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Water.

The 50.00 ppb single component standard solutions of each semivolatile organic compound, i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in water were prepared by pipetting 20.00 µL of 1,250.00 ppm standard methanolic solutions of each semivolatile organic compound into 500.00 mL volumetric flask and was then diluted it to the mark with double distilled water and mix thoroughly.

3.3.7 The 500.00 ppb Standard Mixture Solution of Ethylbenzene, Chlorobenzene,1,2-Dichlorobenzene, 1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Water.

The standard mixture solution containing 500.00 ppb of ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in water was prepared by pipetting 20.00 µL of the 12,500.00 ppm standard solution of the mixture in methanol into a 500.00 mL volumetric flask and was diluted to the mark with double distilled water and mix thoroughly.

3.3.8 The 50.00 ppb Standard Mixture Solution of Ethylbenzene, Chlorobenzene, 1,2-Dichlorobenzene,1,3-Dichlorobenzene and 1,4-Dichlorobenzene in Water.

A standard mixture solution containing 50.00 ppb of ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in water was prepared by measuring 20.00 uL of 1,250.00 ppm standard solution of the mixture in methanol with 50.00 µL microsyringe and transferring it into a 500.00 mL volumetric flask. It was then diluted it to the mark with double distilled water and mix thoroughly.

3.4 Gas Chromatographic Conditions

Table 3.2 The gas chromatographic conditions used in the study of single component solution.

GC Parameters	Compound *				
	ETB	CB	oCB	mCB	pCB
Analytical Column	1.8 m x 3 mm ID, glass column packed with 8.9% FFAP on chromosorb WAW, 100/120 mesh.				
Oven Temperature (^{o}C)	80	110	130	130	130
Flow Rate (mL/min) of					
Carrier Gas (N_2)	40	40	40	40	40
H_2	50	50	50	50	50
Air	500	500	500	500	500
Detector	FID	FID	FID	FID	FID
Detector Temperature (^{o}C)	210	210	210	210	210
Injection Temperature (^{o}C)	210	210	210	210	210

Note * :

ETB = ethylbenzene, CB = chlorobenzene, oCB = 1,2-dichlorobenzene, mCB = 1,3-dichlorobenzene, pCB = 1,4-dichlorobenzene

Table 3.3 The gas chromatographic condition used in the study of standard mixture solution.

GC Parameters	GC Condition
Analytical Column	1.8 m x 3 mm ID, glass column packed with 8.9 % FFAP on chromosorb WAW, 100/120 mesh.
Oven Temperature (^{o}C)	80 ^{o}C for 9 min., then to 110 ^{o}C at 30 ^{o}C/min and hold for 8 min.
Flow Rate (mL/min) of	
Carrier Gas (N_2)	40
H_2	50
Air	500
Detector	FID
Detector temperature (^{o}C)	210
Injection Temperature (^{o}C)	210

3.5 The Study of the Various Parameters on the Sensitivity of Headspace Technique.

The various parameters which have the effect on the sensitivity of the headspace technique including the equilibration time, temperature, phase ratio, injection volume and salting out were studied in order to be able to determine the optimum headspace analysis condition and therefore the procedures for the studies were described as follows :

3.5.1 Equilibration Time

1. pipet 25.00 mL of the 500.00 ppb standard single component in aqueous solution into a series of 60 mL serum vials.

2. Close each vial with aluminum foil, black rubber septum and aluminum cap sequentially, and then tightly crimp it with Manual Hand Operated Crimper .

3. Place the sealed serum vial in a constant temperature water bath which the temperature is set at 40.0 ^{o}C for 0, 3, 5, 10, 20, 30, 60, 120, 180 minutes.

4. Each serum vial is taken from the constant temperature water bath when it reaches the time as set in 3 and it is shaken vigorously for about 1 minute .

5. Withdraw 1.00 mL of vapor phase from the sample vial with a 2.00 mL Pressure-Lok series A2 gas-tight syringe and is then injected into gas chromatograph under the GC condition as described in Table 3.2 .

6. Plot peak area of each studied compound (A_g) against time (min).

3.5.2 Temperature

The procedure for the study of the effect of the temperature i.e., 30.0°, 40.0°, 50.0°, 60.0°, and 70.0 °C on the sensitivity of headspace technique was described as the follow:

1. Pipet 25.00 mL of 500.00 ppb standard single component in aquecus solution into a series of 60 mL serum vials.

2. Close each vial with aluminum foil, black rubber septum and aluminum cap sequentially, and then tightly crimp it with Manual Hand Operated Crimper.

3. Place them in a constant temperature water bath which is set at various temperature, i.e., 30.0°, 40.0°, 50.0°, 60.0°, and 70.0 °C and leave them to stand in the water bath until they reach an equilibration time as found in the section 3.5.1 .

4. Each serum vial is taken out from the constant temperature water bath and it is shaken vigorously for about 1 minute.

5. Withdraw 1.00 mL of vapor phase from each serum vial with a 2.00 mL Pressure-Lok series A2 gas-tight syringe and is injected into gas chromatograph under the GC condition as described in Table 3.2 .

6. Calculate the sensitivity (S) of interested component by dividing the peak area of the interested component by its initial concentration in aqueous phase (C^{o}_{l}).

7. Determine the concentration of interested component in vapor phase (C_g) by means of external standardization method, then calculate the distribution coefficient of each interested component (K).

8. Plot the sensitivity (S) and the distribution coefficient (K) against the temperature (^{o}C).

The optimum temperature of each semivolatile organic compound found in this section would be used in the next study.

3.5.3 Liquid to Gas Phase Ratio

The liquid to gas phase ratios, i.e., 5:55, 10:50, 15:45, 25:35, 35:25, 50:10 of each semivolatile organic compound were studied in order to be able to determine the optimum phase ratio. The procedure for this study was described as follows:

1. Pipet 5.00, 10.00, 15.00, 25.00, 35.00, 50.00 mL of 500.00 ppb standard single component in aqueous solution into a series of 60 mL serum vials.

2. Close each vial with aluminum foil, black rubber septum and aluminum cap sequentially, and then tightly crimp it with Manual Hand Operated Crimper.

3. Place them into a constant temperature water bath which the temperature is set at the optimum temperature as found in section 3.5.2.

4. Each serum vial is taken out from the water bath when it reaches the equilibration time and it is shaken vigorously for about 1 minute .

5. Withdraw 1.00 mL vapor phase from the sample vial with a 2.00 mL Pressure-Lok series A2 gas-tight syringe and is injected into gas chromatograph under the GC condition as described in Table 3.2 .

6. Calculate the sensitivity (S) of interested component by dividing the peak area of the interested component by its initial concentration in aqueous phase (C^{o}_{l}).

7. Determine the concentration of interested component in vapor phase (C_g) by means of external standardization method, then calculate the distribution coefficient of each interested component (K).

8. Plot the distribution coefficient (K) and the sensitivity (S) against the phase ratio (V_l/V_g).

The optimum liquid to gas phase ratio of each semivolatile compound found in this study would be used in the next study.

3.5.4 Injection Volume

The injection volumes of headspace gas for each semivolatile organic compound i.e., 0.50, 1.00, 1.50, 2.00 mL were studied in order to be able to determine the optimum injection volume. The procedure for the study of the injection volume was described as follows :

1. Pipet 25.00 mL of 500.00 ppb standard single component in aqueous solution into a series of 60 mL serum vials.

2. Close each vial with aluminum foil, black rubber septum and aluminum cap sequentially, and then tightly crimp it vial with Manual Hand Operated Crimper .

3. Place them into a constant temperature water bath which the temperature is set at the optimum temperature as found in

section 3.5.2.

4. Each serum vial is taken out from the constant temperature water bath when it reaches the equilibration time and it is shaken vigorously for about 1 minute .

5. Withdraw 0.50, 1.00, 1.50 and 2.00 mL of vapor phases from each vial, respectively, with a 2.00 mL Pressure-Lok series A2 gas-tight syringe and is then injected it into the gas chromatograph under the GC condition as described in Table 3.2.

6. Calculate the sensitivity of each semivolatile organic compound by dividing the peak area of each compound by its initial concentration in aqueous phase (C^{o}_{l}) and then plot the sensitivity of each semivolatile organic compound against the injection volume.

The optimum injection volume of each semivolatile organic compound found in this section would be used in the next study.

3.5.5 Salting Out Effect

The equilibration time, temperature, liquid to gas phase ratio, and injection volume of each semivolatile organic compound were studied and were evaluated. Therefore, they would be used in the study of the effect of adding salt on the percent recovery of headspace technique. The study of the salting out effect was carried out with 50.00 ppb and 500.00 ppb standard mixture solutions and each study was consisted of three systems :-

1. no addition of salt (not salting out)

2. 10.00 g of sodium chloride

3. 10.00 g of anhydrous sodium sulfate

The procedure for this study was described as follow :

1. Weigh 10.00 g of sodium chloride and 10.00 g of anhydrous sodium sulfate in a series of 60 mL serum vials

2. Transfer 25.00 mL of the standard mixture in aqueous solution into three 60 mL serum vials containing no salt, 10.00 g of sodium chloride and 10.00 g of anhydrous sodium sulfate .

3. Close each vial with aluminum foil, black rubber septum and aluminum cap sequentially, and then tightly crimp it with Manual Hand Operated Crimper .

4. Place them into a constant temperature water bath which the temperature is set at 45.0 ^{o}C for 30 min and each vial is occasionally shaken vigorously during the equilibration at 45.0^{o} C.

5. Withdraw 2.00 mL of vapor phase from the serum vial by using a 2.00 mL Pressure-Lok series A2 gas-tight syringe and is then injected into the gas chromatograph under GC condition as described in Table 3.2.

6. Determine the concentration of the interested component in gas phase (C_g) by means of external standardization method, then calculated distribution coefficient (K) and %E of each component.

7. Compare the percent recoveries (%E) of each interested compound against the three systems studied i.e., nonsalting out, 10.00 g of anhydrous sodium salfate salt,and 10.00 g of sodium chloride.

3.6 Quantitative Headspace Analysis (22,65)

Any traditional quantitative gas chromatographic techniques can be used to determine the initial concentration (C^o_l) of a substance in solution from its concentration in the gas phase. The methods of standard addition and external standardization were chosen as the quantitative methods for the determination of the initial concentration of each semivolatile organic compound in unknown aqueous solutions. The principle of these two quantitative methods is described in the following clauses.

3.6.1 The External Standardization Method (22)

The quantitative analysis in the headspace technique can be carried out in two different methods:

3.6.1.1 When the Distribution Coefficient, K, of the Interested Compounds Is Known.

The initial concentration of each interested compound in aqueous solution, C^o_l, can be determined by using Equation 2.16. Since the volume V_l of the liquid phase, the volume V_g of the gas phase, the distribution coefficient, K, of the interested compound is known and the equilibrium concentration of each interested compound , C_g, in the equilibrated unknown sample can be determined by means of external standardization method as described in section 3.7; hence, by substitution the value of C_g, K, V_g, and V_l into Equation 2.16, the initial concentration of the interested compound, C^o_l, in the aqueous solution can be easily calculated.

$$C^{o}_{l} = Cg \left(K + \frac{V_g}{V_l} \right) \qquad (2.16)$$

3.6.1.2 When the Distribution Coefficient, K, of the Interested Compounds Is Not known.

A various concentrations of standard mixture of interested components in aqueous solution are prepared for constructing the standard calibration curves of each interested compound. These standard mixtures in aqueous solution are analyzed by the headspace technique under the identical headspace analytical condition and GC condition as the analyzed sample. Then the peak area of each standard component obtained from the chromatogram ($A_{g,st}$) is plotted against the initial concentration of the standard ($C^{o}_{l,st}$) . The curve should be linear for a particular system. The slope (m) and y-intercept (b) can be calculated by the linear least square method from a linear equation

$$A_{g,st} = m\, C^{o}_{l,st} + b \qquad (3.3)$$

The exact volume of the vapor phase from the equilibrated unknown sample is then chromatographed. Finally, the initial concentration of the interested compound i in the aqueous solution ($C^{o}_{l,i}$) can be determined by substitution the peak area $A_{g,i}$ of the interested component into the equation (3.3).

3.6.2 The Method of Standard Addition (65)

The standard addition method should be used when it is impossible to suppress interferences from matrix elements. To quantify the unknown headspace sample with this method, two serum vials containing the same volume of the identical analyzed sample are prepared. A small amount of analyte solution of known concentration is spiked into one of the two serum vials, then the headspace analysis are made on the unspiked sample and the spiked sample using the same headspace analysis condition, instrument parameters, and procedure. If a gas chromatographic response, A_g, is obtained from a sample solution of unknown initial concentration, C^o_1, and a gas chromatographic response A_{g+st} from the sample solution to which a known concentration, C_{st}, of analyte has been added, then C^o_1 can be calculated from the following relation

$$\frac{C^o_1}{C^o_1 + C_{st}} = \frac{A_g}{A_{g+st}} \qquad (3.7)$$

It is always advisable to check the result with at least one other standard addition. Addition of analyte equal to twice and one-half the amount of analyte in the original sample are optimum statistically. All solution should be diluted to the same final volume so any interference in the sample matrix will have an identical effect on each solution.

3.7 The Determination of Equilibrium Concentration of the Interested Compound in Gas Phase .

In order to determine the equilibrium concentration of the interested components in vapor phase ($C_{g,i}$), the calibration curve of each interested component must be constructed. Thus, a series of standard solutions containing the known weight of the components in carbon disulfide were prepared and chromatographed under the identical GC condition as the analyzed sample. Then the peak area of each standard component obtained from the chromatogram ($A_{g,st}$) was plotted against the weight of the standard component ($W_{g,st}$) . The curve should be linear for a particular system. The slope (m) and y-intercept (b) can be calculated by the linear least square method from a linear equation

$$A_{g,st} = m W_{g,st} + b \qquad (3.1)$$

The exact volume of the vapor phase from the equilibrated headspace sample (v_g) was then chromatographed. The computation of weight of the interested component i in gas phase ($W_{g,i}$) can be compared graphically to the constructed calibration curve of that interested component or calculated by substitution the peak area of the interested component i ($A_{g,i}$) into Equation (3.1); and, the equilibrium concentration of the interested component i in vapor phase can be calculated by dividing the weight of interested compound ($W_{g,i}$) by the injection volume of vapor phase (v_g), therefore:

$$C_{g,i} = \frac{W_{g,i}}{v_g} \qquad (3.2)$$

where $C_{g,i}$ = Equilibrium concentration of the interested component i in gas phase.

v_g = Injection volume of gas phase.

The calibration curves of each standard compound including ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene in carbondisulfide used in the determination of the weight of the interested component were shown in Figures 3.1, 3.2, 3.3, 3.4, and 3.5, respectively.

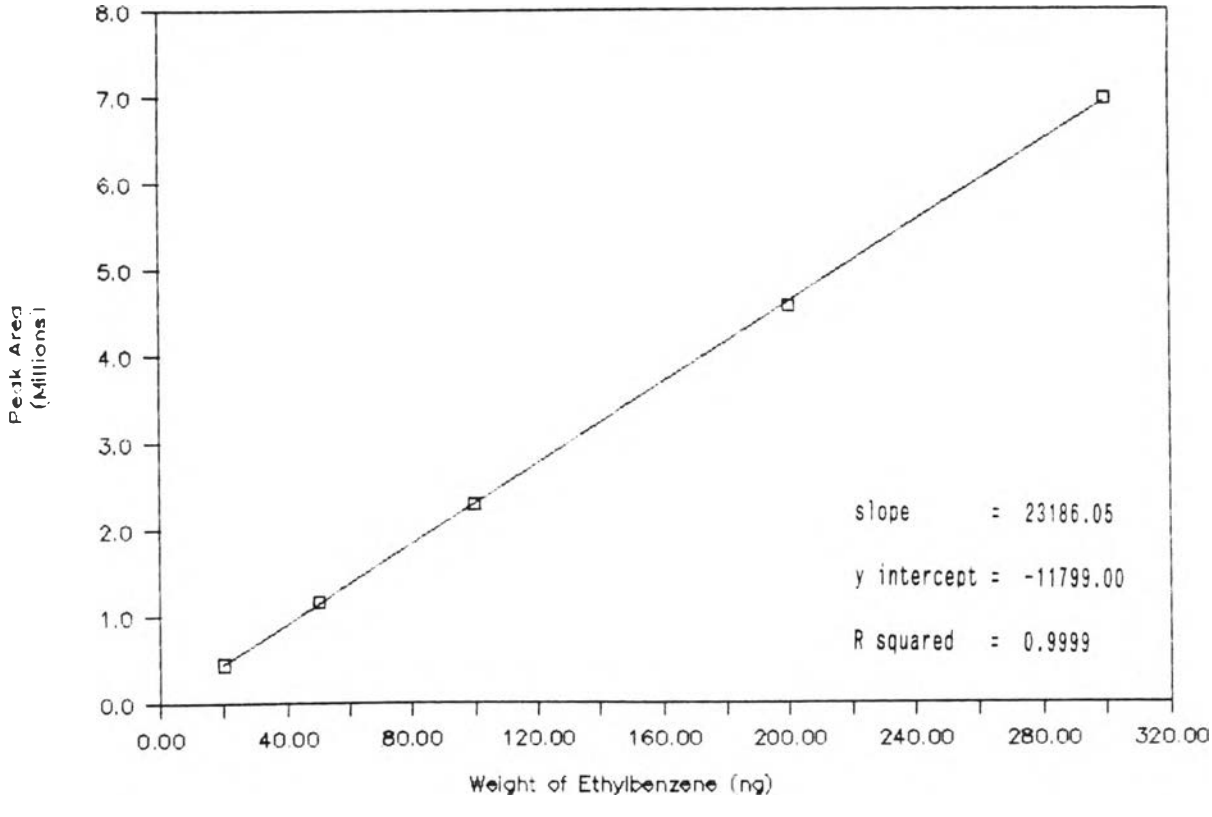

Figure 3.1 The calibration curve of ethylbenzene in carbon disulfide.

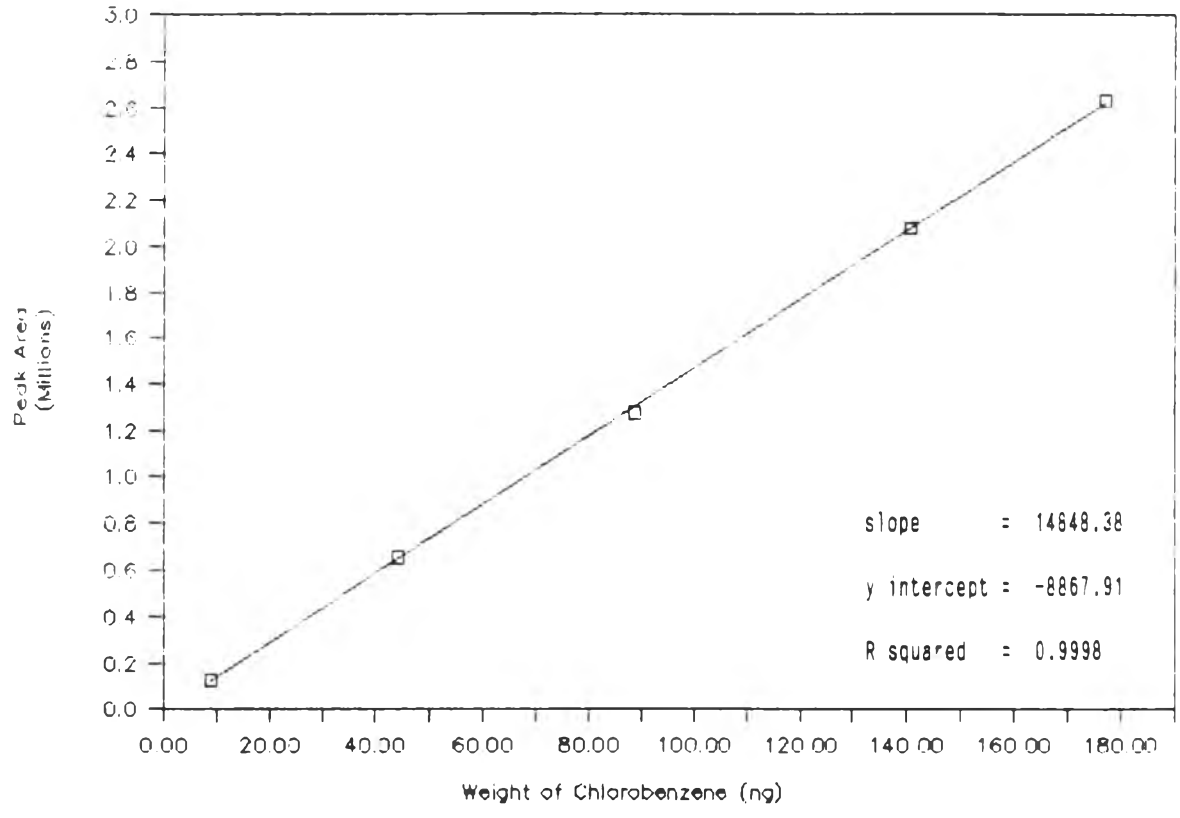

Figure 3.2 The calibration curve of chlorobenzene in carbon disulfide.

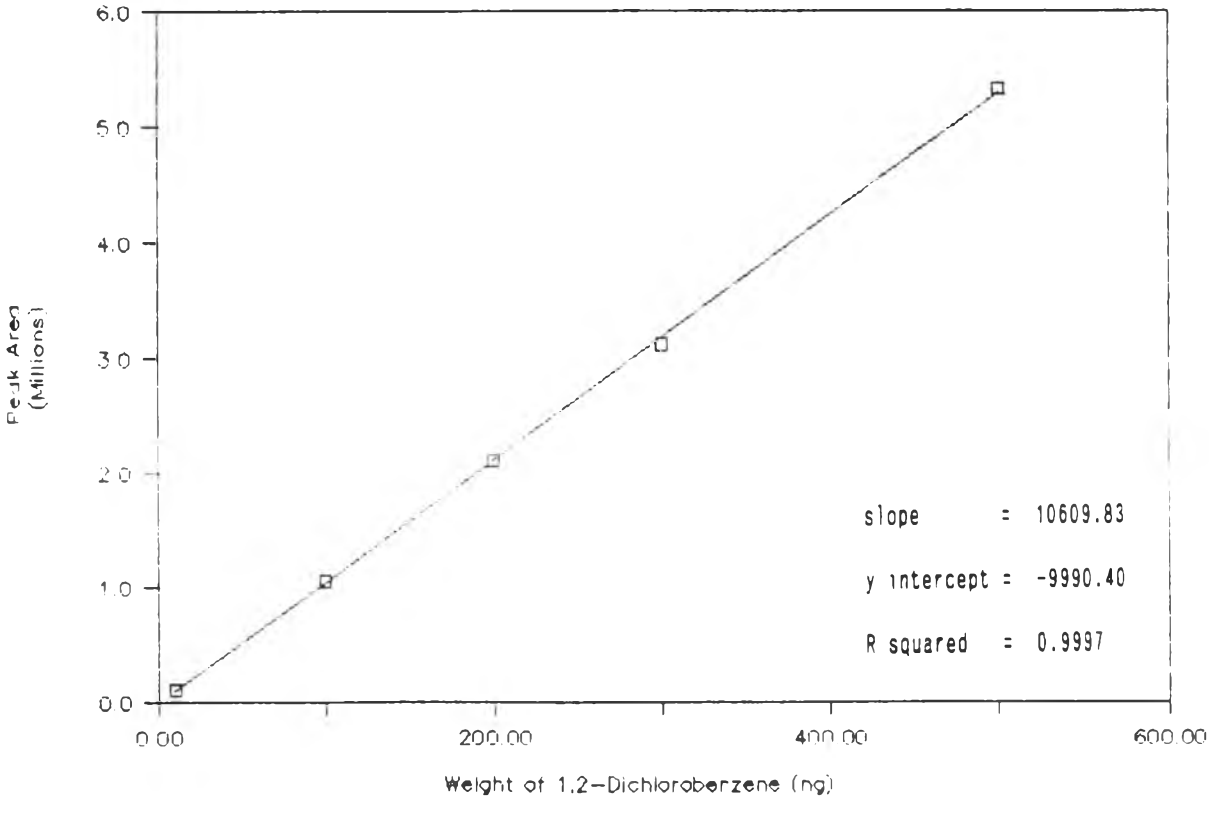

Figure 3.3 The calibration curve of 1,2-dichlorobenzene in carbon disulfide.

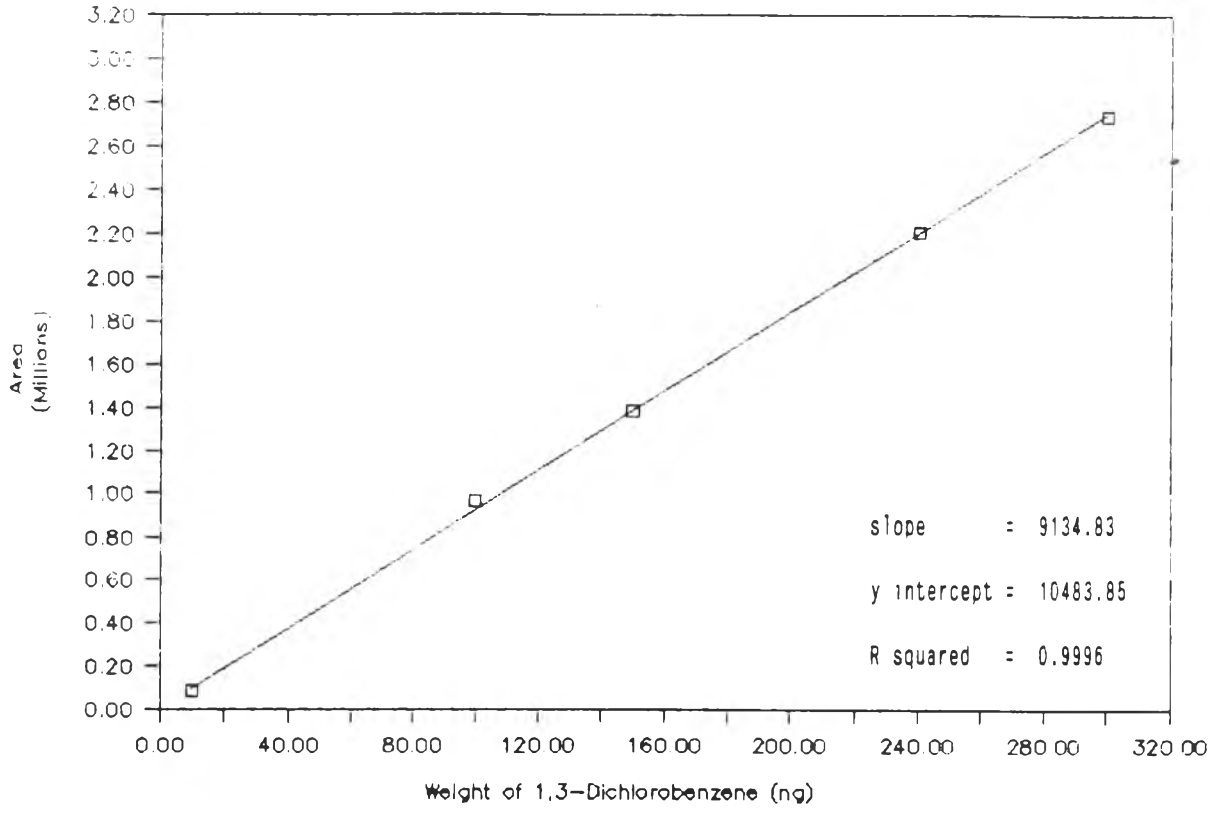

Figure 3.4 The calibration curve of 1,3-dichlorobenzene in carbon disulfide.

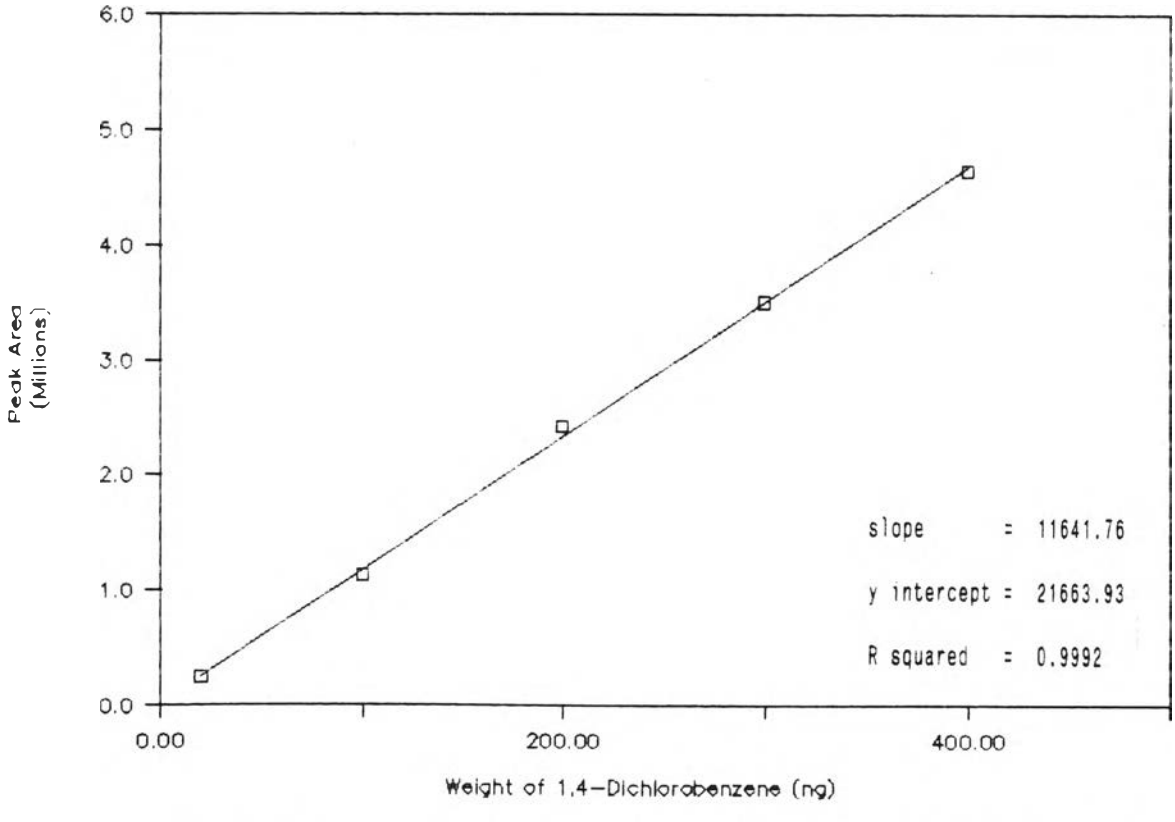

Figure 3.5 The calibration curve of 1,4-dichlorobenzene in carbon disulfide.

3.8 The Procedure for Checking the Accuracy of Headspace Analysis Technique

To evaluate the accuracy of this technique, the synthetic unknown mixture solution in methanol were prepared. The concentration of each semivolatile organic compound in the synthetic unknown solution was determined by means of the external standardization method as described in section 3.6.1.2 and standard addition method under the optimum headspace analysis condition found in the previous studied These two procedures were described as follow :

3.8.1 The Quantitative Headspace Analysis by External Standardization Method

1. Pipet 20.00 μL of the synthetic unknown solution in methanol into a 500.00 mL volumetric flask, and is then diluted to the mark with double distilled water and mix it well.

2. Pipet 25.00 mL of the unknown in aqueous solution into a 60 mL serum vial containing 10.00 g of anhydrous Na_2SO_4.

3. Close the vial with aluminum foil, black rubber septum and aluminum cap sequentially, and then tightly crimp the serum vial with Manual Hand Operated Crimper .

4. Place it into a constant temperature water bath which the temperature is set at 45.0 ^{o}C for 30 min and a vial is shaken vigorously in occasion during the equilibration at 45.0 ^{o}C.

5. Withdraw 2.00 mL of vapor phase from the serum vial by using a 2.00 mL Pressure-Lok series A2 gas-tight syringe and

is then injected into gas chromatograph under the GC condition as described in Table 3.3 .

6. Determine the initial concentration of each semivolatile organic compound in aqueous solution (C^{o}_{l}) from the absolute calibration curves as shown in Figures 3.6-3.10.

3.8.2 The Quantitative Headspace Analysis by Standard Addition Method

To quantify the components in the synthetic unknown sample with standard addition method, two serum vials are needed to prepare the following samples

1. unspiked sample,
2. spiked sample.

The procedure of preparing the above samples and quantifying the interested components was described as the follow :

1. Pipet 20.00 μL of the synthetic unknown solution in methanol into a 500.00 mL volumetric flask. Dilute to the mark with double distilled water and mix them well.

2. Add 10.00 g of anhydrous sodium sulfate and 25.00 mL of the synthetic unknown in aqeous solution sequentially in each vial and spike known amount of standard mixture solution in methanol into the spiked sample vial.

3 Close the vials with aluminum foils, black rubber septa and aluminum caps sequentially, and then tightly crimp the serum vials with Manual Hand Operated Crimper.

4. Place them into a constant temperature water bath which the temperature is set at 45.0 ^{o}C for 30 min and each

vial is shaken vigorously in occasion during the equilibration at 45.0°C.

5. Withdraw 2.00 mL of gas phase from the serum vial by using a 2.00 mL Pressure-Lok series 2A gas-tight syringe and is then injected into gas chromatograph under the GC condition as described in Table 3.3 .

6. Determine the initial concentration of the interested component i, $C^{o}_{l,i}$, in the unknown aqueous solution by standard addition method.

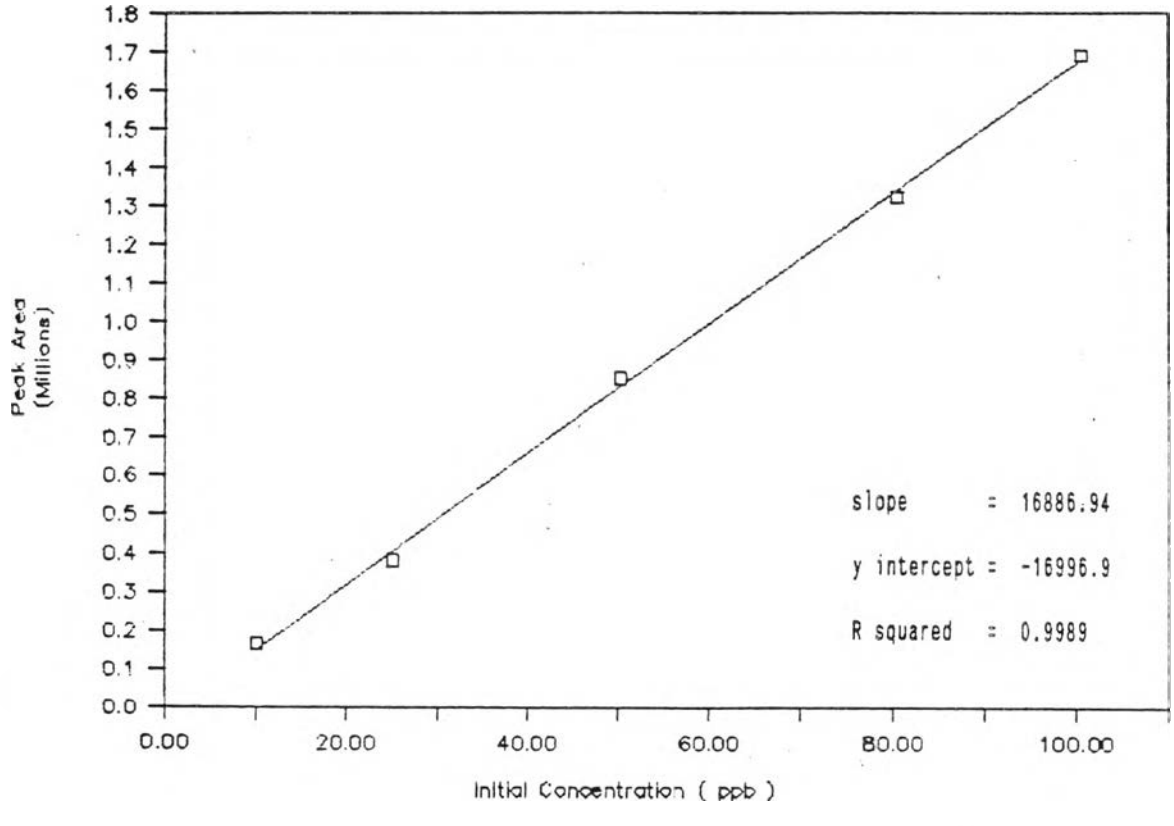

Figure 3.6 The absolute calibration curve of ethylbenzene in aqueous solution.

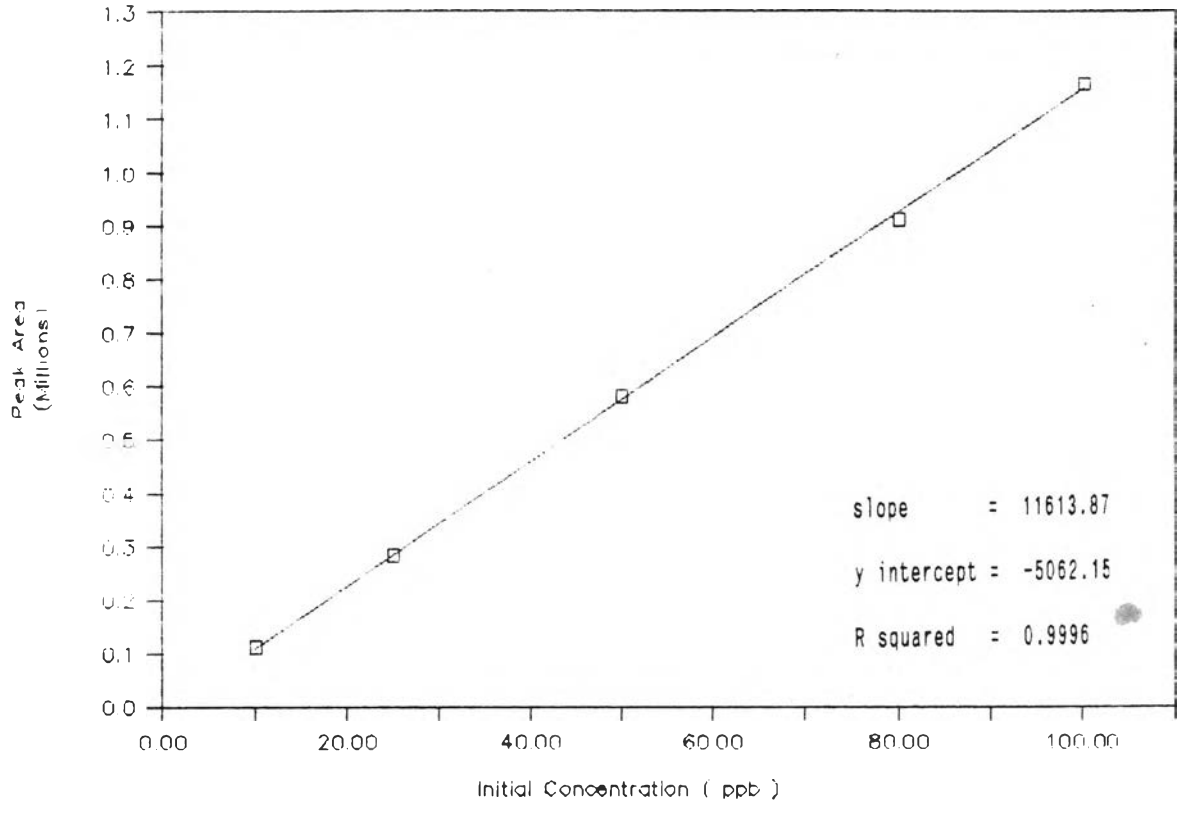

Figure 3.7 The absolute calibration curve of chlorobenzene in aqueous solution.

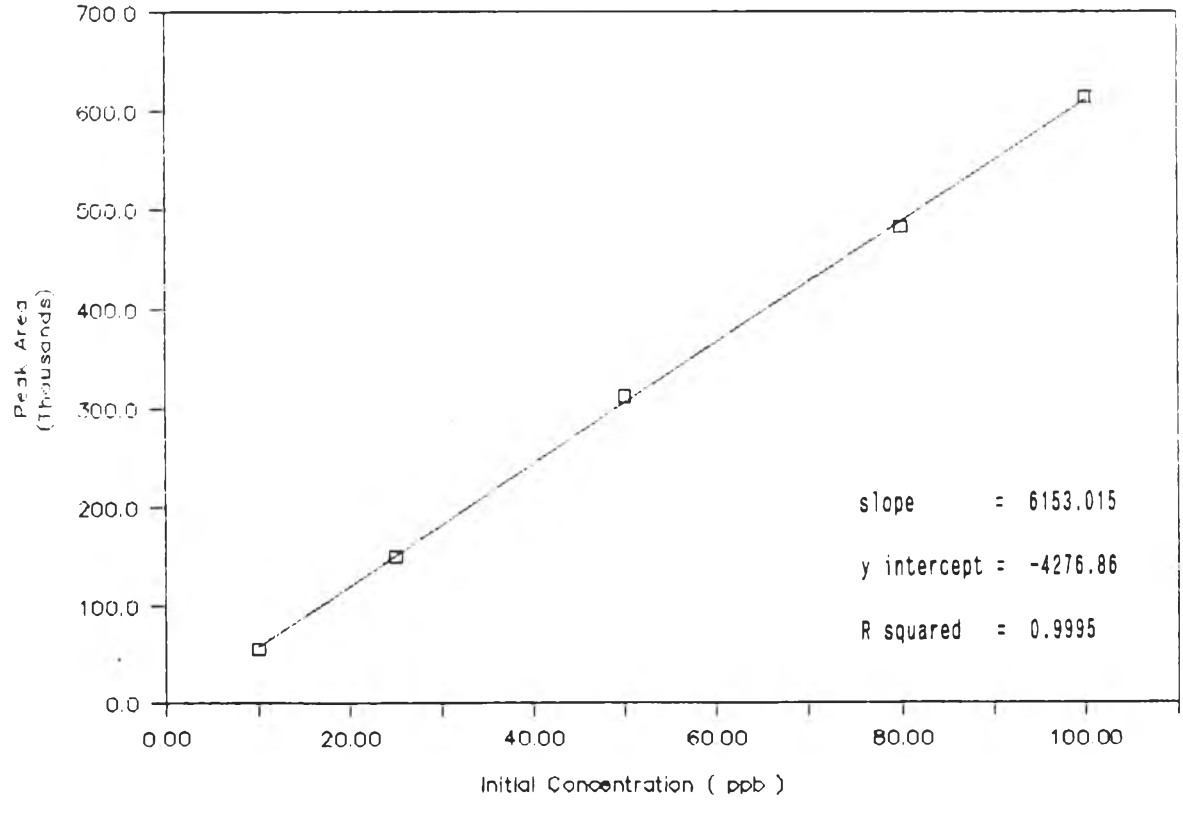

Figure 3.8 The absolute calibration curve of 1,3-dichlorobenzene in aqueous solution.

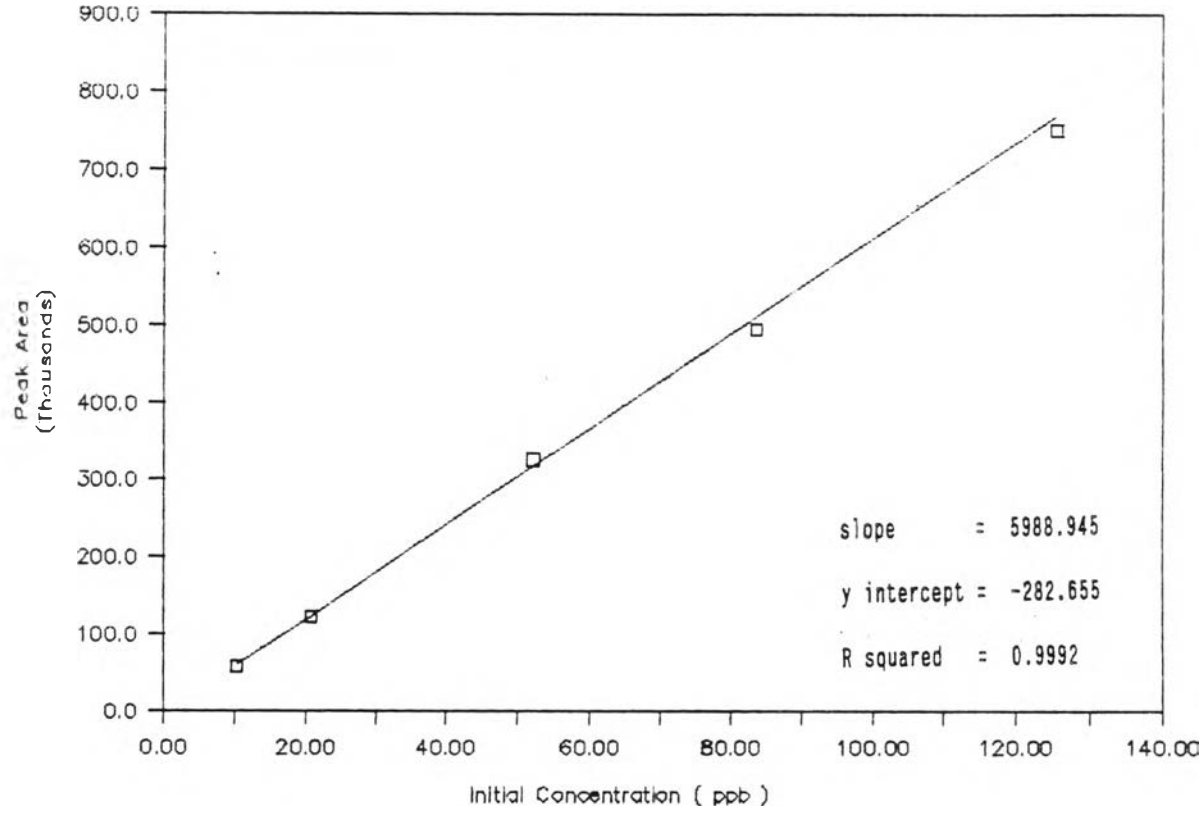

Figure 3.9 The absolute calibration curve of 1,4-dichlorobenzene in aqueous solution.

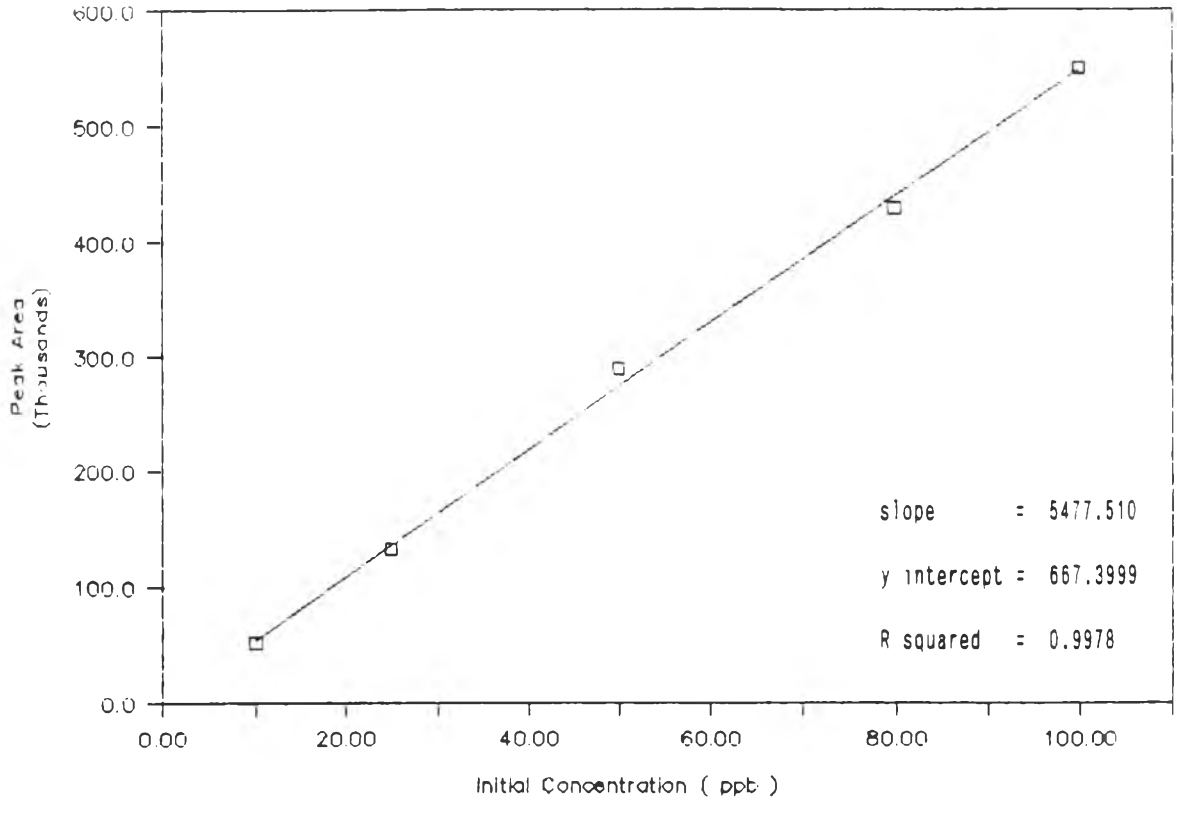

Figure 3.10 The absolute calibration curve of 1,2-dichlorobenzene in aqueous solution.