

APPENDICES

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่

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APPENDIX A

The physical properties of carbaryl

Table 1 The physical properties of carbaryl [8-12].

Molecular formula	$C_{12}H_{11}NO_2$
Molar mass	201.22 g mol ⁻¹
Appearance	Colorless crystalline solid
IUPAC name	1-naphthyl methylcarbamate
Melting point	142°C
Vapor pressure	< 0.005 mmHg at 26°C
Specific gravity	1.23
Solubility in water	40 ppm at 30°C
Solubility in organic solvent at 20°C	250 ppm in n-Heptane 9860 ppm in Xylene 87500 ppm in Methanol 175000 ppm in Ethyl acetate
Half life (in orange)	14 days
MRL (Thailand)	15 mg kg ⁻¹

APPENDIX B

The physical properties of dimethoate

Table 2 The physical properties of dimethote [8, 22-24].

Molecular formula	$C_5H_{12}NO_3PS_2$
Molar mass	229.26 g mol ⁻¹
Appearance	Grey-white crystalline solid
IUPAC name	O,O-dimethyl S-[2-(methylamino)-2-oxoethyl] dithiophosphate
Melting point	43-45 °C (316-318 K)
Boiling point	117 °C (390 K) at 0.01 kPa
Flash point	107 °C
Density	1.3 g cm ⁻³ , solid
Specific gravity	1.28 at 20 °C
Solubility in water	2.5 g/100 mL
Solubility in organic solvent	Soluble in methanol and cyclohexane Slightly soluble in aliphatic hydrocarbons, aromatic hydrocarbons, diethyl ether, carbon tetrachloride, hexane and xylene Very soluble in chloroform, benzene, toluene, alcohols, esters, ketones, methylene chloride, acetone and ethanol

Table 2 (Continued)

Insoluble	petroleum ether
Vapor pressure	8.50 x 10 ⁻⁶ mmHg at 25 °C 1.85 x 10 ⁻⁶ mmHg at 20 °C 2.90 x 10 ⁻⁴ mmHg at 50 °C
Half life (in orange peel)	13-14 days
MRL (Thailand)	5 mg kg ⁻¹

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APPENDIX C

The physical properties of fenvalerate

Table 3 The physical properties of fenvalerate [8, 35-36].

Molecular formula	$C_{25}H_{22}ClNO_3$
Molar mass	419.9 g mol^{-1}
Appearance	Yellow-brown viscous liquid
IUPAC name	(RS)-alpha-Cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate
Density	1.175 g cm^{-3} at $25 \text{ }^\circ\text{C}$
Vapor pressure	0.037 mPa at $25 \text{ }^\circ\text{C}$
Solubility in water	$2 \text{ } \mu\text{g L}^{-1}$
Solubility in organic solvent	$> 500 \text{ g L}^{-1}$ in acetone, chloroform, cyclohexanone, ethanol, methanol, and xylene at $23 \text{ }^\circ\text{C}$ and 134 g L^{-1} in hexane at $23 \text{ }^\circ\text{C}$.
Half life (in plant surface)	14-28 days
MRL (Thailand)	$2 \text{ } \mu\text{g L}^{-1}$

APPENDIX D

Literatures review of extracting solvent for class of pesticide

Table 4 Literatures review of extracting solvent for different class of pesticide.

Organochlorine	Carbamate	Organophosphate	Pyrethroid	Organochlorine
	n-hexane [115]	DCM [116]	EtOAc [117]	
	MeOH [118]	Acetone [116]	DCM [119, 120]	
	Light petroleum-DCM (1:1) [121]	Hexane [116]	ACN-Hexane [122]	
	CH ₃ Cl ₂ [123]	Toluene [124]	Toluene-Water [125]	
		ACN [126]	Hexane-Acetone (1:1) [127]	
	Acetone-DCM [128]		Acetone following petroleum ether [129]	
	Petroleum ether and DCM [7:3, v/v] [130]			
	EtOAc [131]			
	Cyclohexane [131]			
	ACN [131]			
	DCM [131]			
	Acetone-Methylene chlorine (1:1, v/v) [132]			
	Acetone [133]			
	ACN [133]			
	n-haxane [134]			

APPENDIX E

UV cutoff point

Table 5 UV cutoff point of solvents [135].

Solvent	UV Cutoff (nm)
Acetonitrile	190
Pentane	190
Water	190
Hexane	195
Cyclopentane	198
Cyclohexane	200
Heptane	200
Isopropyl Alcohol	205
Methanol	205
Ethyl alcohol	210
2-Methoxyethanol	210
Methyl <i>t</i> -Butyl Ether	210
<i>n</i> -Propyl Alcohol	210
Trifluoroacetic acid	210
Tetrahydrofuran	212
<i>n</i> -Butyl Alcohol	215
1,4-Dioxane	215
Ethyl Ether	215
Iso-Octane	215

Table 5 (continued)

Solvent	UV Cutoff (nm)
<i>n</i> -Butyl Chloride	220
Isobutyl Alcohol	220
Propylene Carbonate	220
Ethylene Dichloride	228
1,1,2-Trichlorotrifluoroethane	231
Dichloromethane	233
Chloroform	245
<i>n</i> -Butyl Acetate	254
Ethyl acetate	256
Dimethyl Acetamide	268
<i>N,N</i> -Dimethylformamide	268
Dimethyl Sulfoxide	268
Toluene	284
<i>N</i> -Methylpyrrolidone	285
Chlorobenzene	287
<i>o</i> -Xylene	288
<i>o</i> -Dichlorobenzene	295
1,2,4-Trichlorobenzene	308
Methyl Ethyl Ketone	329
Acetone	330
Methyl Isoamyl Ketone	330
Methyl <i>n</i> -Propyl Ketone	331
Methyl Isobutyl Ketone	334

APPENDIX F

Peak area of dimethoate as analyzed by GC using of EtOAc as extracting solvent

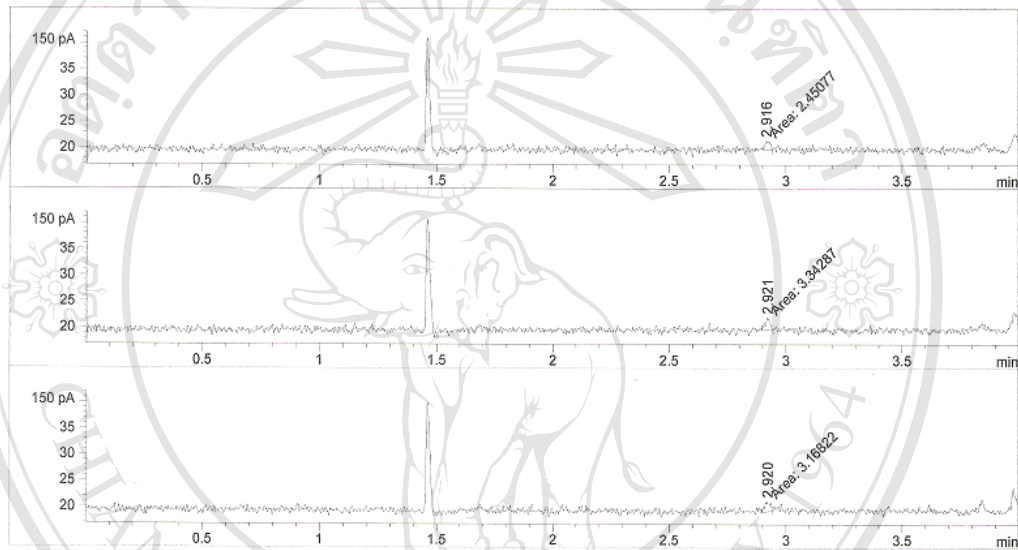


Figure 1 Peak area of dimethoate in un-spiked sample.

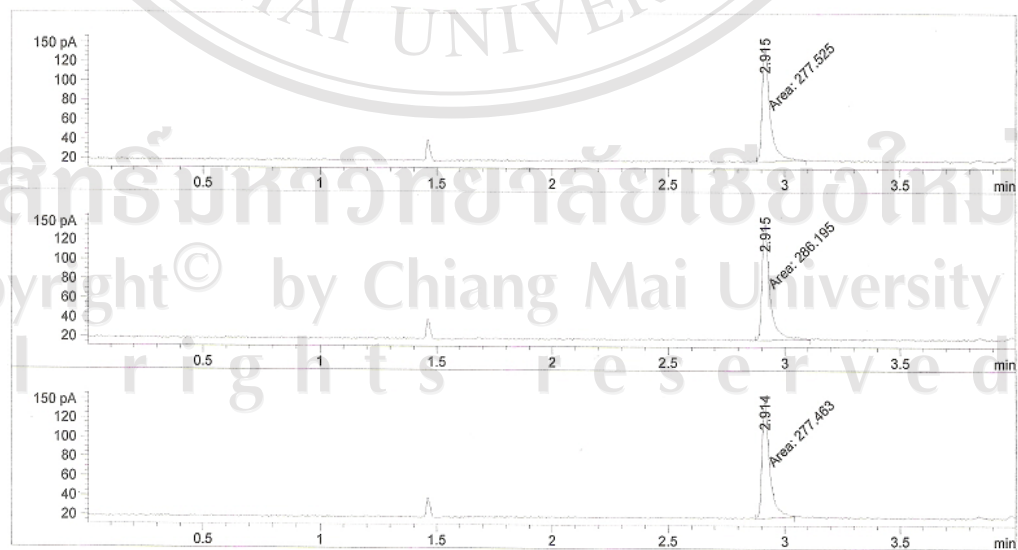


Figure 2 Peak area of dimethoate in spiked sample.

APPENDIX G

Peak areas of dimethoate as analyzed by GC at sonication time 15 minutes

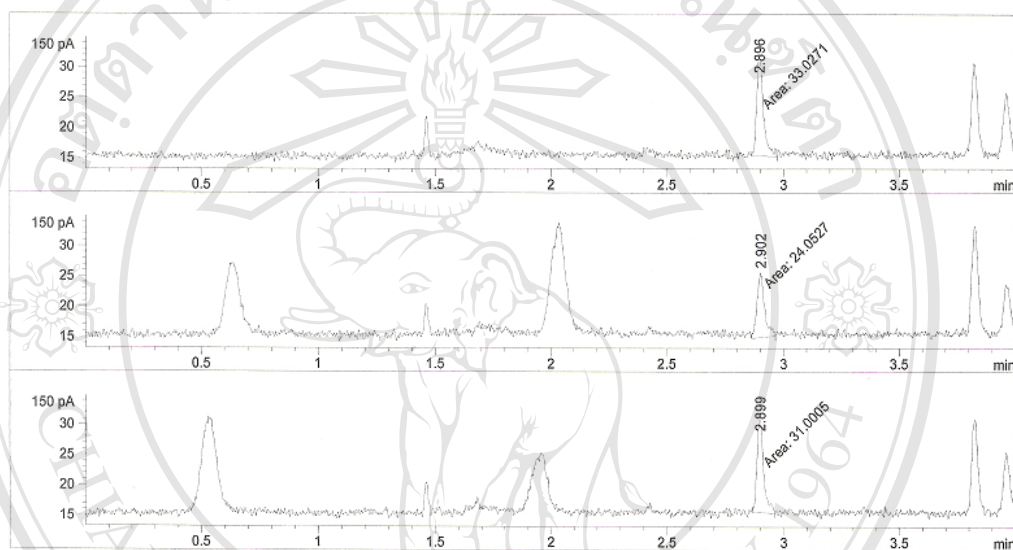


Figure 3 Peak area of dimethoate in un-spiked sample.

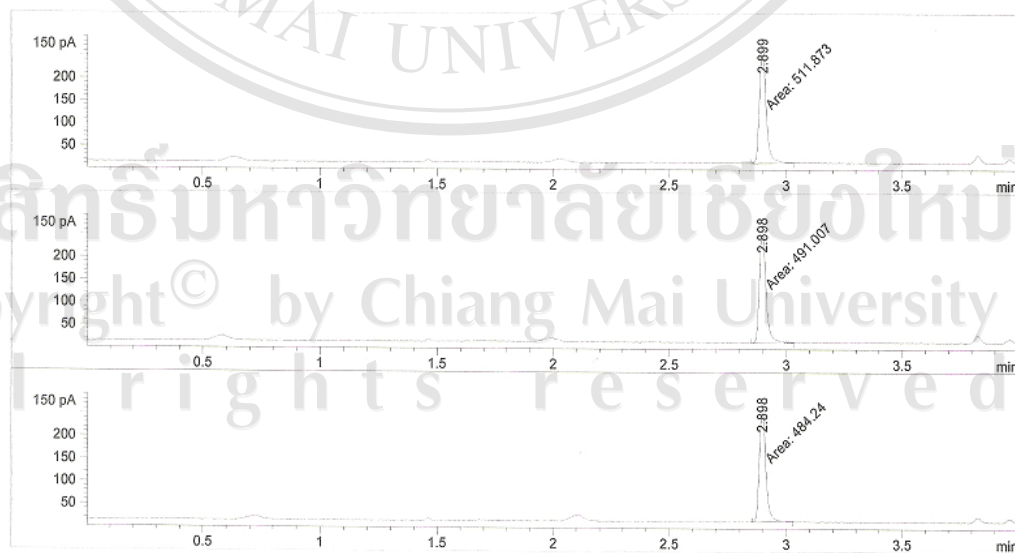


Figure 4 Peak area of dimethoate in spiked sample.

APPENDIX H

Residual silanol group on C18 sorbent

Reverse Phase SPE [136]

Reverse phase separations involve a polar or moderately polar sample matrix and a nonpolar stationary phase. The analyte of interest is typically mid- to nonpolar. Several SPE materials, such as the alkyl- or aryl-bonded silicas (LC-18, ENVI-18, LC-8, ENVI-8, LC-4 and LC-Ph) are in the reversed phase category. Here, the hydrophilic silanol groups at the surface of the raw silica packing (Figure 5) have been chemically modified with hydrophobic alkyl or aryl functional groups by reaction with the corresponding silanes.

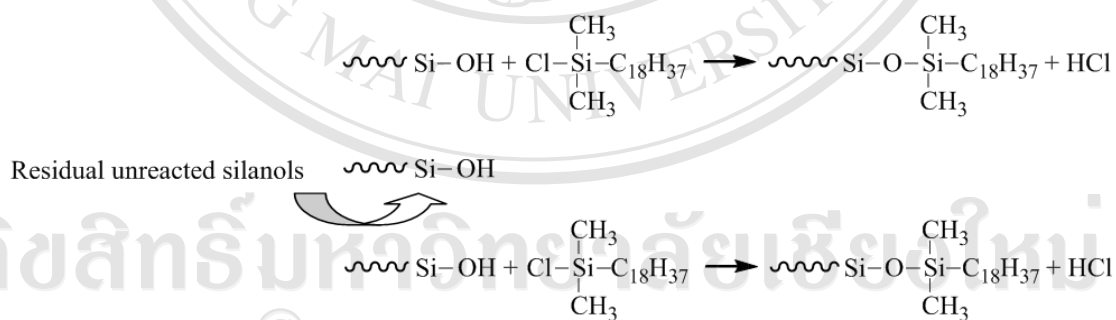


Figure 5 Hydrophilic silanol group at the surface of the raw silica packing.

Retention of organic analytes from polar solutions (e.g. water) onto these SPE materials is due primarily to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the silica surface. These nonpolar-nonpolar attractive forces are commonly called van der Waals forces or dispersion forces. To elute an adsorb compounds from a reverse phase SPE tubes or disk, use a nonpolar solvent to disrupt the forces that bind the compound to the packing. LC-18 and LC-8 are standard, monomerically bonded silicas. Polymerically bonded materials, such as ENVI-18 and ENVI-8, result in a more complete coverage of the silica surface and higher carbon loading. Polymeric bonding is more resistant to pH extremes and thus is more suitable for environmental applications for trapping organic compounds from acidified aqueous samples. All silica based bonded phases have some percentage of residual unreacted silanols that act as secondary interaction sites. These secondary interactions may be useful in the extraction or retention of highly polar analytes or contaminants but may also irreversibly bind analytes of interest.

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APPENDIX I

Literatures review of wavelength

Many research expressed the λ_{max} of dimethoate, carbaryl and fenvalerate in routine analysis. From the experiment, the suitable wavelength for the simultaneous dimethoate, carbaryl and fenvalerate detection was found to be 220 nm which conformed to literature review that reported the maximum wavelength of dimethoate and carbaryl almost found in the range of 199.0 - 225.5 nm (Table 4).

Table 6 The maximum wavelength of dimethoate, carbaryl and fenvalerate.

Pesticide	λ , (nm)	ϵ_1 ($\times 10^3$)	λ , (nm)	ϵ_1 ($\times 10^3$)	ϵ_{221} ($\times 10^3$)	Ref.
Dimethoate	199.0	11.3	221.0	4.1	4.1	137
Carbaryl	225.5	25.8	221.0	24.6	24.6	137
	225.0					138
	222.0					138, 139
	254.0					29
Fenvalerate ^a	240.0	-	-	-	-	-
Multi - pesticide	221	-	-	-	-	1
	(190.0 - 205.0) ^b	-	(220.0, 247.0 or 280.0) ^c	-	-	79

Note; UV detection from ^a the experiment, ^b the first absorption maxima and ^c secondary absorption maxima

APPENDIX J

Calculation of limit of detection by Miller-Miller method

Table 7 Limit of detection of dimethoate as analyzed by HPLC.

Conc. (mg L ⁻¹)	Y ₁	Y ₂	Y ₁ -Y ₂	Y ₁ -Y ₂ ²
0.13	4.87	4.56	0.31	0.0961
0.27	26.95	28.50	1.55	2.4025
0.50	67.21	67.83	0.62	0.3844
0.80	124.98	119.12	5.86	34.3396
1.0	149.32	153.32	4.00	16.0000
$\Sigma Y_1 - Y_2 $				53.2226
S_y / x				17.7409
LOD				0.07

According to Figure 3.18, the linear regression equation is $y = 170.99x - 17.67$.

$$\begin{aligned}
 S_{y/x} &= [53.2226/(5-2)]^{1/2} \\
 &= 17.7409 \\
 \text{LOD} &= (3 \times 17.709)/170.99 \\
 &= 0.07 \text{ mg L}^{-1}
 \end{aligned}$$

The limit of detection of carbaryl and fenvalerate are also calculated in the same way.

So, in consecutive solution 4.00 mL containing of carbaryl = $4.00 \times 0.41 = 1.64 \mu\text{g}$
 $\frac{1.64}{4.00}$
 1.00

Therefore, the percentage of recovery of carbaryl = $(1.64/3.00) \times 100 = 54.7\%$

1.3 Calculation of the percentage of recovery of fenvalerate

According to Figure 3.20, the linear regression equation is $y = 272.55x + 13.99$.

If $y = 97.25$ (Table 3.15) then $x = 0.31 \text{ mg L}^{-1}$

It means that in solution 1.00 mL containing of fenvalerate $0.31 \mu\text{g}$

So, in consecutive solution 4.00 mL containing of fenvalerate = $4.00 \times 0.31 = 1.24 \mu\text{g}$
 $\frac{1.24}{4.00}$
 1.00

Therefore, the percentage of recovery of fenvalerate = $(1.24/4.00) \times 100 = 31.00\%$

APPENDIX L

Calculation of percentage of recovery as analyzed by LC/MS

1.1 Calculation of the percentage of recovery of dimethoate

According to Figure 3.29, the linear regression equation is

$$y = 71,449.20 x + 17,744.40$$

If $y = 264,472$ (Table 3.28) then $x = 3.45 \text{ mg L}^{-1} = 3.45 \text{ } \mu\text{g mL}^{-1}$

It means that in solution 1.00 mL containing of dimethoate 3.45 μg

Due to 1.00 mL of the solution was obtained from adjusting volume of the residues to 10 mL after evaporation so in the solution 10.00 mL was also containing of dimethoate

3.45 μg .

Therefore, the percentage of recovery of dimethoate = $(3.45/5.00) \times 100 = 69\%$

1.2 Calculation of the percentage of recovery of carbaryl

According to Figure 3.30, the linear regression equation is

$$y = 660,357.00 x + 2,311.90$$

If $y = 705,229$ (Table 3.28) then $x = 1.06 \text{ mg L}^{-1} = 1.06 \text{ } \mu\text{g mL}^{-1}$

It means that in solution 1.00 mL containing of carbaryl 1.06 μg

Due to 1.00 mL of the solution was obtained from adjusting volume of the residues to 10 mL after evaporation so in the solution 10.00 mL was also containing of carbaryl 1.06 μg .

Therefore, the percentage of recovery of carbaryl = $(1.06/1.50) \times 100 = 71\%$

1.3 Calculation of the percentage of recovery of fenvalerate

According to Figure 3.31, the linear regression equation is

$$y = 104,062.50 x - 5,052.20$$

If $y = 212,603$ (Table 3.28) then $x = 2.09 \text{ mg L}^{-1} = 2.09 \text{ } \mu\text{g mL}^{-1}$

It means that in solution 1.00 mL containing of fenvalerate 2.09 μg

Due to 1.00 mL of the solution was obtained from adjusting volume of the residues to 10 mL after evaporation so in the solution 10.00 mL was also containing of fenvalerate 2.09 μg .

Therefore, the percentage of recovery of fenvalerate = $(2.09/2.00) \times 100 = 105\%$

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National Research University Project of Thailand, Office of
the Higher Education Commission

List of Publication

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Jitmanee, *Journal of Srinakharinwirot University*, **3** (2011)
332-337.

List of presentation

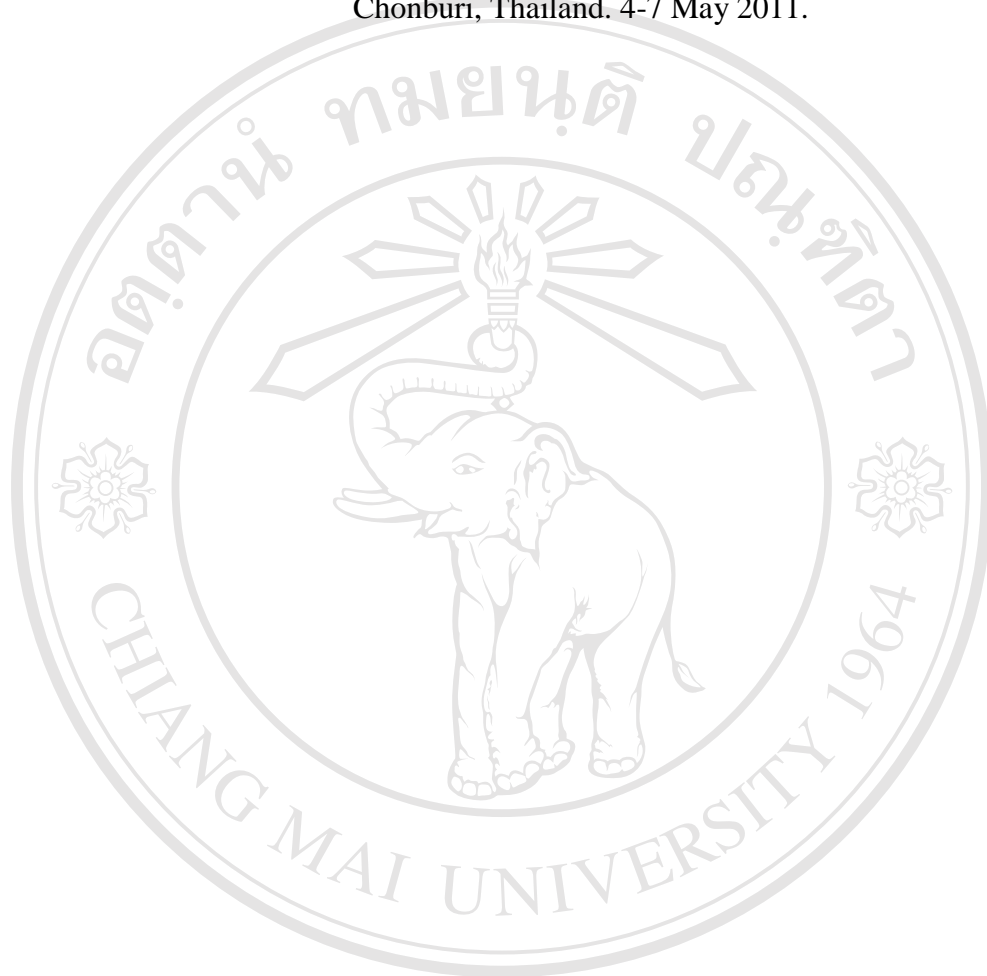
Poster presentation. “Determination of Arsenite and
Arsenate in Water Sample by Spectrophotometry” at the
31st Congress on Science and Technology of Thailand,
Suranaree University, Nakhon Ratchasima, Thailand. 19-21
October 2005.

Poster presentation. “Development of simultaneous
determination of dimethoate, carbaryl and fenvalerate by
liquid chromatography-mass spectrometry” at the
PACCON Congress, Miracle Grand Hotel, Bangkok,
Thailand. 5-7 January 2011.

Oral presentation. “Development of Simultaneously
Carbaryl, Dimethoate, and Fenvalerate Residual Extraction
in Tangerine (Sai Nam Pung) by using SPE Technique and
Detection with HPLC and LC/MS” at the 7th PERCH-CIC

Congress VII, Jomtien Palm Beach Hotel & Resort Pattaya,

Chonburi, Thailand. 4-7 May 2011.



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