APPENDIX A

Calculation for the preparation of standard insecticide solutions

A-1 Preparation of standard cypermethrin solution, 1000 mg/L (100 mL)

1000 mL of solution contains 1000 mg of cypermethrin

100 mL of solution contains 100 mg of cypermethrin

but, purity of cypermethrin standard solution was 98.8% (w/w)

100 g of cypermethrin contains 98.8 g

prepared 100 mg of cypermethrin

thus, weight of standard cypermethrin $= \frac{100mg \times 100g}{98.8g} =$ 101.21 mg

A-2 Preparation of standard fenvalerate solution, 1000 mg/L (100 mL)

1000 mL of solution contains 1000 mg of fenvalerate

100 mL of solution contains 100 mg of fenvalerate

but, purity of standard fenvalerate solution was 98.0% (w/w)

100 g of fenvalerate contains 98.0 g

prepared 100 mg of fenvaerate

thus, weight of standard fenvalerate $= \frac{100mg \times 100g}{98.0g} =$ 102.04 mg

APPENDIX B

Validation method

The validation method was presented n term of percent recovery, standard deviation (SD), relative standard deviation (RSD) and detection limit

B-1 Percent recoveries of extraction method

The percent recovery can be calculated as follows

$$\% \text{ Recovery} = \frac{\text{Peak area of the extract}}{\text{Peak area of standard solution}} \times 100 \quad (1)$$

For example, the calculation for percent recoveries as shown in Table B-1 and B-2

B-2 Standard deviation [37,38]

The most common measure of the error or a statistical measure of precision in an experimental quantity is SD of a set of data. SD defines a series of n measurements of the same measure and, the quantity is characterizing the dispersion of the results and given by the formula:

$$SD = \left[\sum (X_i - \overline{X})^2 / (n-1)\right]^{1/2} \quad (2)$$

Where X_i = the result of the i measurement

$\overline{X}$ = the arithmetic mean of the n results considered

n = the number of measurement

The definition is estimated the standard deviation for n values of a sample of a population and is always calculated using n-1. If the analysis was repeated several times to produce several sample sets of data, it would be expected that each set of measurements would have a different mean and a different estimate of the standard deviation.

B-3 Relative standard deviation

The most useful test parameter is the precision of replicate injections of the analytical reference solution, prepared as directed under the individual reagent. The precision of replicate injections is expressed as the relative standard deviation as follows:

$$\%RSD = (SD / \overline{X}) \times 100 \qquad (3)$$

Where SD = standard deviation

$\overline{X}$ = the mean of data

B-4 Relative error

The relative error can be calculated from the following equation (4)

$$\%\ \text{Error} = \frac{\text{Measured value} - \text{True value}}{\text{True value}} \times 100 \qquad (4)$$

Calculation of percent recovery of extraction method

An example for calculation of the percent recovery of cypermethrin from spiked in cabbage sample (0.5 mg/L) using acetone, *n*-hexane and ethyl acetate at the ratio 1:1:1 by volume

Table B-1 Amount of cypermethrin insecticide detected after spiked cypermethrin standard in cabbage sample (0.5 mg/L)

Trial No	Cypermethrin found, X_i (mg/L)	$\left(X_i - \overline{X}\right)$	$\left(X_i - \overline{X}\right)^2$
1	0.43	-0.0360	0.0013
2	0.47	0.0040	0.0000
3	0.49	0.0240	0.0006
4	0.53	0.0640	0.0041
5	0.41	-0.0560	0.0031
	$\overline{X} = 0.4660$		$\Sigma = 0.0091$

By using equation (1)

$$\%\ \text{Recovery} = \frac{0.4660}{0.50} \times 100$$

$$= 93$$

The statistic SD is calculated by

$$SD = \left[\sum (X_i - \overline{X})^2 / (n-1)\right]^{1/2}$$

$$SD = \left[(0.0091)/(5-1)\right]^{1/2}$$

$$SD = 0.05$$

From equation (3)

$$\% RSD = (SD / \overline{X}) \times 100$$

$$\% RSD = (0.048/0.4660) \times 100$$

$$\% RSD = 10$$

From equation (4)

$$\% Error = \frac{\text{Measured value} - \text{True value}}{\text{True value}} \text{ X } 100$$

$$\% Error = \frac{0.4660 - 0.5}{0.5} \times 100$$

$$\% Error = -7$$

Table B-2 Amount of cypermethrin insecticide detected after spiked cypermethrin standard in cabbage sample (3.0 mg/L)

Trial No	Cypermethrin found, X_i (mg/L)	$(X_i - \overline{X})$	$(X_i - \overline{X})^2$
1	3.34	0.2380	0.0566
2	2.89	-0.2120	0.0449
3	2.99	-0.1120	0.0125
4	3.26	0.1580	0.0250
5	3.03	-0.0720	0.0052
	$\overline{X}$ = 3.1020		Σ = 0.1443

By using equation (1)

$$\% \text{ Recovery} = \frac{3.1020}{3.0} \times 100$$

$$\% \text{ Recovery} = 103$$

The statistic SD is calculated by

$$SD = \left[\sum (X_i - \overline{X})^2 / (n-1)\right]^{1/2}$$

$$SD = \left[(0.1443)/(5-1)\right]^{1/2}$$

$$SD = 0.19$$

From equation (3)

$$\% \text{ RSD} = (SD / \overline{X}) \times 100$$

$$\% \text{ RSD} = (0.1899/3.1020) \times 100$$

$$\% \text{ RSD} = 6$$

From equation (4)

$$\% \text{ Error} = \frac{\text{Measured value} - \text{True value}}{\text{True value}} \text{ X } 100$$

$$\% \text{ Error} = \frac{3.1020 - 3.0}{3.0} \times 100$$

$$\% \text{ Error} = 3$$

The results are given in Table B-1 and B-2, it can be concluded that percent recovery of cypermethrin from spiked in cabbage sample (0.5 and 3.0 mg/L) using acetone, *n*-hexane and ethyl acetate at the ratio 1:1:1 by volume was in the range 93-103 SD, % RSD and % error were found to be 0.05-0.19, 6-10 and 3-7 respectively.

B-5 Detection limit

A definition of limit of detection (LOD) is based on the concentration, which give signal equal to the blank signal plus three standard deviations of the blank. LOD was calculated from the calibration curve by means of the blank signal, which can be used as an estimation of the calculated intercept, plus three standard deviations of the blank. It can be used as an estimation of the calculated value from the regression line. The limit of detection was calculated by using Linear least Squares' Line procedure.

$$Y = a + bx \quad (5)$$

where Y = Instrument signals

x = concentrations

a = intercept

b = slope of the straight line

$$Y_L = Y_B + kS_B \quad (6)$$

where Y_L = lowest detectable instruments signals

Y_B = Y intercept, a

K = constant depending on definition such as

k = 1, 5, 3 of 10 according to IUPAC, in calculation of limit of detection, k = 3 was used in this work

S_B = blank signal standard deviation

$S_{y/x}$ can be calculated from the equation

$$S_{y/x} = \{\sum[Yi - \hat{Y}i]^2 /(n-2)\}^{1/2} \quad (7)$$

where Y_i = response value from instrument corresponding to the individual x value

$\hat{Y}i$ = value of y on the instrument corresponding to the individual x value

n = number of point on the calibration line

From equation (6) and (7)

$$Y_L = a + 3\ S_{y/x} \quad (8)$$

$$Y_L = a + b\ C_L \quad (9)$$

Thus,

$$a + 3\ S_{y/x} = a + b\ C_L$$

$$C_L = 3\ S_{y/x} /b \quad (10)$$

The values lower than LOD was called non-detected

An example for calculation of the detection limit of cypermethrin

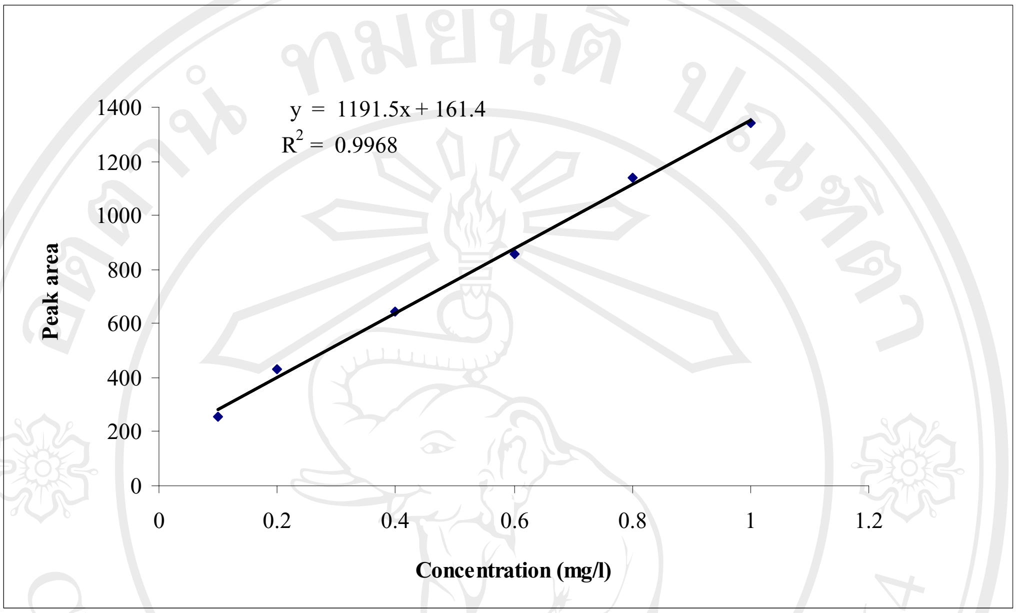

Figure B-1 Calibration curve of cypermethrin for calculating of the detection limit at optimum condition

Linear regression of Figure B-1; $y = 1191.5x + 161.4$

$R^2 = 0.9968$

Table B-3 The data used for calculation of the detection limit of cypermethrin

Concentration (mg/L)	Y_i	$\hat{Y}_i$	$\left[Y_i - \hat{Y}_i\right]$	$\left[Y_i - \hat{Y}_i\right]^2$
0.1	253.3	280.55	-27.25	742.56
0.2	429.5	399.70	29.80	888.04
0.4	644.1	638.00	6.10	37.21
0.6	857.2	876.30	-19.10	364.81
0.8	1138.1	114.60	23.40	547.56
1.0	1340.5	1352.90	-12.90	166.41

$$\therefore \quad \sum\left[Y_i - \hat{Y}_i\right]^2 = 2580.18$$

By using equation (9) and (10)

$$S_{y/x} = \{\sum[Yi - \hat{Y}i]^2/(n-2)\}^{1/2}$$

$$S_{y/x} = \{2580.18/(6-2)\}^{1/2}$$

$$S_{y/x} = 25.3977$$

and $C_L = 3\, S_{y/x}/b$

$$C_L = (3\times25.3977)/1191.5$$

$$C_L = 0.064$$

$\therefore$ Limit of detection for cypermethrin is 0.064.

APPENDIX C

Determination of cypermethrin and fenvalerate insecticide residues in cabbage sample using a standard addition method

Example for calculation of the amount of cypermethrin in sample No. 3

From figure 3.5, the amount of cypermethrin in sample No.3 can be calculated as in the following :

regression equation, $y = 10374x + 4575.3$

concentration of cypermethrin $= 0.4410$ mg/L

1000 mL of solution contains 0.4410 mg of cypermethrin

1μL of solution injected contains $\frac{0.4410 \times 10^{-3}}{1000}$ mg of cypermethrin

hence 5 mL of final solution contains $\frac{0.4410 \times 5}{1000}$ mg of cypermethrin

In the extraction step, 2 mL was used from 5 mL of final extracts

2 mL of extract contains $= \frac{0.4410 \times 5}{1000}$ mg of cypermethrin

so 5 mL of final extract contains $= \frac{0.4410 \times 5 \times 5}{1000 \times 2}$ mg of cypermethrin

$= 2.205 \times 10^{-3}$ mg of cypermethrin

In this work, 10.00 g of cabbage sample was used

then 10.00 g of cabbage sample contains = 2.205×10^{-3} mg of cypermethrin

1000 g of cabbage sample contains = 0.221 mg of cypermethrin

$\therefore$ Cypermethrin content in cabbage sample (sample No. 3) = 0.221 mg/kg

APPENDIX D

Desorption study

D-1 Calculation for the concentration of insecticides

D-1.1 Cypermethrin insecticide solution 35% (w/v)

	100 mL of solution contains	35 g of cypermethrin
so,	1 mL of solution contains	$\frac{35}{100}$ g of cypermethrin
if we prepared	1000 mL of solution contains	0.35 g of cypermethrin
or	1000 mL of solution contains	350 mg of cypermethrin

thus we obtained, 350 mg/L of cypermethrin insecticide solution

D-1.2 Fenvalerate insecticide solution 10% (w/v)

	100 mL of solution contains	10 g of fenvalerate
so,	1 mL of solution contains	$\frac{10}{100}$ g of fenvalerate
if we prepared	1000 mL of solution contains	0.10 g of fenvalerate
or	1000 mL of solution contains	100 mg of fenvalerate

thus we obtained, 100 mg/L of fenvalerate insecticide solution

D-2 Calculation of amount of the analytes after desorption study

An example for calculation of the desorption of cypermethrin insecticide in water at 10 min (or 0.41 $h^{1/2}$) in room temperature (28 °C)

initial volume of water = 900 mL

water sample = 5 mL

final volume of extract water = 5 mL

volume of extract water injected = 1 µL

peak area (y) = 2163.36

Table D-1 The data used for constructed calibration curve and desorption study of cypermethrin at room temperature (28 °C)

Concentration (mg/L)	Peak area
0.1	90.3
0.2	290.1
0.3	505.7
0.5	812.6
0.7	1530.8
1.0	2270.3
1.5	3771.1
2.0	5370.7

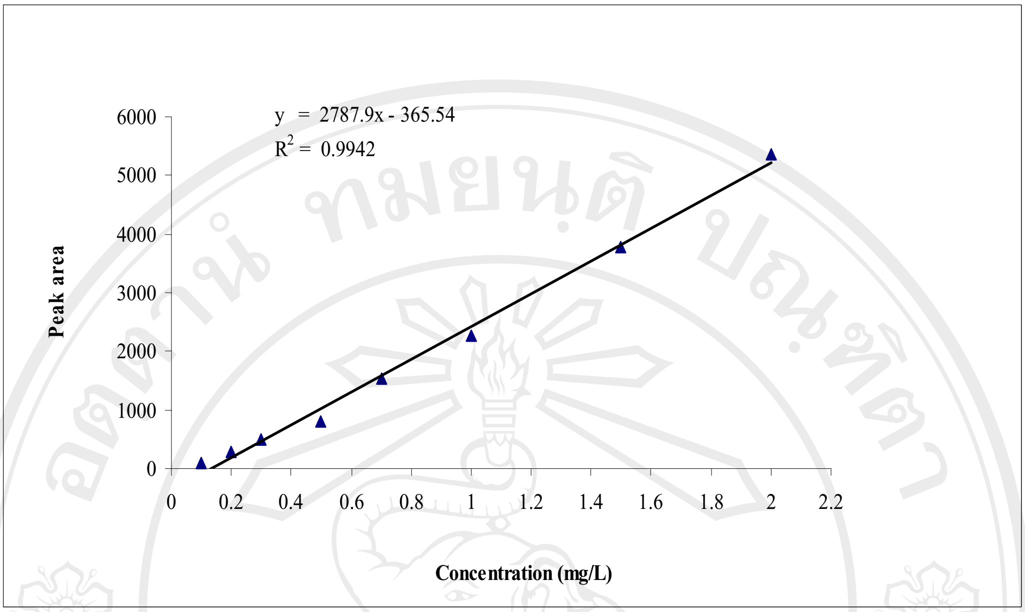

Figure D-1 Calibration curve of standard cypermethrin solution (0.1-2.0 mg/L) for desorption study at room temperature (28 °C)

From calibration curve

regression equation, $y = 2787.9x - 365.54$

$x = 0.9071$ mg/L

1000 mL of solution contains 0.9071 mg of cypermethrin

1 μL of extract water injected contains $\frac{0.9071 \times 10^{-3}}{1000}$ mg of cypermethrin

5 mL of final extract water $\frac{0.9071 \times 5}{1000}$ mg of cypermethrin

so, 5 mL of extract water sample contained cypermethrin $= \frac{0.9071 \times 5}{1000}$ mg

From results, calculated the amounts of cypermethrin desorbed

	900 mL of water solution	$\frac{0.9071 \times 900}{1000}$ mg of cypermethrin
	1000 mL of water solution	$\frac{0.9071 \times 900 \times 1000}{1000 \times 900}$ mg of cypermethrin
or,	1000 mL of water solution	0.9071 mg of cypermethrin

In desorption step, 390.00 g cabbage was used

thus, the amounts of cypermethrin desorbed $= \frac{0.9071}{390.00}$ mg/g

$\therefore$ the amounts of cypermethrin desorbed $= 2.3 \times 10^{-3}$ mg/g

Table D-2 The data used for constructed calibration curve and desorption study of cypermethrin at 90 °C

Concentration (mg/L)	Peak area
0.1	209.8
0.2	550.0
0.3	727.5
0.5	960.3
0.7	1544.7
1.0	2297.8
1.5	3797.5
2.0	5188.9

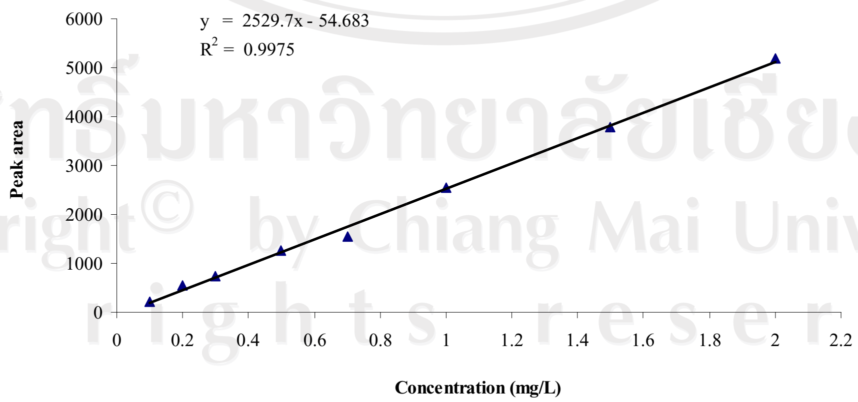

Figure D-2 Calibration curve of standard cypermethrin solution (0.1-2.0 mg/L) for desorption study at 90 °C

Table D-3 The data used for constructed calibration curve and desorption study of fenvalerate at room temperature (28 °C)

Concentration (mg/L)	Peak area
0.1	162.1
0.2	390.5
0.3	711.9
0.5	888.2
0.7	1562.2
1.0	2426.9
1.5	3729.4
2.0	5467.4

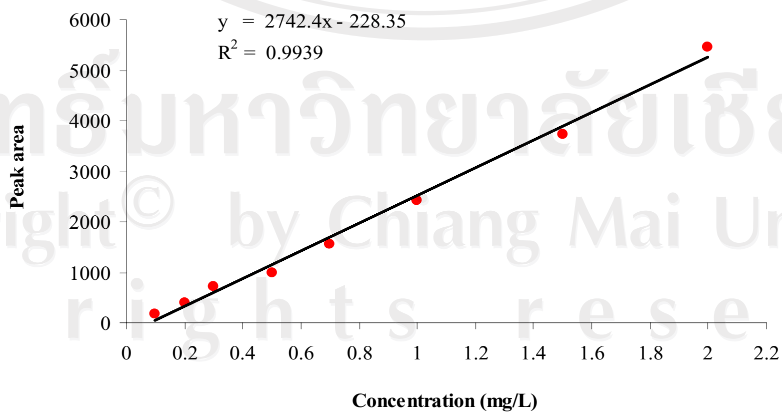

Figure D-3 Calibration curve of standard fenvalerate solution (0.1-2.0 mg/L) for desorption study at room temperature (28 °C)

Table D-4 The data used for constructed calibration curve and desorption study of fenvalerate at 90 °C

Concentration (mg/L)	Peak area
0.1	249.9
0.2	578.4
0.3	1398.2
0.5	2400.1
0.7	2945.2
1.0	5670.5
1.5	8290.5
2.0	11710.3

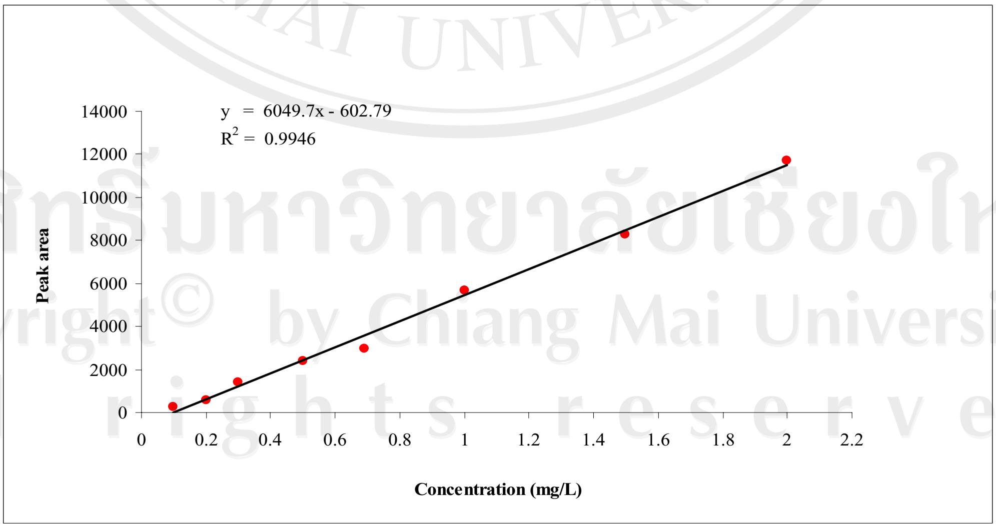

Figure D-4 Calibration curve of standard fenvalerate solution (0.1-2.0 mg/L) for desorption study at 90 °C

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