			TABLES OF CONTENTS		
				Page	
А	CKNOWLED	OGEM	IENT	iii	
А	BSTRACT (E	ENGL	JSH)	iv	
A	BSTRACT (1	THAI)		vi	
L	IST OF TABI	LES		xi	
L	IST OF FIGU	RES		xvi	
A	BBREVIATI	ONS .	AND ACRONYMS	xviii	
500	HAPTER 1	INT	RODUCTION	1502	
		1.1	Statement and significance of the problem	1708	
		1.2	Purposes of the research	2	
		1.3	Scope of Research	2	
		1.4	Education and application advantage	2	
c	CHAPTER 2	LIT	ERATURE REVIEWS	3	
		2.1	Insecticide	3	
		2.2	Fipronil	3	
		2.3	Physical-chemical properties of fipronil	4	
		2.4	Mode of Action	6	
		2.5	Toxicity of fipronil	6	
		2.6	The sample preparation for GC analysis	8	
		2.7	The validity for analytical methods	10	
		2.8	Gas chromatography	K C 13	
		2.9	Gas chromatography-mass spectrometry	26	
C	CHAPTER 3	MA	TERIALS AND METHOD	Una6vers	
		3.1	Apparatus and instruments	36	
		3.2	Materials and chemicals	e 36 e	
		3.3	The preparation of chemicals	37	

		3.3.1	Standard	solution preparation	37
			3.3.1.1	Preparation of stock solution	37
			3.3.1.2	Preparation of mixed standard solution	on37
			3.3.1.3	Preparation of mixed intermediate	
				solutions	37
			3.3.1.4	Preparation of working standard	
				solutions	38
	3.4	Resear	ch Metho	dology	38
		3.4.1	Cultivatio	on of sweet peppers and	
			Procedu	res in the experimental plot land	38
		3.4.2	Validatio	n of analytical method	40
			3.4.2.1	Linearity range	40
			3.4.2.2	Precision and accuracy	40
			3.4.2.3	Limit of detection	41
			3.4.2.4	Limit of quantification	41
		3.4.3	Determin	ation of fipronil and its derivatives	
			residues	in sweet peppers by GC-MS	41
		3.4.4	Analysis	of insecticide residues in sweet	
			peppers		43
CHAPTER 4	RES	ULTS			44
	4.1	Valida	tion of the	analytical method	44
		4.1.1	Linearity	range	44
		4.1.2	The accu	racy and the precision	
			of the m	ethod	48
		4.1.3	Limit of	detection and limit of quantification	73
	4.2	Optim	um condit	ion for analyzing fipronil and its	
		deriva	tives by G	C-MS	87
	4.3	Compa	arison of t	wo types of SPE for cleaning up	88
		the sa	mples extr	racts	
			TS		

		4.3.1	Using alumina SPE for cleaning up the extracts	88
		4.3.2	Using PSA (primary-secondary-amine) SPE	
			for cleaning up the extracts	93
	4.4	Analy	sis of residues of fipronil and its derivatives in	
		sweet	peppers at the recommended rate	94
	4.5	Analy	sis of residues of fipronil and its derivatives	
		in swe	et peppers at double concentration rate	
		of reco	ommendation	98
CHAPTER 5	DIS	CUSSI	ONS AND CONCLUSION	102
REFERENCE	S			104
APPENDIX				107
CURRICULU	M VI	TAE		113

ลิ<mark>ปสิทธิ์มหาวิทยาลัยเชียงใหม่</mark> Copyright[©] by Chiang Mai University All rights reserved

LIST OF TABLES

Tabl	e Salar S	Page	
2.1	Physical-chemical properties of fipronil. All parameters are at 25°C		
	unless specified	5	
2.2	Selection of adsorbents in SPE cartridge	9	
2.3	Criteria for analysis of pesticide residues	11	
4.1	linearity range of fipronil	44	
4.2	linearity range of fipronil-sulfide	45	
4.3	linearity range of fipronil-sulfone	46	
4.4	linearity range of fipronil-desulfinyl	47	
4.5	Percentage recovery and the precision of fipronil in sweet pepper		
	samples blank added with 0.002 mg/kg of fipronil standard using		
	GC-MS for analysis	49	
4.6	Percentage recovery and the precision of fipronil in sweet pepper		
	samples blank added with 0.02 mg/kg of fipronil standard using		
	GC-MS for analysis	50	
4.7	Percentage recovery and the precision of fipronil in sweet pepper		
	samples blank added with 0.2 mg/kg of fipronil standard using		
	GC-MS for analysis	51	
4.8	The precision of fipronil in sweet pepper samples blank added		
	with 0.002 mg/kg of fipronil standard using GC-MS for analysis	52	
4.9	The precision of fipronil in sweet pepper samples blank added		
	with 0.02 mg/kg of fipronil standard using GC-MS for analysis	53	
4.10	The precision of fipronil in sweet pepper samples blank added		
	with 0.2 mg/kg of fipronil standard using GC-MS for analysis	54	
4.11	Percentage recovery and the precision of fipronil-sulfide in sweet		
	pepper samples blank added with 0.002 mg/kg of fipronil-sulfide		
	standard using GC-MS for analysis	55	

4.12	Percentage recovery and the precision of fipronil-sulfide in sweet	
	pepper samples blank added with 0.02 mg/kg of fipronil-sulfide	
	standard using GC-MS for analysis	56
4.13	Percentage recovery and the precision of fipronil-sulfide in sweet	
	pepper samples blank added with 0.2 mg/kg of fipronil-sulfide	
	standard using GC-MS for analysis	57
4.14	The precision of fipronil-sulfide in sweet pepper samples blank	
	added with 0.002 mg/kg of fipronil-sulfide standard using GC-MS	
	for analysis	58
4.15	The precision of fipronil-sulfide in sweet pepper samples blank	
	added with 0.02 mg/kg of fipronil-sulfide standard using	
	GC-MS for analysis	59
4.16	The precision of fipronil-sulfide in sweet pepper samples blank	
	added with 0.2 mg/kg of fipronil-sulfide standard using GC-MS	
	for analysis	60
4.17	Percentage recovery and the precision of fipronil-sulfone in	
	sweet pepper samples blank added with 0.002 mg/kg of	
	fipronil-sulfone standard using GC-MS for analysis	61
4.18	Percentage recovery and the precision of fipronil-sulfone	
	in sweet pepper samples blank added with 0.02 mg/kg of	
	fipronil-sulfone standard using GC-MS for analysis	62
4.19	Percentage recovery of fipronil-sulfone in sweet pepper samples	
	blank added with 0.2 mg/kg of fipronil-sulfone standard	
	using GC-MS for analysis	63
4.20	The precision of fipronil-sulfone in sweet pepper samples blank	
	added with 0.002 mg/kg of fipronil-sulfone standard using	
	GC-MS for analysis	64
4.21	The precision of fipronil-sulfone in sweet pepper samples blank	
	added with 0.02 mg/kg of fipronil-sulfone standard using	
	GC-MS for analysis	65

xii

4.22	The precision of fipronil-sulfone in sweet pepper samples blank	
	added with 0.2 mg/kg of fipronil-sulfone standard using	
	GC-MS for analysis	66
4.23	Percentage Recovery of fipronil-desulfinyl in sweet pepper samples	
	to study the repeatability at 0.002 mg/kg of concentration level	67
4.24	Percentage recovery and the precision of fipronil-desulfinyl in	
	sweet pepper samples blank added with 0.02 mg/kg of	
	fipronil-desulfinyl standard using GC-MS for analysis	68
4.25	Percentage recovery and the precision of fipronil-desulfinyl in	
	sweet pepper samples blank added with 0.2 mg/kg of	
	fipronil-desulfinyl standard using GC-MS for analysis	69
4.26	The precision of fipronil-desulfinyl in sweet pepper samples blank	
	added with 0.002 mg/kg of fipronil-desulfinyl standard using	
	GC-MS for analysis	70
4.27	The precision of fipronil-desulfinyl in sweet pepper samples blank	
	added with 0.02 mg/kg of fipronil-desulfinyl standard	
	using GC-MS for analysis	71
4.28	The precision of fipronil-desulfinyl in sweet pepper samples blank	
	added with 0.2 mg/kg of fipronil-desulfinyl standard using	
	GC-MS for analysis	72
4.29	The standard deviation value of fortified sample at 0.005 mg/kg	
	of fipronil repeating analysis 10 times	75
4.30	The peak areas of fortified sample of fipronil at 0.001 mg/kg	
	that shown 3 times of the noise (LOD)	76
4.31	The peak areas of fortified sample of fipronil at 0.002 mg/kg	
	that shown 10 times of the noise (LOQ)	77
4.32	The standard deviation value of fortified sample at 0.005 mg/kg	
	of fipronil-sulfide repeating analysis 10 times	78
4.33	The peak areas of fortified sample of fipronil-sulfide at 0.001 mg/kg	
	that shown 3 times of the noise (LOD)	79

4.34	The peak areas of fortified sample of fipronil-sulfide at 0.002 mg/kg	
	that shown 10 times of the noise (LOQ)	80
4.35	The standard deviation value of fortified sample at 0.005 mg/kg	
	of fipronil-sulfone repeating analysis 10 times	81
4.36	The peak areas of fortified sample of fipronil-sulfone at 0.001 mg/kg	
	that shown 3 times of the noise (LOD)	82
4.37	The peak areas of fortified sample of fipronil-sulfone at 0.002 mg/kg	
	that shown 10 times of the noise (LOQ)	83
4.38	The standard deviation value of fortified sample at 0.005 mg/kg	
	of fipronil-desulfinyl repeating analysis 10 times	84
4.39	The peak areas of fortified sample of fipronil-desulfinyl at 0.001 mg/k	g
	that shown 3 times of the noise (LOD)	85
4.40	The peak areas of fortified sample of fipronil-desulfinyl at 0.002 mg/k	g
	that shown 10 times of the noise (LOQ)	86
4.41	Percentage recovery of fipronil in sweet pepper samples added with	
	mixed standard of fipronil at 0.002 mg/kg and cleaned up with	
	alumina SPE	89
4.42	Percentage recovery of fipronil-sulfide in sweet pepper samples addeed	i
	with mixed standard of fipronil at 0.002 mg/kg and cleaned up with	
	alumina SPE	90
4.43	Percentage recovery of fipronil-sulfone in sweet pepper samples added	d
	with mixed standard of fipronil at 0.002 mg/kg and cleaned up with	
	alumina SPE	91
4.44	Percentage recovery of fipronil-desulfinyl in sweet pepper samples	
	added with mixed standard of fipronil at 0.002 mg/kg and cleaned up	
	with alumina SPE	92
4.45	The amount of fipronil and its derivatives residues in sweet peppers	
	harvested 7 times for analysis by GC-MS after spraying once with	
	fipronil at recommended rate	94

xiv

The amount of fipronil and its derivatives residues in sweet peppers 4.46 harvested 7 times for analysis by GC-MS after spraying twice with fipronil at recommended rate 95 4.47 The amount of fipronil and its derivatives residues in sweet peppers harvested 7 times for analysis by GC-MS after spraying 3 times with 96 the fipronil at recommended rate The amount of fipronil and its derivatives residues in sweet peppers 4.48harvested 7 times for analysis by GC-MS after spraying with once 98 fipronil at double concentration rate of recommendation 4.49 The amount of fipronil and its derivatives residues in sweet peppers harvested 7 times for analysis by GC-MS after spraying with twice fipronil at double concentration rate of recommendation 99 4.50 The amount of fipronil and its derivatives residues in sweet peppers harvested 7 times for analysis by GC-MS after spraying 3 times fipronil

at double concentration rate of recommendation

100

ลิ<mark>ปสิทธิ์มหาวิทยาลัยเชียงใหม่</mark> Copyright[©] by Chiang Mai University All rights reserved

LIST OF FIGURES

Figu	re	Page
2.1	The structure of fipronil	4
2.2	Derivatives of fipronil	4
2.3	The selection of SPE, considering from the solubility of the sample	
	Substance	10
2.4	Diagram of a gas chromatograph	16
2.5	The rule of ten in gas chromatography	22
2.6	A gas chromatography oven, open to show a capillary column	24
2.7	GC-MS schematic	27
2.8	Interpreting spectra	35
2.9	Library search results	35
4.1	Linearity of fipronil	45
4.2	Linearity of fipronil-sulfide	46
4.3	Linearity of fipronil- sulfone	47
4.4	Linearity of fipronil - desulfinyl	48
4.5	LOD of fipronil and its derivatives	73
4.6	LOQ of fipronil and its derivatives	74
4.7	Chromatogram of fipronil residues in the sweet pepper samples added	
	with 0.002 mg/kg of fipronil and cleaned up with alumina SPE	88
4.8	Chromatogram of fipronil residues in sweet pepper samples added	
	0.002 mg/kg of fipronil and cleaned up with PSA-SPE	93
4.9	Disintegration of fipronil and its derivatives in sweet peppers after 1	
	sprays at the recommended rate harvesting 7 times for analysis	95
4.10	Disintegration of fipronil and its derivatives in sweet peppers after 2	
	sprays at the recommended rate harvesting 7 times for analysis	96

4.11	Disintegration of fipronil and its derivatives in sweet peppers after 3	
	sprays at the recommended rate harvesting 7 times for analysis	97
4.12	Disintegration of fipronil and its derivatives in sweet peppers after 1	
	sprays at double concentration rate of recommendation harvesting 7 time	s
	for analysis	99
4.13	Disintegration of fipronil and its derivatives in sweet peppers after 2	
	sprays at double concentration rate of recommendation harvesting 7	
	times for analysis	100
4.14	Disintegration of fipronil and its derivatives in sweet peppers after 3	
	sprays at double concentration rate of recommendation harvesting 7	
	times for analysis	101
A-1	Weigh the sweet pepper samples at 10 gram/each and put them in	
	50-ml centrifuge tubes	108
A-2	Add 10 ml of acetonitrile and put them in 50-ml centrifuge tubes	108
A-3	Add 2 grams of sodium chloride for increase the efficiency of extraction	109
A-4	The extraction by homogenizer for extraction	109
A-5	Centrifuge samples at the speed of 5000 rpm for 5 minutes	110
A-6	The cleaning up the samples by SPE alumina	110
A-7	The extracts for the clean up	111
A-8	Evaporate samples by nitrogen evaporator	111
A-9	The analyte samples by GC-MS	112

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่ Copyright[©] by Chiang Mai University All rights reserved