CHAPTER V
DISCUSSIONS AND CONCLUSION

In this study, fipronil and its derivatives were determined by GC-MS. Two microlitres of mixed standard solution or sample solution were injected into a HP-5 capillary column (5% phenyl-methylpolysiloxane, 30 m x 250 um (id) x 0.25 um film thickness) the operating conditions were as follows: GC-MS, Quadrupole type HP 6890N model connected with 5975C MSD, using helium (carrier gas) with a flow rate of 1 ml/min. The injector and detector temperatures were 250 °C and 300°C respectively. The oven temperature was programmed from 50 °C, hold 1 min; ramped at 10 °C/min to 100 °C hold 1 min; ramped at 20 °C /min to 240 °C, hold 2 min, ramped at 25 °C /min to 280 °C (0 min). Linear calibration curve was obtained over the fipronil concentration range from 0.002-0.2 mg/L with the correlation coefficient at 0.9984-0.9999.

The mixed standard solution (0.002 mg/L) of fipronil was added into sweet pepper sample and extracted with acetonitrile. Then the sample solution was cleaned up by using two types of SPE cartridges; alumina SPE and PSA-SPE. The samples cleaned up by using alumina SPE gave better % recoveries and precisions (70-110%) with the % RSD of 4.48-5.02 as shown in Tables 4.42-4.45 than that obtained by using PSA-SPE (% recovery 67.02%). Moreover, the alumina SPE is less expensive than PSA-SPE and also used shorter time for cleaning up samples. Therefore, alumina SPE was chosen for cleaning up the samples in this investigation.

The extraction methods in this research had LOD value at 0.001 mg/kg which could measure the concentrations of the fipronil and its derivatives lower than the methods used by Pei *et al.*, (2004) and Liu *et al.*, (2008). Moreover, the LOQ value obtained by this extraction method was at 0.002 mg/kg which was lower than the LOQ of the extraction methods used by Pei *et al.*, (2004) and Liu *et al.*, (2008).

With the lower values of LOD and LOQ obtained by this extraction method, the accuracy and precision for determination of fipronil and its derivatives in sweet

pepper samples showed good % recoveries. This advantage came from using alumina SPE for extraction and using GC-MS for the samples.

Two experiments using Split Plot design were on spraying fipronil at recommended rate and double concentration rate for 1, 2 and 3 times respectively. The fruit yields were randomly harvested to be extracted and determined for the residues of fipronil and its derivatives at 0 (2 hrs), 1, 3, 5, 7, 10 and 14 days. The alumina SPE method of extraction and the GC-MS were used to analyse the residues. The results showed that spraying sweet pepper plants with fipronil at recommended rate at 5 day-intervals at 1 time takes 3 days, 2 times take 5 days and 3 times take 7 days for safety harvesting. Spraying fipronil at recommended rate 3 times continuously at 5 day-intervals, the harvested fruits can be safe for consumption after 7 days with the residue at 0.016 mg/kg (Codex MRL = 0.02 mg/kg). For its derivatives fipronil (fipronil-sulfide, fipronil-desulfinyl and fipronil-sulfone) after spraying 3 times, the residues were very little (0.017, 0.009 and 0.004 mg/kg) only 3 days after third spraying the time which was lower than Codex MRL level. When the double rate of fipronil concentration was sprayed, the results of residues from analysis were double of that obtained from spraying fipronil at recommended rate. Using fipronil at double concentration rate of fipronil, spraying 3 times continuously at 5 day-intervals, it takes longer time for safety harvesting (1 spray takes 7 days; 2 sprays take 10 days and 3 sprays take > 10 days. It can be concluded that the appropriate method for determination of fipronil residues and its derivatives in sweet peppers was obtained. The alumina SPE showed effective extraction while GC-MS showed reliable determination of fipronil and its derivatives residues, at low concentrations enough for comparison with Codex MRL. Analysis of the residues in sweet pepper indicates safety harvesting dates after spraying fipronil at various times and concentrations. It is useful not only for the farmers to know what concentration should be used and how long they should leave the residues to disintegrate but also for the consumers to have good health with food safety.