

CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

This thesis describes detailed development of a new sample preparation technique for the determination of the herbicide glyphosate and its metabolite, aminomethylphosphonic acid (AMPA), followed by the analysis by high-performance liquid chromatography (HPLC) with post-column derivatization and fluorescence detection.

A polymer based hollow fiber membrane commercially available; Accurel polypropylene Q3/2 was selected for the extraction. This hydrophobic membrane was used in a supported liquid membrane format in a three phase membrane extraction system. Because both analytes are very polar and hydrophilic, a carrier-Aliquat 336 (methyltrioctylammonium chloride) (Figure 5.1) was added to the membrane solvent to facilitate the extraction process which resulted in increased method sensitivity. The transport mechanism is summarized in Figure 5.2.

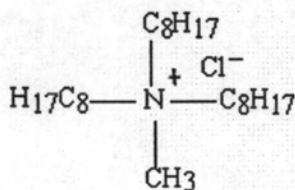


Figure 5.1 Chemical structure of Aliquat 336 (methyltrioctylammonium chloride).

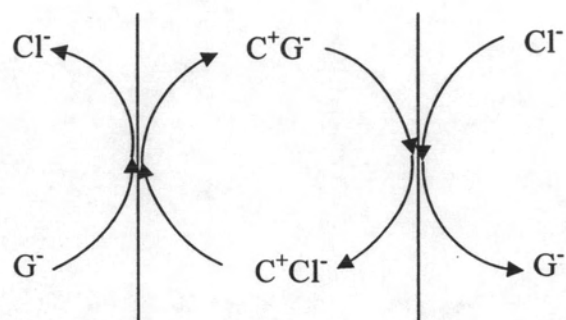


Figure 5.2 Transport mechanism of glyphosate and AMPA (G^- = anion analytes, C^+ = carrier, Cl^- = chloride ion).

The three phase HF-LPME set-up is illustrated in Figure 5.3. Detailed description of HF-LPME device set-up and operation is summarized in the flow chart of Figure 5.4.

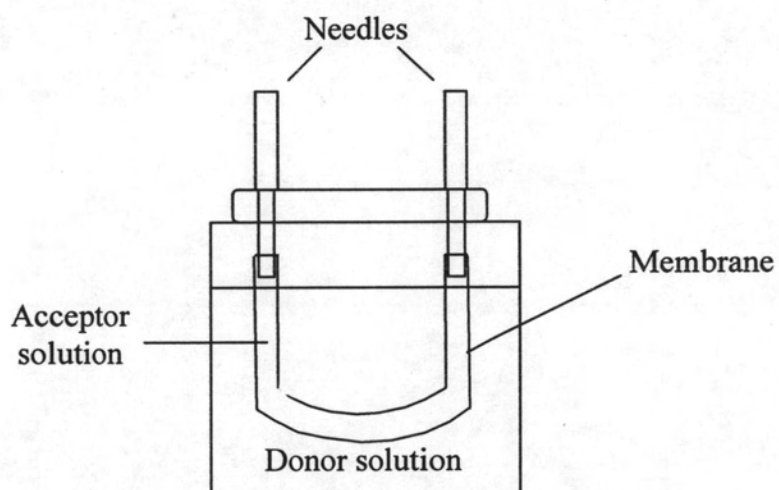


Figure 5.3 The schematic diagram of HF-LPME.

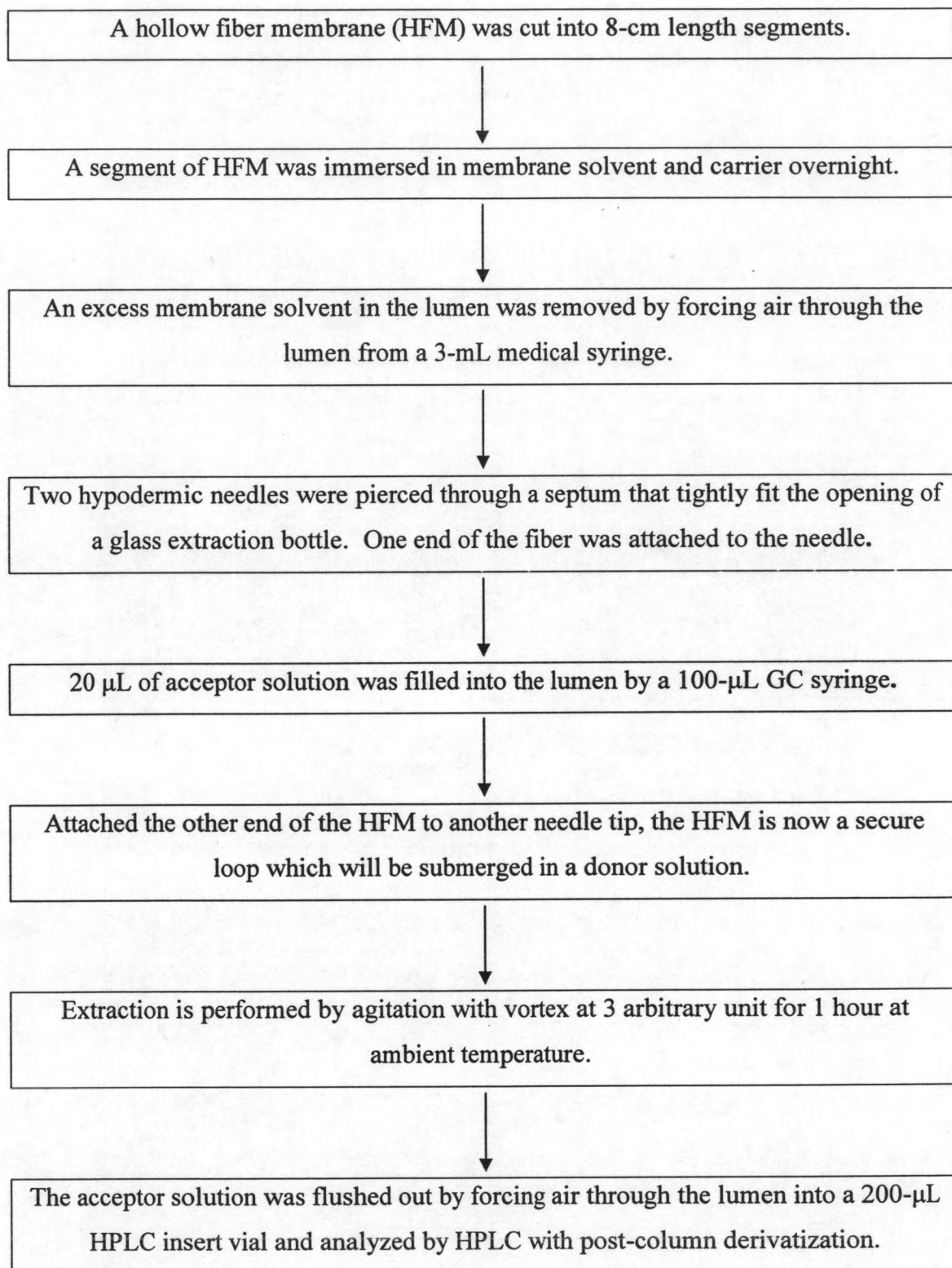


Figure 5.4 Construction and operation of HF-LPME device.

The device was fine-tuned by varying key parameters to obtain optimum extraction condition. The procedure was fully validated and tested on spiked ground-water samples.

Optimization was a procedure that searched for the best parameters of HF-LPME that influence the extraction process. The immersion time, donor solution pH, carrier concentration, acceptor solution type, acceptor solution concentration, acceptor solution volume, donor solution volume, agitation and extraction time were optimized. Each parameter provided specific maximum enrichment factor that adding to provide optimum method sensitivity and reproducibility. The optimum condition was summarized in Table 5.1.

Table 5.1 Optimum extraction condition of HF-LPME.

Parameters	Extraction condition
Donor pH	9.0
Donor volume	20.0 mL
Acceptor	1.0 M KCl
Acceptor volume	20.0 μ L
Aliquat 336 concentration	0.20 M
Immersion time	Overnight
Agitation	Vortex 3
Extraction time	60 min

Table 5.2 Characteristic validation data consists of method detection limit, method quantitation limit, linearity range, and correlation coefficient (R^2).

	Compound	
	Glyphosate	AMPA
MDL ($\mu\text{g/L}$)	0.3	1.5
MQL ($\mu\text{g/L}$)	1.0	5.0
Linearity range ($\mu\text{g/L}$)	1-1,000	5-605
Correlation coefficient	0.996	0.997

Table 5.2 showed the characteristic validation data of the HF-LPME procedure. The method showed good analytical characteristics, having $R^2 > 0.99$ from 1-1,000 $\mu\text{g/L}$ for glyphosate and from 5-605 $\mu\text{g/L}$ for AMPA. The method precision was studied at two concentration levels (MQL and 5-MQL) in spiked water samples. The satisfactory precision of this method was achieved with obtained %RSD values lower than the values calculated from Horwitz equation. The method accuracy was satisfied because percent recoveries were within the recommended range of the AOAC Manual for Peer Verified Methods Program.

Once the procedure was validated to test its reliability, it was tested on real samples. Four samples of ground water were collected from provinces of Thailand and extracted by HF-LPME. Because the two analytes were not detected in these samples, glyphosate and AMPA standards were spiked at MQL concentrations. Percent recoveries were calculated and compared followed the AOAC standard. The results were within the acceptable range and demonstrated good capability of this new sample preparation technique to real water samples.

In conclusion, the developed u-shaped supported liquid membrane HF-LPME provided high enrichment factors of glyphosate and AMPA. The enrichment factors are 814 and 141, respectively. Comparing to the planar membrane module, the memory effect of the HF-LPME is totally eliminated because the membrane was discarded after one use. Also, it was unnecessary to use a peristaltic pump to circulate

the donor and acceptor solutions, therefore operation cost is much lower and the procedure is simpler and very easy to do. Other than being easy, fast and inexpensive; the procedure is also environmental friendly. Method validation results showed the capability of the developed HF-LPME procedure for routine analysis of real water.

It would be interesting to apply HF-LPME method for the determination of glyphosate and AMPA in any other matrices such as wheat, milk, rice, etc., which may interfere with glyphosate. Joint FAO/WHO Meeting on Pesticide Residues reported new recommended maximum residue limits of glyphosate in many agricultural products in October 2005 (42). These regulations proposed lower trace pesticides to 0.05 ppm which is difficult to detect by some traditional method. The developed HF-LPME can be used to enrich both analytes in these matrices and provide simple detection without high expensive analytical instrument such as mass spectrometry. These new proposed thresholds put new challenge to analytical chemists implying that analyte enrichment procedure will become more necessary than ever.

It should be stated here that the use of glass bottle as the extraction device may not be totally acceptable. This is because both glyphosate and AMPA can be adsorbed by silanol groups on glass surface and may affect or interrupt the mass transfered process. Plastic containers are therefore more preferable.