

Chapter Six

Conclusions

6. Conclusions

This extensive research programme aimed to improve current analytical methods of detection of selected priority agrochemicals named in the Water Framework Directive (2000) using UPLC-MS/MS and Solid Phase Extraction. Focus was directed towards improvements in speed, sensitivity and resolution compared with previous research outputs, and on the application of the developed methods to water samples obtained from the Rivers Wye, Ogmore, Ely and Taff. The analytes chosen for investigation were a combination of triazine, phenylurea and chloroacetanilide agrochemicals.

This research established three separate method development programmes:-

1. The chromatographic separation of the above analytes in simulated and real water samples under experimentally established optimum conditions (Chapter 2);
2. The extraction of the above analytes from simulated and real water samples using multi-mode solid phase extraction (Chapter 4);
3. The detection of the above analytes by tandem mass spectrometry using an electrospray ionisation interface and multiple reaction monitoring of primary and secondary transitions (Chapter 3).

It is believed that this may be the first attempt to analyse this specific set of agrochemical analytes by UPLC-MS/MS. Simultaneous separation of all analytes occurred within 7 minutes using this new method (*mei128*); this represents a

significant improvement in retention time compared to previous US EPA methods of analysis where similar types of agrochemical compounds are separated.

Extraction of the target analytes from the sample and simulated matrices was achieved through SPE; three different sorbent chemistries were investigated and it was concluded that the mixed mode cation exchange cartridge was able to recover (extract) all analytes, with varying but consistent extraction efficiencies approximately between 15 and 90%.

An extensive investigation into the selection of suitable molecular and fragment ions was conducted in multiple reaction monitoring (MRM, tandem mass spectrometry) mode. The use of primary and secondary transitions was made throughout and special attention was paid to co-eluting compounds from *mei128*; the co-eluting compounds, isoproturon and diuron, could then be identified using unique primary to secondary ion transitions for each co-eluting compound. (Isoproturon $[M+H]^+ = 207.1$ - primary ion transition = 165.1 – secondary ion transition = 134.0). Diuron $[M+H]^+ = 233.0$ – primary ion transition = 72.0 – secondary ion transition = 159.9). This illustrates a further benefit of tandem mass spectroscopic analysis over UV detection methods.

The calibration curves were produced over the region of 10 to 1000 $\mu\text{g l}^{-1}$ for all analytes based upon the primary MRM ion response. The correlation coefficients varied between 0.985 and 0.999, illustrating excellent reproducibility in signal response, given all analytes were measured in a single injection.

Studies on the river water samples show:-

1. The methods developed in chapters 2, 3 and 4 were fit for purpose in the extraction and analysis of the target analytes.
2. The instrument limit of detection and limit of quantitation values while not being specifically designed to achieve the lowest detection limits are capable of delivering results down at the levels of the European drinking water directive.
3. It would appear that the concentrations of the priority pesticides in each of other rivers studies were below the limits of the drinking water regulations of $0.1 \mu\text{g l}^{-1}$.
4. It would appear that although some metabolites can be detected, when compared to the US FDA 40 CFR full method detection limits, the concentrations in the river waters were below the limit regardless of the location of origin of the sample, e.g. rural, agricultural or industrial areas. The average percentage recovery for all compounds against the MDL for the River Wye was 3.9% with atrazine desisopropyl between 10.4% and 30.3%. For the River Ogmore the average percentage recovery for all compounds against the MDL was 4.9%, atrazine desisopropyl ranged from 15.6% to 44.5%. The atrazine desethyl MDL for the same river ranged between 10.1% and 23.7%. The River Ely average percentage recovery against MDL was 2.1%, atrazine desisopropyl was between 4.4% and 11.3% and atrazine desethyl between 4.9 and 9.3%. As the compounds atrazine desisopropyl and atrazine desethyl are formed from the breakdown of other compounds such as atrazine, propazine, simazine and cyanazine, it is an indication of the presence of one or more of these parent compounds in the environment.

Whilst this programme has been extensive in the areas outlined above, it is acknowledged that improvements to the methodology may be made through additional specific investigations.

A more detailed experimental procedure could be used for the extraction and clean up of the river waters. The optimisation in this study used only three different types of sorbent for the solid phase extraction of water and proved successful in extracting the analytes of interest. There are other sorbents manufacturers and other sorbent chemistries on the market that could be investigated further.

At the outset of this research the size and type of UPLC chromatography separation columns available were limited. New thinner and longer chromatography columns of the same chemistry type used in this study have since been developed. The use of these columns in conjunction with the method developed in this research could lead to increasing separation efficiency of the analytes. New columns chemistries have also been developed which have been designed to separate more specific groups of analytes of interest from the background matrix. However whilst these columns may be very successful in separating specific compounds, a general purpose column with the chemistry type used in this study may prove better at separating different groups of compounds.

The results presented here refer only to the analyses of samples collected on the days of sampling and therefore different results may be obtained if samples were collected on other days. Further studies in the application of this method for monitoring rivers

could investigate agrochemical levels in the water over daily, weekly or monthly periods. A regime to periodically monitor the river systems could indicate whether seasonal weather changes adversely affect the river water quality. It could be determined if weather has adverse effects on pollutants in the water due to heavy rainfall or if drought conditions cause concentrations to rise.

Water sampling points were taken no more than two meters from the river bank and no more than one metre below the surface level. The concentration profiles may change as you approach the centre of the river and depth concentration profiles change towards the river bed. Further studies could concentrate on the analyses of the river at specific depths and distances from the river bank across its whole width for a more detailed view of the compounds present.

Whilst this method was applied to river water samples it could equally apply to other forms of aqueous monitoring such as drainage streams, irrigation canals and sewage sludge with the appropriate clean up procedures.

The studies outlined throughout this thesis have achieved the aims and objectives of the research question.