Determination of Priority Substances in Water: Quantifying a drop (or two) in the Ocean

John Quick, Sam Towers, Aaron Lewis
ALS Environmental Ltd, Torrington Avenue, Coventry, CV4 9GU

Introduction
The EU Water Framework Directive (WFD) legislation requires the analysis of some Priority Substances in environmental waters at the parts-per-quadrillion (ppq) level. As part of our participation in the UK Chemical Investigation Programme (CIP) ALS have developed a series of robust analytical methods using state-of-the-art instrumentation that is capable of meeting these challenging criteria. Herein we describe the analysis of the pyrethroid insecticide Cypermethrin at less than 10ppq/L using GC-MSMS with negative chemical ionisation and the perfluorinated compounds PFOS and PFOA at less than 0.1ng/L using High Resolution / Accurate Mass (HRAM) LC-MS on an Orbitrap instrument. The latter method employs an on-line SPE technique and requires a sample size of only 5ml. We show that these methods are robust and easily capable of meeting the limits of detection, precision and bias targets stipulated under the WFD legislation. The scope of the methods can be expanded to incorporate other WFD Priority Substances not covered in the CIP project.

Cypermethrin
Cypermethrin is a pyrethroid insecticide which has been designated a priority substance under the WFD legislation, and an environmental quality standard (EQS) of 80pg/L in inland surface waters has been established for this compound. The Quality Assurance / Quality Control directives stipulate that the limit of quantification (LOQ) should be no more than 10% of the EQS value. This implies a target LOD (of detection 0.01LOQ) of one seventh of the EQS in this case the target LOD is 10ppq/L. A means of detection that is both extremely sensitive and very selective is required to meet this target. GC-MSMS with electron impact (EI) ionisation is a widely used technique to measure trace levels of GC amenable pesticides in complex matrices. However, it proved difficult to accurately quantify Cypermethrin at the required level in environmental samples using this technique without resorting to an impracticably large sample size and/or time consuming clean-up techniques. It was therefore decided to employ GC-MSMS with negative chemical ionisation (NCI) as the preferred technique for this analysis. The use of NCI allows for lower detection limits when compared to EI mode. It is a highly selective process whereby electron capture takes place for halogenated compounds and this enables a relatively higher selectivity of the analyte versus matrix interferences than would be observed in EI mode. Using this technique it was possible to develop a method involving the extraction of 400mls of sample withhexane followed by GC-MSMS with NCI, without any clean-up step, that delivered a LOD of less than 10ppq/L with excellent precision and bias statistics. An Agilent 7890A GC-MS System was used for this work.

Method performance Statistics

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method LOD</th>
<th>Reporting limit</th>
<th>Spike Recovery</th>
<th>Spike RSD</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEWAGE EFFLUENT</td>
<td>0.006ng/L</td>
<td>0.010ng/L</td>
<td>99.8%</td>
<td>3.4%</td>
<td>7.04%</td>
</tr>
<tr>
<td>SURFACE WATER</td>
<td>0.05ng/L</td>
<td>0.08ng/L</td>
<td>95.4%</td>
<td>5.5%</td>
<td>14.47%</td>
</tr>
</tbody>
</table>

Comparison of Sensitivity and Selectivity of GC-MSMS with NCI and EI for Cypermethrin
The chromatograms below demonstrate the difference in the detectability of Cypermethrin using the different ionisation modes in a real sample of surface water containing Cypermethrin at about 0.009ng/L (9pg/L). In the first (NCI) chromatogram the peaks representing Cypermethrin are clearly visible whereas in the second (EI) chromatogram no peaks can be distinguished.

LC-MSMS Detection of Non-Target Compounds
As mentioned previously one advantage of a HRAM approach over MSMS is that it enables the analysis of a wide range of non-target compounds. Other pesticides and pharmaceutical compounds are commonly found. These chromatograms show the detection of the PFCs Perfluorosulfonic acid (PFHxS) and Perfluorooctanoic acid (PFOA) and the herbicide Diuron along with PFOS in a sewage treatment works effluent.

Conclusions
ALS Environmental have developed a series of robust methodologies that enable the quantification of priority pollutants in environmental samples at ultra-trace (ppq) levels. These methods have been applied to the analysis of samples that form part of the UK Chemical Investigation Project (CIP). The methods utilise techniques such as GC-MSMS with negative chemical ionisation and HRMS with high resolution mass spectrometry on an Orbitrap system. The methods are extendable to other WFD priority substances that do not form part of the CIP project and the use of high resolution full scan GC-MS also makes possible the retrospective interrogation of the data for the identification of non-target compounds.