

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

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## 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 10pg/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 programme.

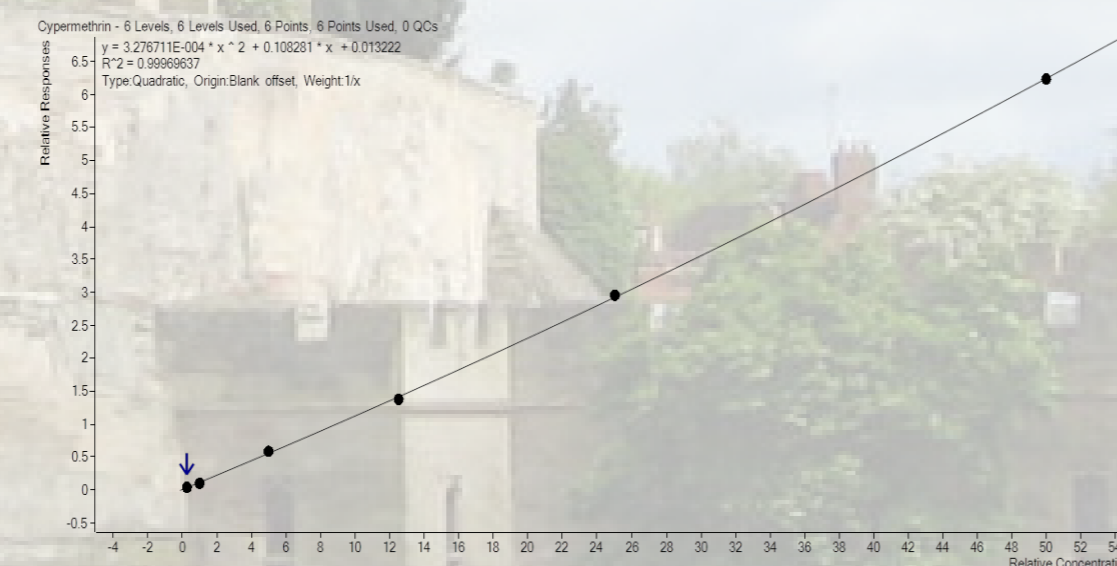
## Cypermethrin

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 (ppq) in inland surface waters has been established for this compound. The Quality Assurance / Quality Control directive stipulates that the limit of quantitation (LOQ) should be no more than 1/3 of the EQS value, this implies a target limit of detection (LOD) of one seventh of the EQS, in this case the target LOD is 10pg/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 in which 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 with hexane followed by GC-MSMS with NCI, without any clean-up step, that delivered an LOD of less than 10pg/L with excellent precision and bias statistics. An Agilent 7000C GC-MSMS system was used for this work.

### Method performance Statistics

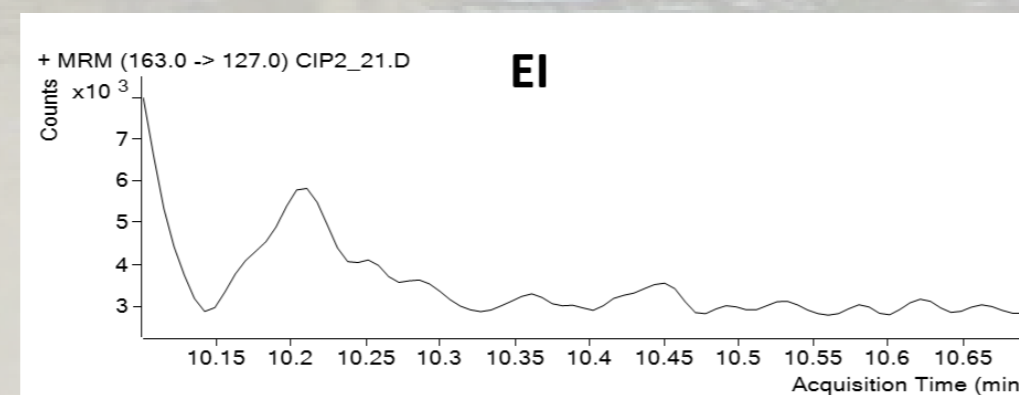
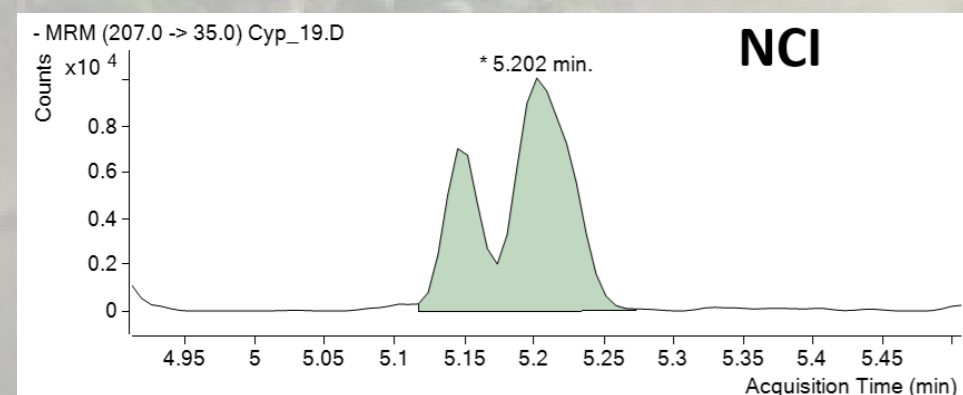
CYPERMETHRIN	
Method LOD	0.0068ng/L
Reporting Limit	0.010ng/L
SURFACE WATER	
Spike Recovery	99.8%
Spike RSD	3.41%
Uncertainty	7.04%
SEWAGE EFFLUENT	
Spike Recovery	98.3%
Spike RSD	4.85%
Uncertainty	12.76%

### Calibration Curve



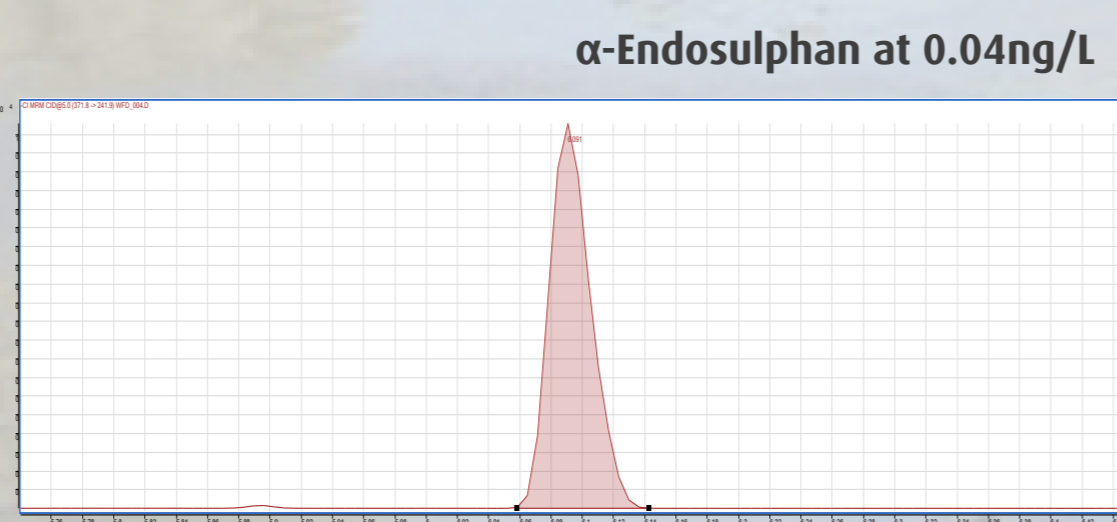
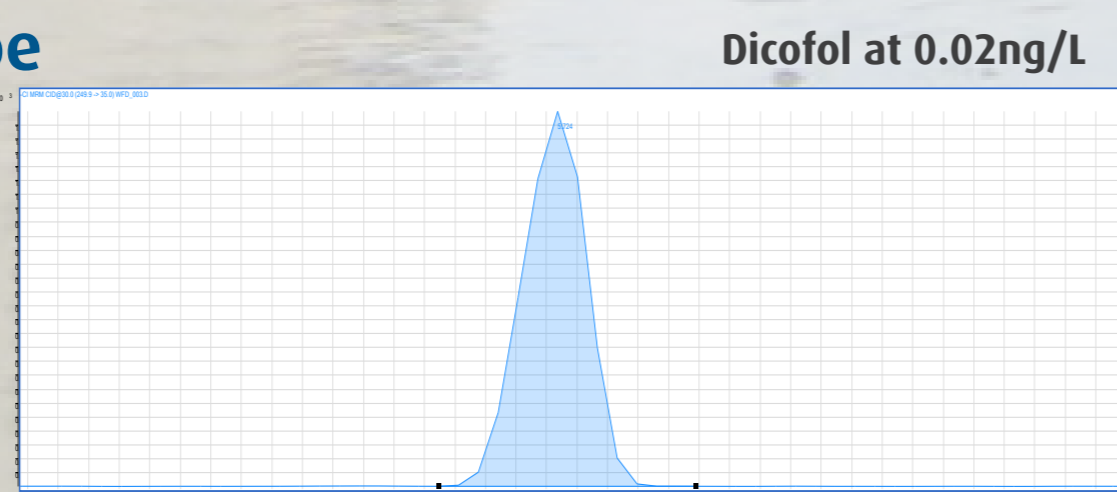
## Comparison of Sensitivity and Selectivity of GC-MSMS with NCI and EI for Cypermethrin

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.



## GC-NCI-MSMS Expansion of Scope

The suitability of the technique for other chlorinated pesticides identified as priority substances under the WFD legislation has been investigated. The accompanying chromatograms show Dicofol and  $\alpha$ -Endosulphan at the equivalent of 0.02 and 0.04ng/L respectively. These levels are lower than the lowest EQS values for these compounds and demonstrate the feasibility of expanding the method to cover these priority substances.



## PFOS and PFOA by LC-HRAM-MS

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are examples of a group of chemicals known as perfluorinated compounds or PFCs. PFOS has been used in the past in fire fighting foams whilst PFOA has been used in the manufacture of Teflon. Technical PFOS and PFOA as used in commercial products consist of a mixture of linear and branched isomers. They are persistent in the environment where they pose a potential risk both for the environment and for human health, consequently PFOS has been designated as a priority substance under the WFD legislation and assigned an EQS value of 0.65ng/L in inland surface waters. The UK CIP project requires the analysis of PFOS and PFOA to a limit of detection of 0.09ng/L. In order to meet this target ALS have developed a method utilising HPLC with high resolution accurate mass (HRAM) mass spectrometry on a Thermo Exactive Plus Orbitrap system. The use of HRAM MS offers several advantages over the more conventional LC-MSMS approach for this analysis. Orbitrap mass spectrometers are highly sensitive and selective detectors capable of operating at mass resolutions in excess of 100,000 FWHM. Since acquisition is full scan they are capable both of trace level quantitative analysis of target compounds in complex matrices and of screening for unexpected compounds in a single analytical run. An additional advantage of this approach for PFC analysis is that an even response is observed between linear and branched isomers in contrast to LC-MSMS, resulting in the more reliable quantification of total PFOS & PFOA. The method developed by ALS involves the direct loading of 5ml of sample onto an on-line SPE system, the trapped analytes are then backflushed onto the analytical column for separation and detection. MS analysis is carried out on a Thermo Exactive Plus Orbitrap mass spectrometer with an electrospray ionization (ESI) source. Full scan data is acquired at m/z 200-800 simultaneously in both positive and negative ionization modes at a resolution of 70,000 FWHM.

### Method performance Statistics

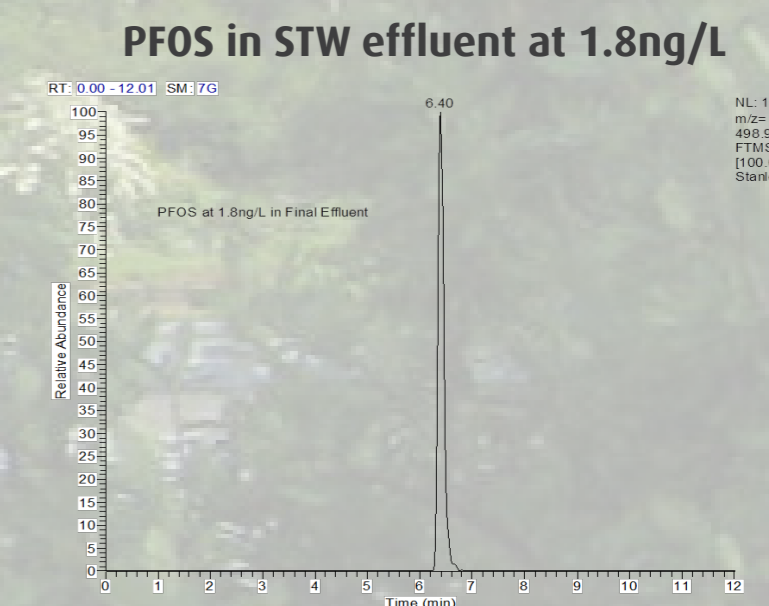
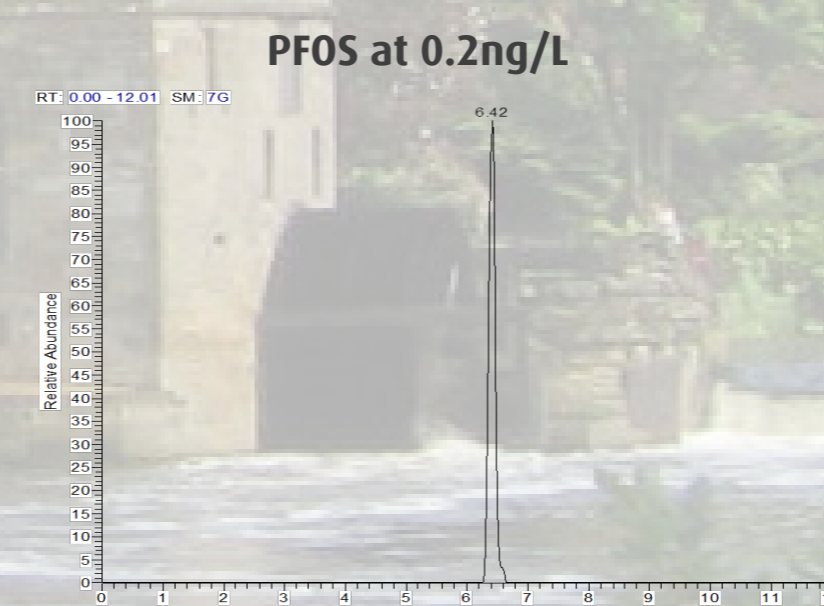
	PFOS	PFOA
Method LOD	0.068ng/L	0.054ng/L
Reporting Limit	0.09ng/L	0.09ng/L
SURFACE WATER		
Spike Recovery	94.4%	95.9%
Spike RSD	5.53%	5.17%
Uncertainty	16.65%	14.47%
SEWAGE EFFLUENT		
Spike Recovery	96.9%	94.8%
Spike RSD	4.15%	2.38%
Uncertainty	11.41%	10.00%

### Exacte Plus Orbitrap Mass Spectrometer



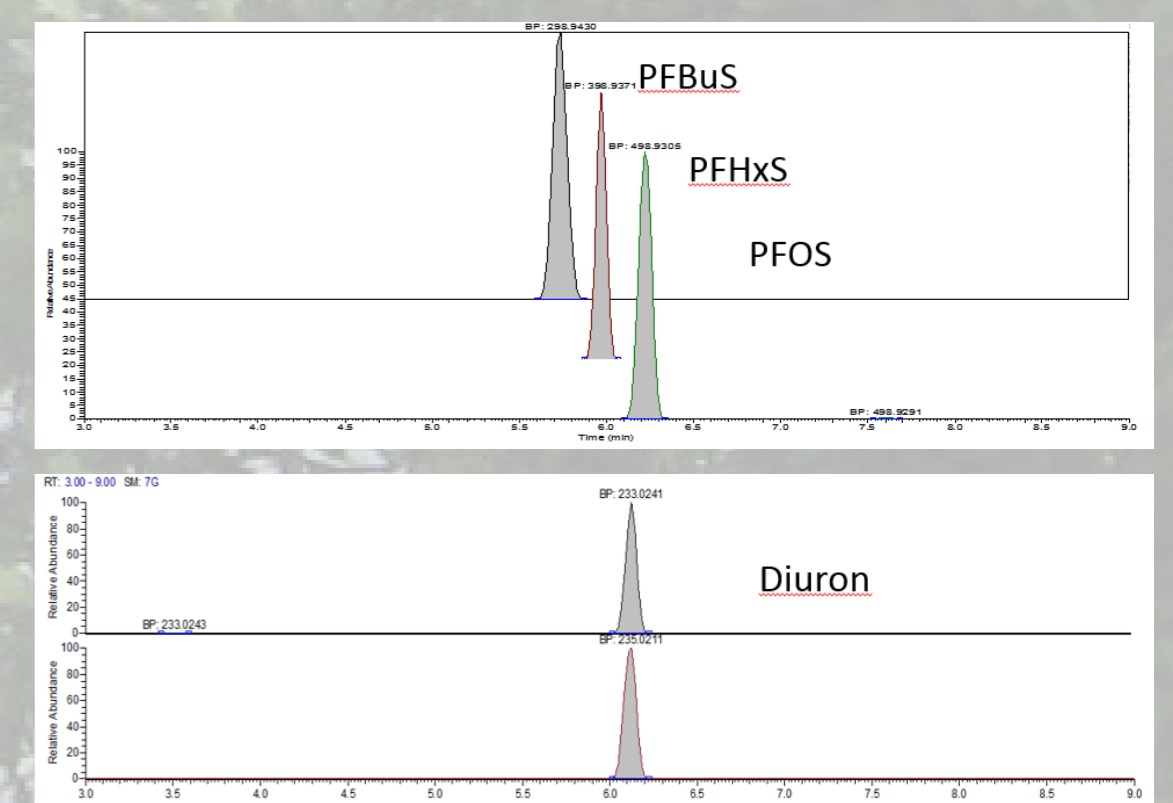
## Sensitivity and Selectivity of LC-HRAM-MS for PFOS

The chromatograms below illustrate the high degree of sensitivity and selectivity obtainable for PFOS analysis in environmental samples using LC-HRAM-MS on an Orbitrap mass spectrometer. The first shows a calibration standard at 0.2ng/L. The second, PFOS detected in a sewage treatment works effluent at 1.8ng/L.



## LC-HRAM-MS Detection of Non-Target Compounds

As mentioned previously one advantage of a HRAM approach over MSMS is that it enables the retrospective examination of the data for a wide range of non-target compounds. Other PFCs, pesticides and pharmaceutical compounds are commonly found. These chromatograms show the detection of the PFCs Perfluorobutane Sulfonic acid (PFBS) and Perfluorohexane Sulfonic acid (PFHS) 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 Programme (CIP). The methods utilise techniques such as GC-MSMS with negative chemical ionisation and HPLC 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 LC-MS also makes possible the retrospective interrogation of the data for the identification of non-target compounds.