Environmental

Analysis of Non-Polar Organic Compounds in Water by GC-MSMS

ALS Environmental Europe

John Quick – Principal Scientist

February 2013

RIGHT SOLUTIONS RIGHT PARTNER

Background

- STL was purchased by ALS from Severn Trent Water on 8th February 2013.
- STL is now ALS Environmental Ltd.
- Wakefield laboratory – Potable & Wastewater samples
- Coventry laboratory – Wastewater & Contaminated Land samples
- Bridgend laboratory – remained with Severn Trent Water

ALS Company History

Soap & Chemical Company Established

Listed on ASX

Modern Era

1863

1952

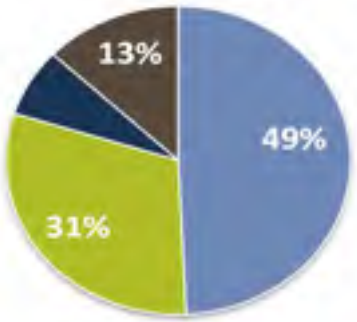
2012

ALS Limited – Today

- Market Capitalization GBP2.3 billion
- Fourth largest public listed TIC company in the world
- ASX 100 participant (Sept 2011)
- Annual Revenues GBP +1 billion
- 14,000 Staff
- Operations in 56 countries on 6 continents
- Conservative Funding – 29% gearing
- Commitment to training - promotion

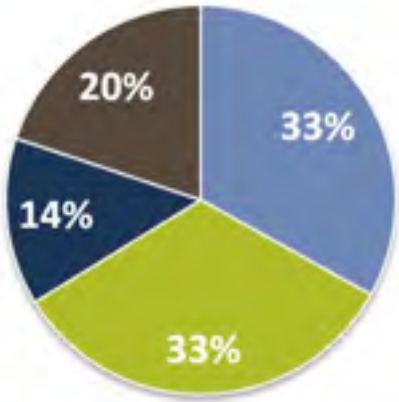
ALS Divisional Structure

- Four Global Divisions
- Ten Business Streams



Revenue 2012 – GBP 0.9 billion

Strategy



Revenue 2017 – GBP 1.3 billion

Introduction

- Recent work to transfer a number methods for, principally, non-polar organic analytes from GC and GC-MS to GC-MSMS across sample matrix types.
- Drivers
  - Efficiency improvements
    - Shorter chromatographic runs
    - Simpler data processing
    - Scope for simplifying sample preparation procedures
  - Enhanced service to clients
    - Ability to meet challenging LODs even in difficult matrices
    - Unambiguous identification of target analytes.
- Examples
  - Pesticides in Potable waters
  - Pesticides/PBDEs and PAHs in dirty environmental waters
  - NDMA – not non-polar!!
  - Potential simple screening method using MEPS

Potable Water Analysis

- Pesticides
  - PCV of 0.1ug/l for individual pesticides.
  - Required LODs <0.025ug/l (<0.01ug/l preferred).
  - Precision target – 12.5%
  - Need for efficient robust methodologies
  - Analysis of the more polar pesticides usually undertaken by LC-QQQ systems.
  - Non-polar pesticide analysis is now being transferred from single quadrupole instruments to GC-QQQ

Non-polar suite of compounds

- 51 compounds
  - LogPs are generally >3
  - Mostly organochlorine
  - Large volatility range

1,2,4-Trichlorobenzene	p,p'-DDE	PCB 28
Hexachlorobutadiene	Dieldrin	PCB 52
Dichlobenil	o,p'-TDE	PCB 101
alpha-HCH	Endrin	PCB 118
beta-HCH	beta-Endosulphan	PCB 153
Hexachlorobenzene	p,p'-TDE	PCB 138
gamma-HCH	o,p'-DDT	PCB 180
delta-HCH	p,p'-DDT	Cyfluthrin
Chlorothalonil	Methoxychlor	Cypermethrin
Heptachlor	Captan	Fenvalerate
Aldrin	EPTC	Deltamethrin
Isodrin	Tecnazene	Phorate
cis-Heptachlor Epoxide	Trifluralin	Tri-allate
trans-Heptachlor Epoxide	Disulphoton	Chlorpyrifos-Methyl
o,p'-DDE	Fenitrothion	Parathion-Ethyl
alpha-Chlordane	cis-Permethrin	Chlorpyrifos-Ethyl
alpha-Endosulphan	trans-Permethrin	Carbophenothion

Non-Polars - Previous Method

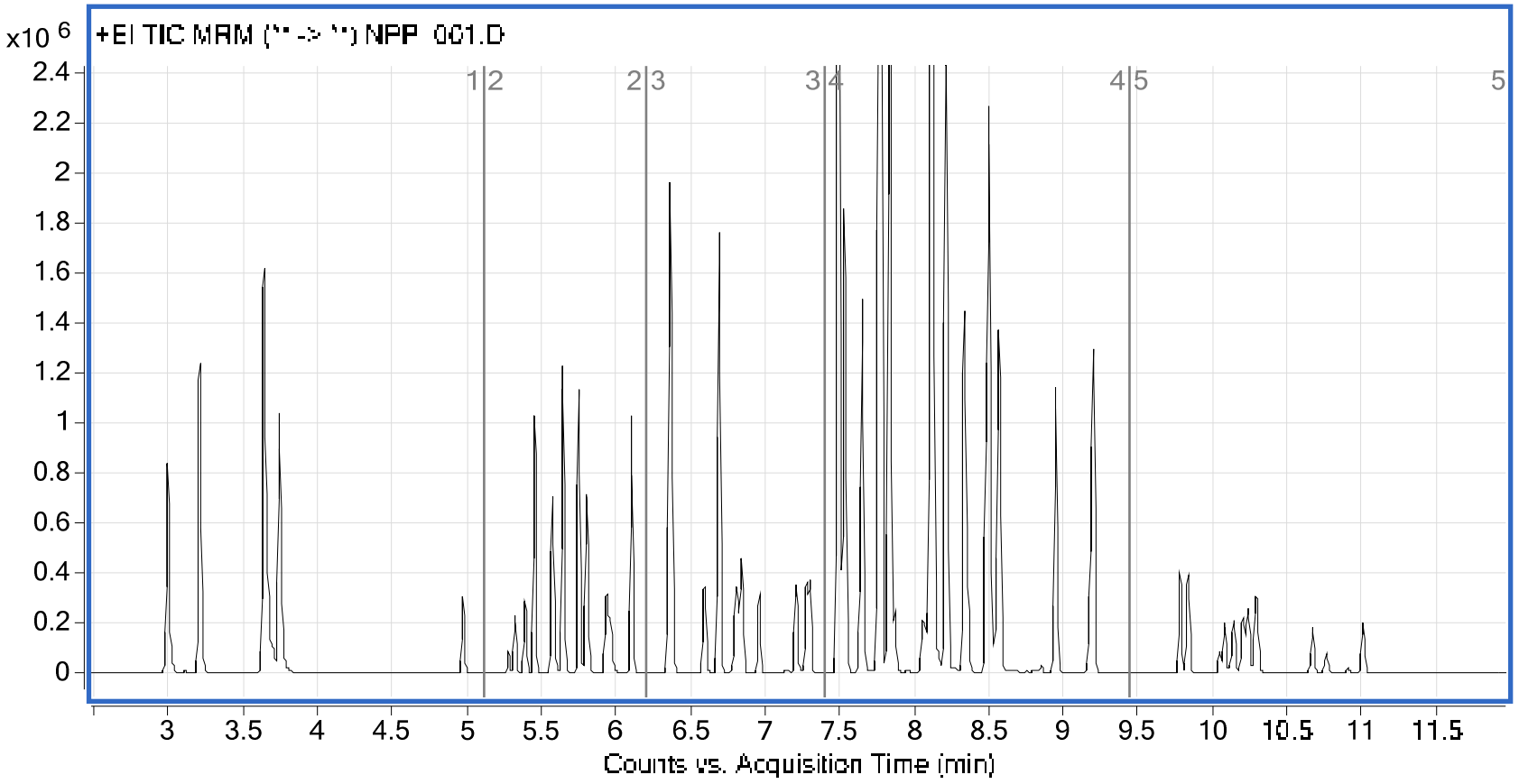
- Simple Extraction
  - 500ml of sample shaken with 5ml hexane
  - Transfer portion of extract directly to autosampler vial – no blow down
- Instrumental Analysis
  - GC-MS/ECD – Microfluidic splitter device used
  - 20ul on-column injection
  - 30 minutes cycle time
- Quantitation
  - Most analytes from MS but some – mainly the Pyrethroids – from the ECD signal
  - Significant resource devoted to reprocessing

Non-Polars – GC-QQQ Method

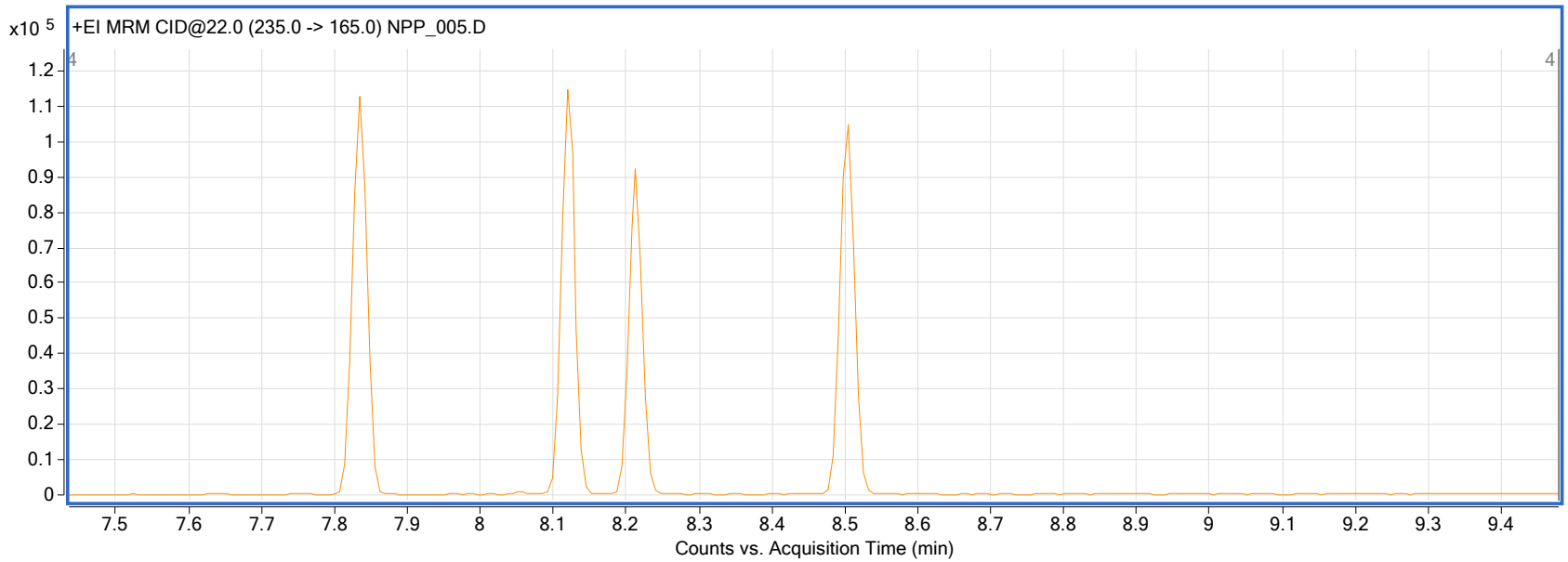
- Extraction
  - Only modified slightly – 10ml of Hexane:Ethyl Acetate (1:1) used as the extraction solvent.

- Instrumental Analysis
  - 25ul injected onto GC-QQQ system
  - Multi-mode inlet - Solvent vent mode utilised
  - 2 MRM transitions per analyte
  - Calibration range – 10 to 120ng/L
  - DB1 or column for good separation of DDT isomers
  - Fast run time – 12 minutes
  - Cycle time - <15 minutes with cryo cooling, ~19mins without.

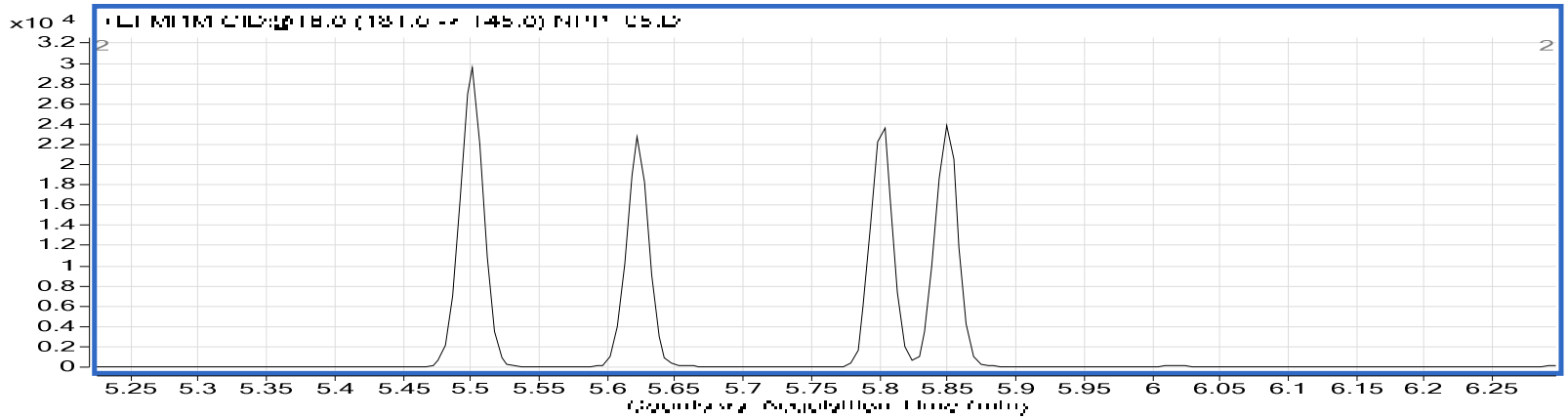
GC-QQQ Method – TIC Chromatogram @ 120ng/L

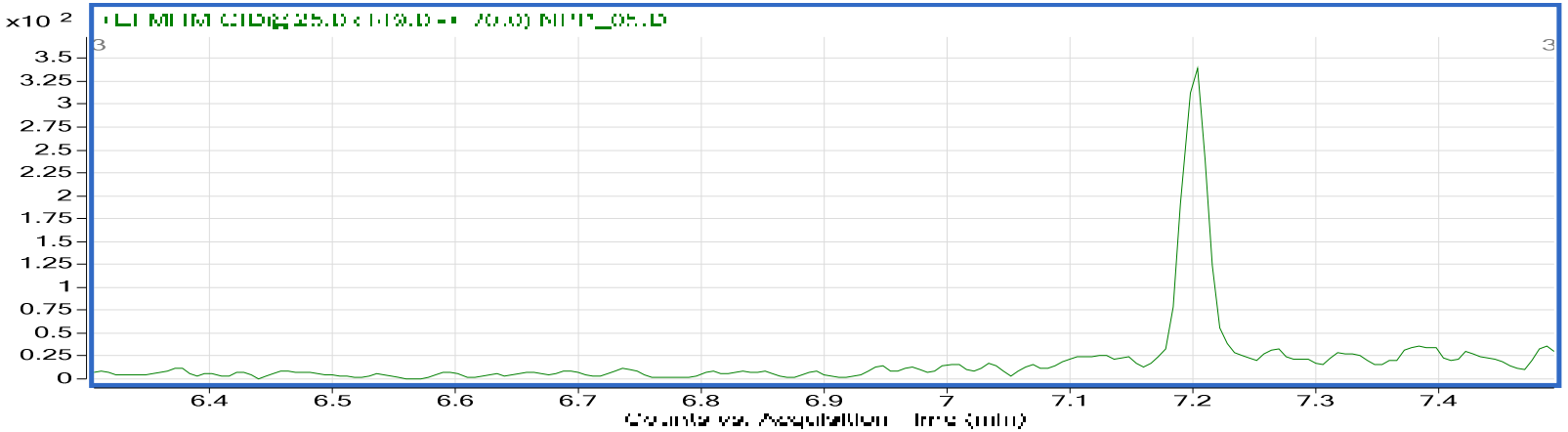


Separation of DDTs at 10ng/L

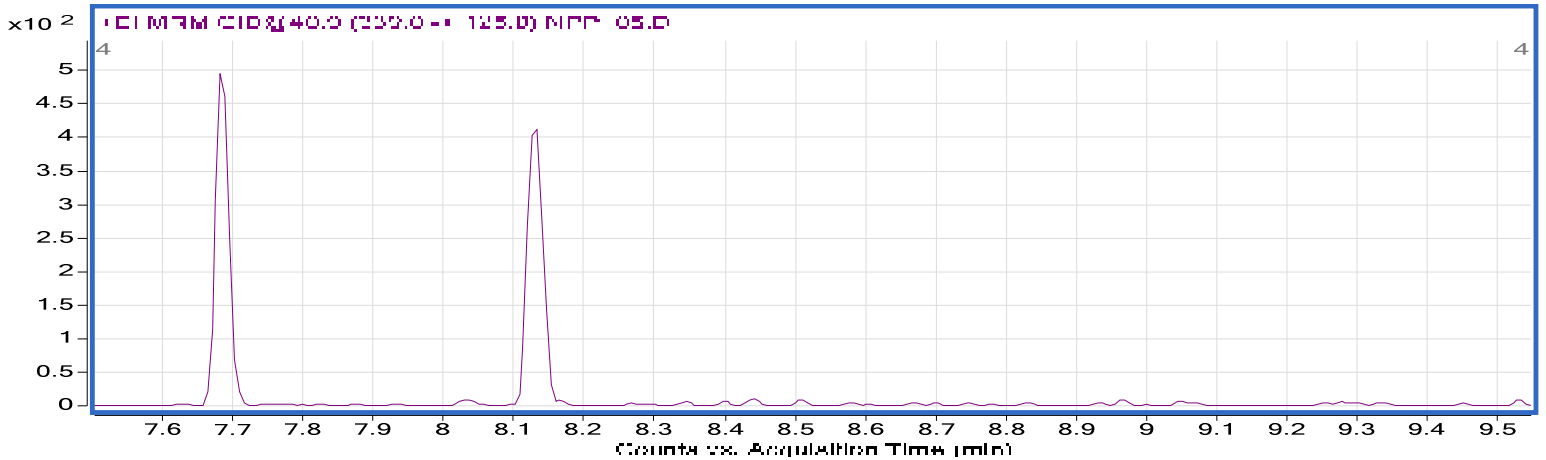


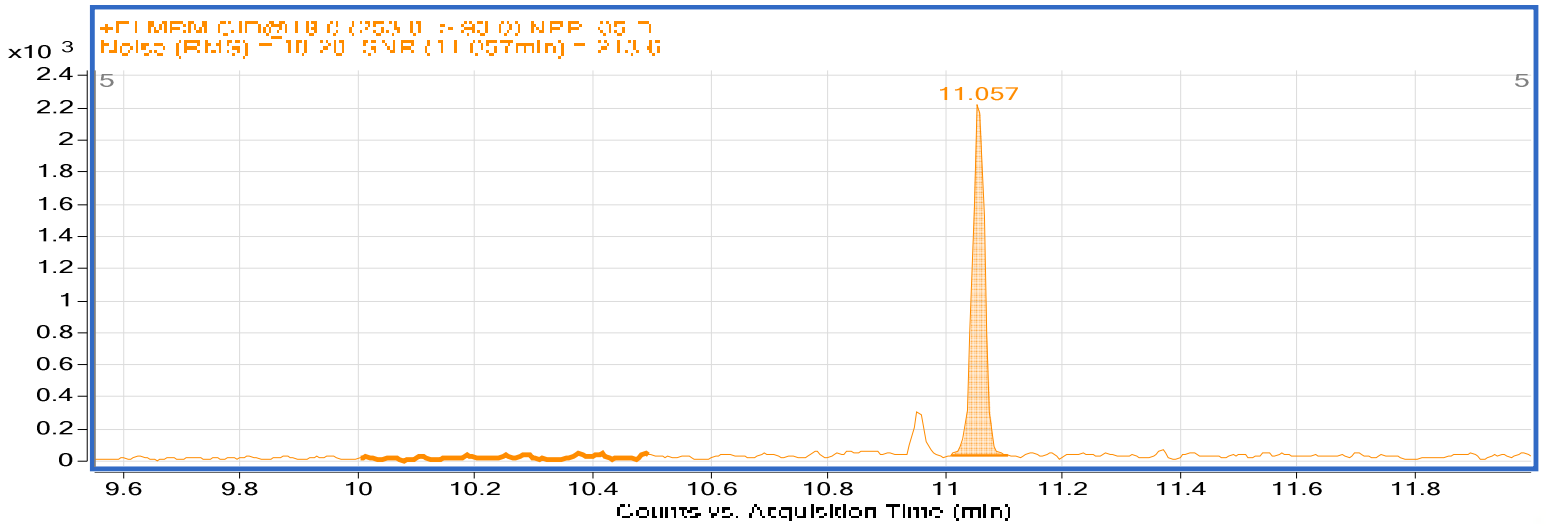
Sensitivity at 10ng/L – HCHs/Captan





Sensitivity at 10ng/L – Endosulphans/Deltamethrin

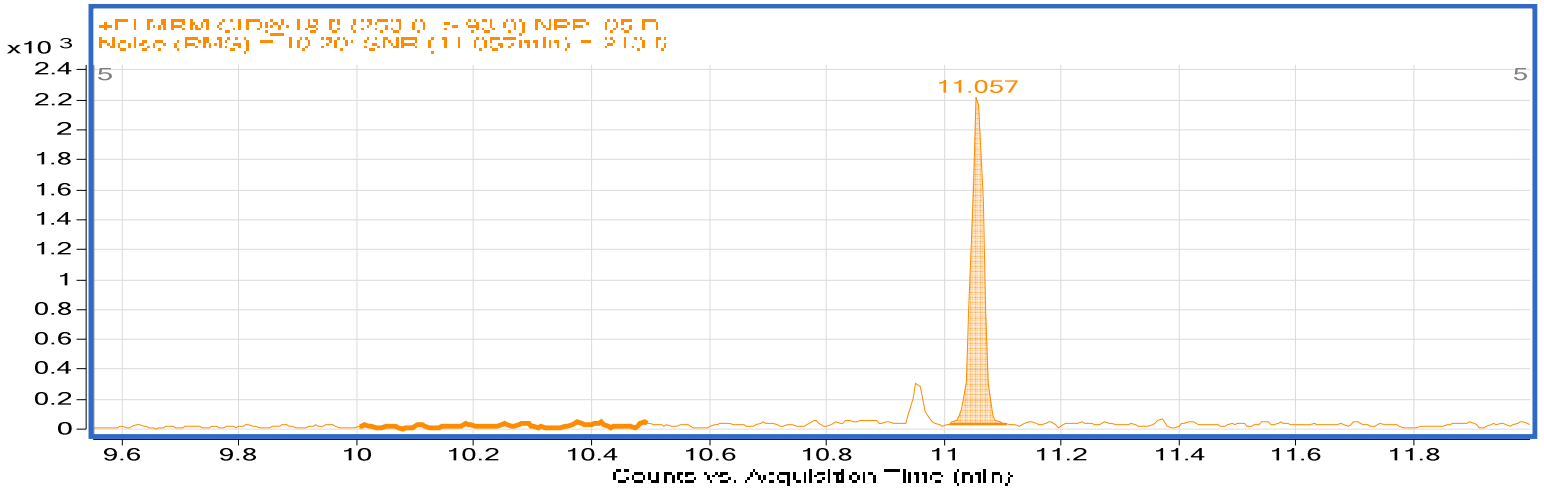


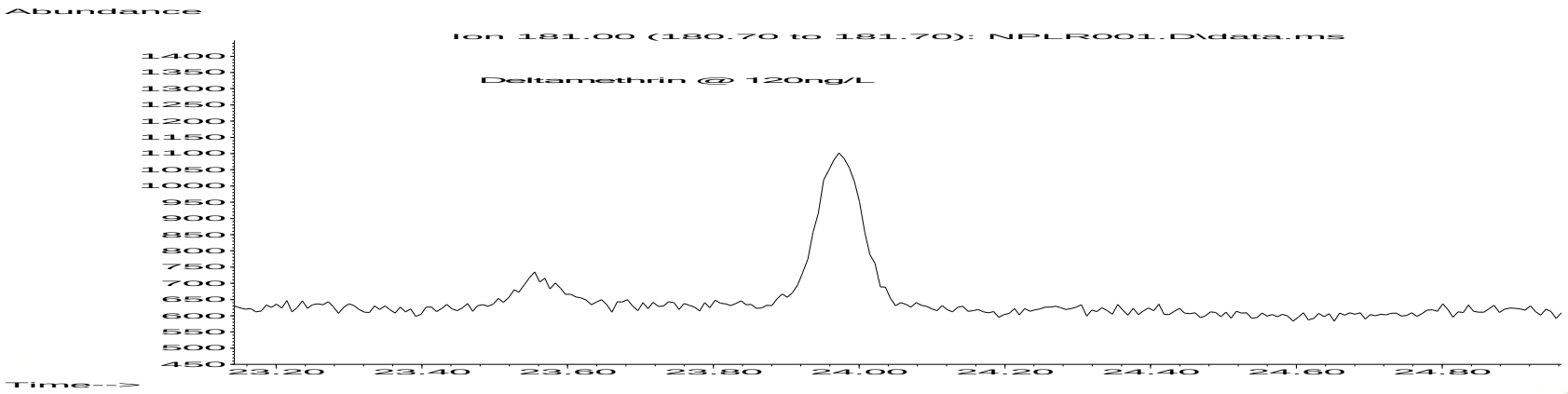


Comparison of GC-MS and GC-MSMS

Top – Deltamethrin at 10ng/L GC-QQQ

Bottom - Deltamethrin at 120ng/L GC-MSD

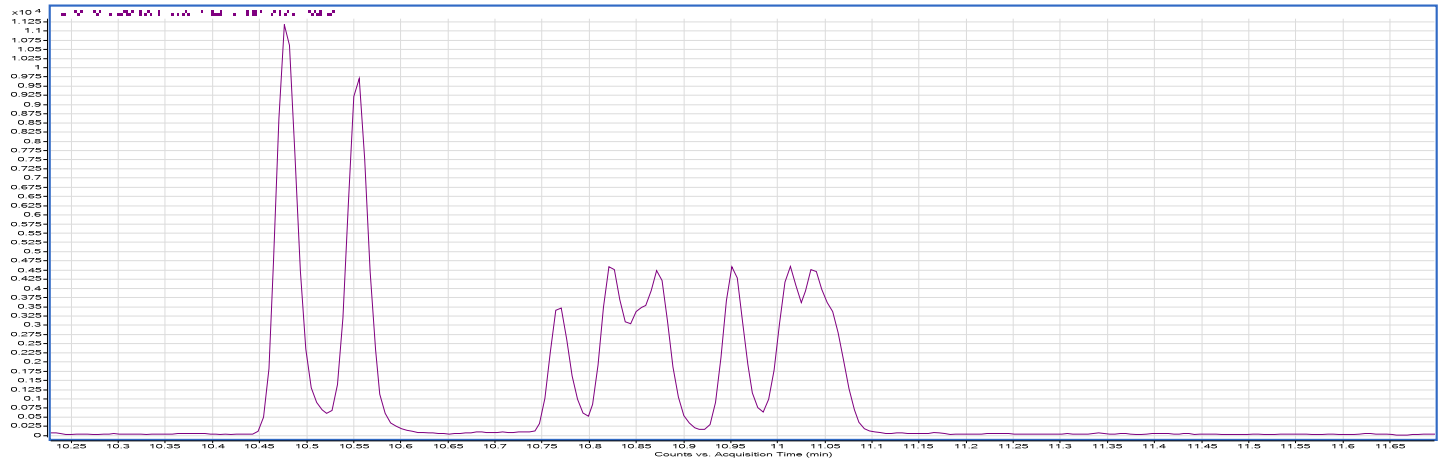


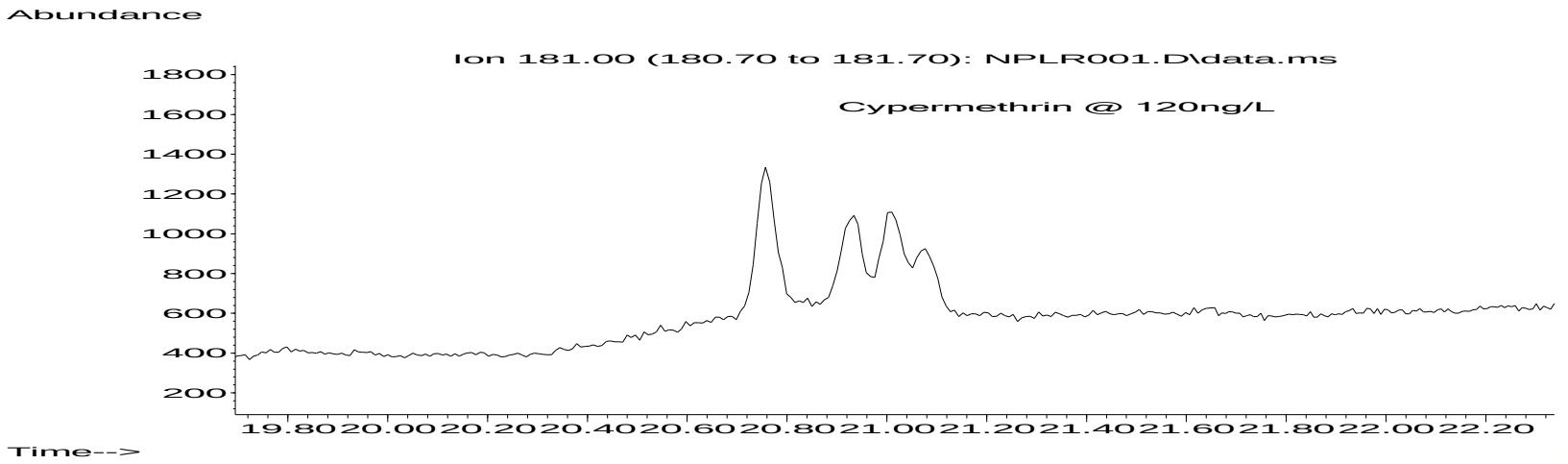


Comparison of GC-MS and GC-MSMS

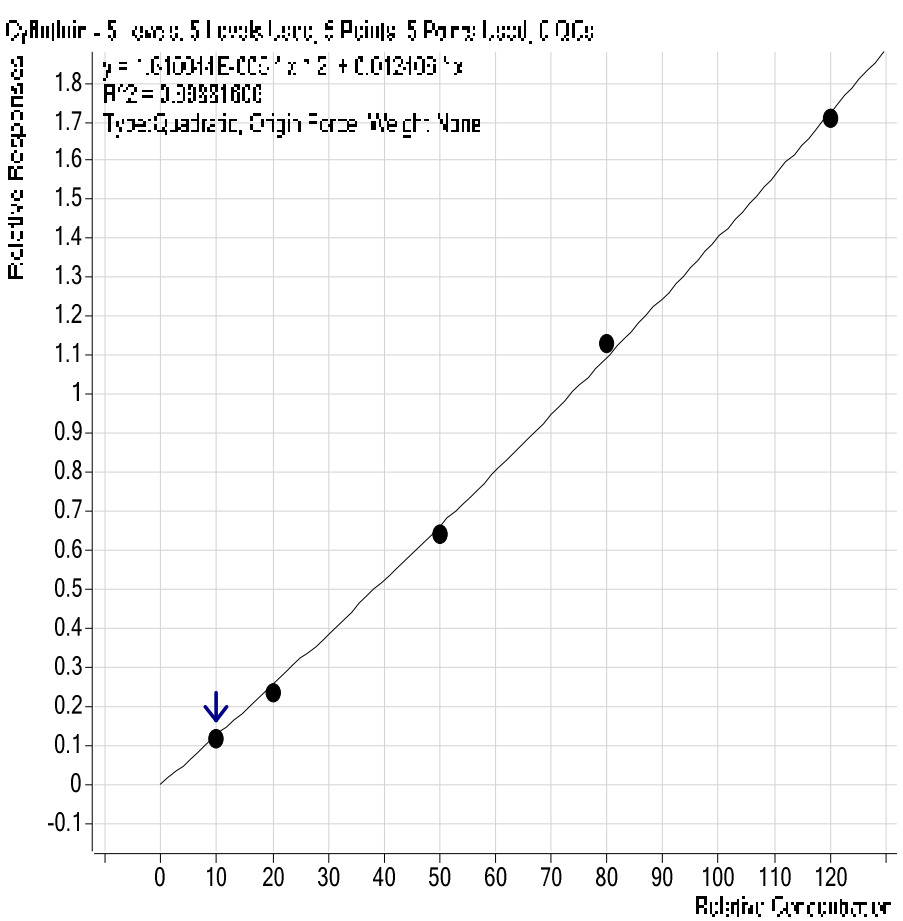
Top – Cypermethrin at 10ng/L GC-QQQ

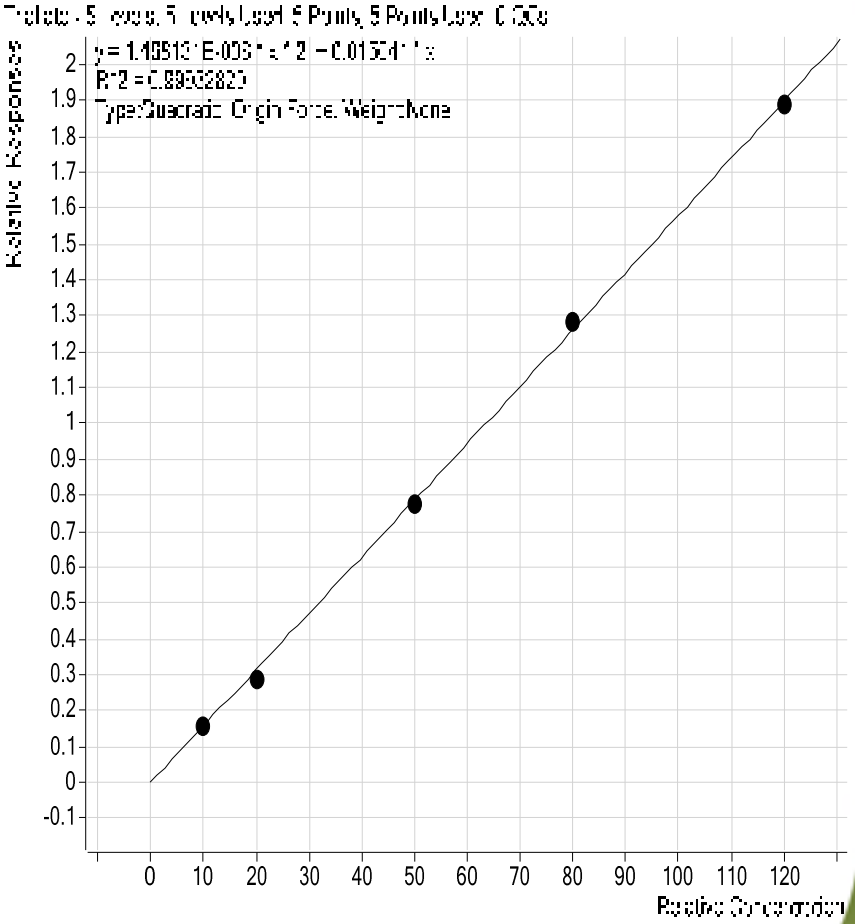
Bottom - Cypermethrin at 120ng/L GC-MSD



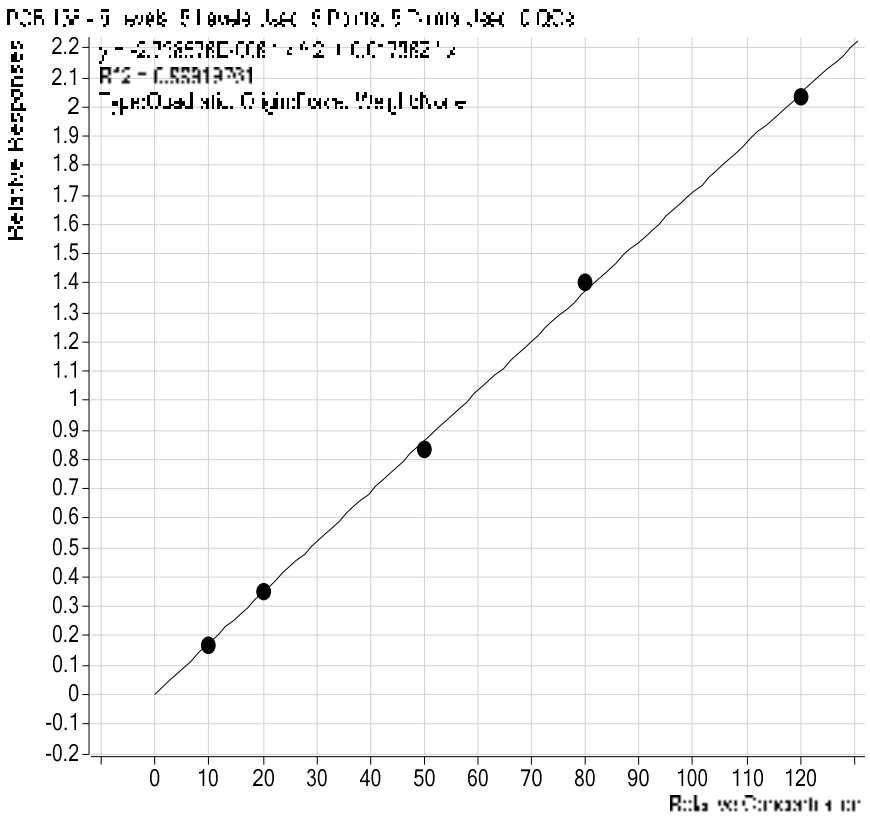


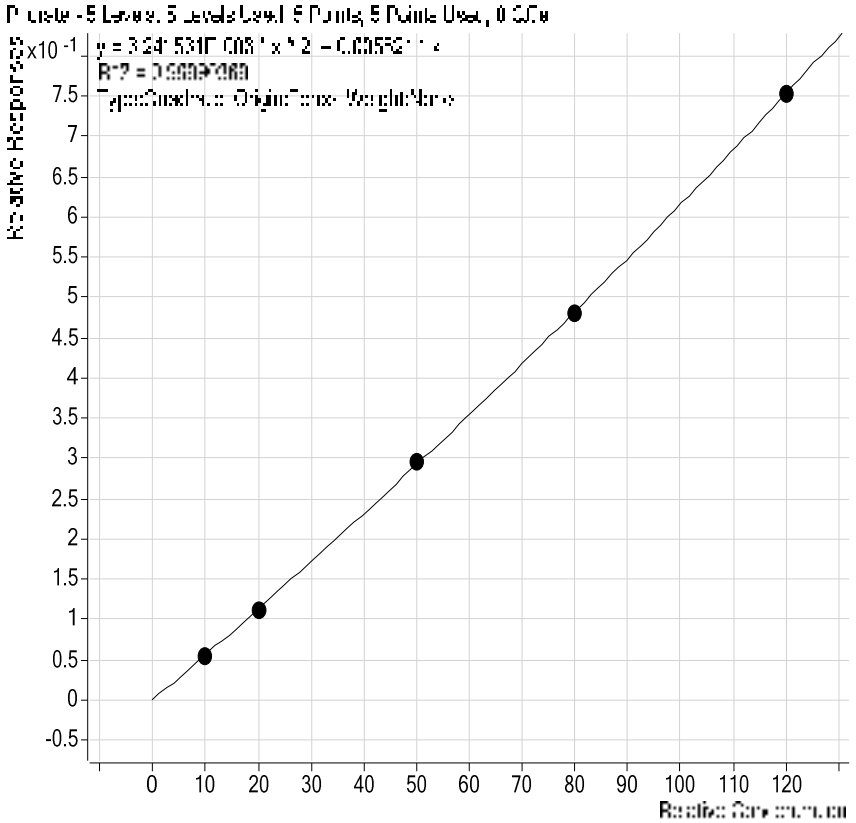
Calibration – Cyfluthrin/Triallate





Calibration – PCB 138/Phorate





Non-Polars – Method Validation

- Method validated on 5 matrices
  - Potable – Soft, Medium, Hard
  - Raw – Borehole, Surface

- Summary of Results
  - Highest LOD was Captan at 3ng/L all others 2ng/L or less
  - Excellent recoveries and precision for all compounds – majority of RSDs <5% at the PCV Level.

- Method accredited by UKAS

- Method has been “live” at the Bridgend laboratory for 9 months and is performing well.

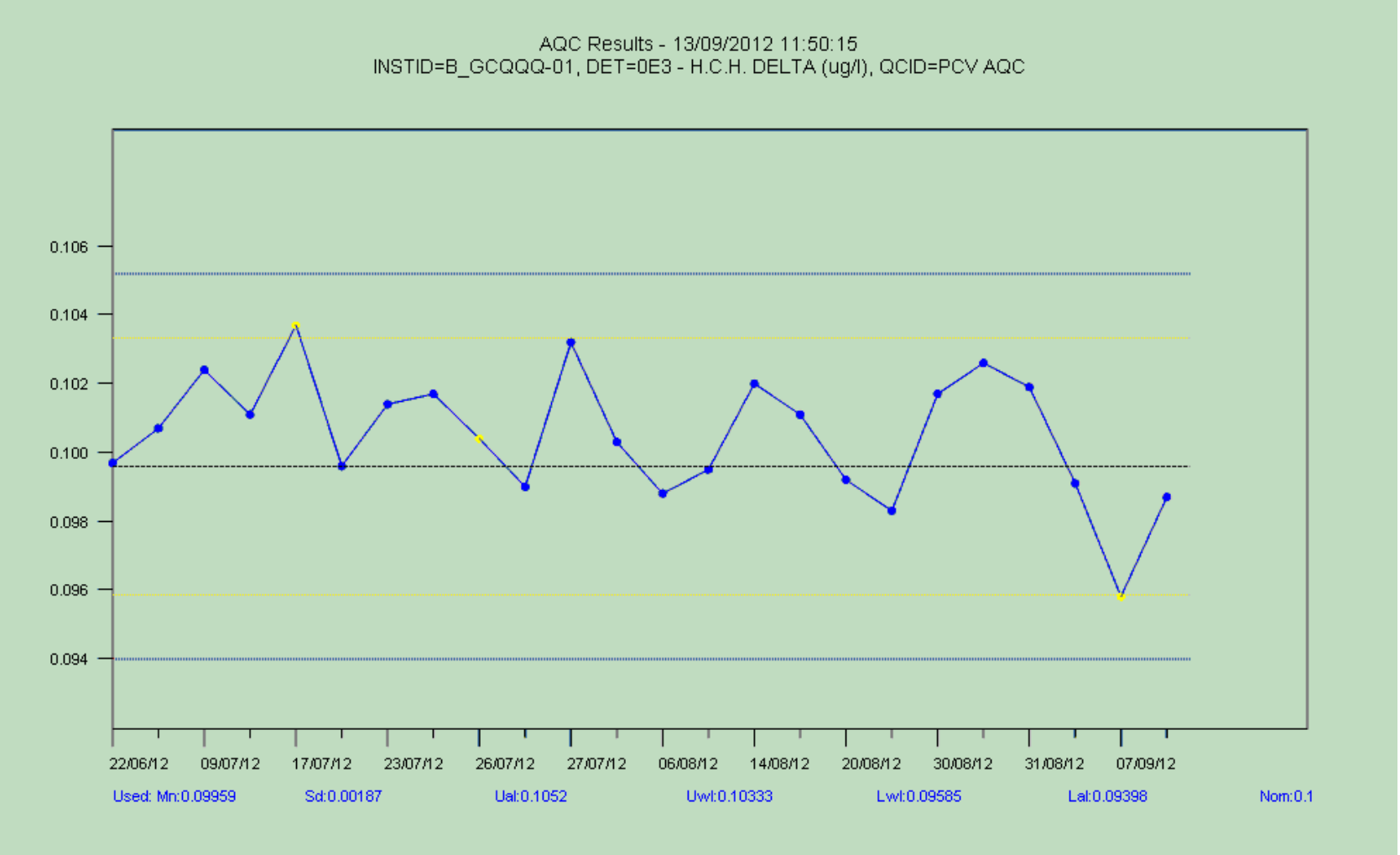
Method Validation Results – Medium water

	Med. Water - PCV Spike			Med. Water - PCV Spike			Med. Water - PCV Spike	
Name	**Recovery**	**RSD**	**Name**	**Recovery**	**RSD**	**Name**	**Recovery**	**RSD**
EPTC	105.1%	2.9%	trans-Heptachlor Epoxide	104.0%	6.8%	Methoxychlor	100.7%	6.3%
124-TCB	100.3%	3.3%	Dieldrin	100.6%	8.3%	PCB 180	100.9%	4.8%
Hexachlorobutadiene	101.6%	5.2%	Isodrin	101.8%	4.5%	cis-Permethrin	102.2%	3.5%
Dichlobenil	103.1%	3.5%	op-DDE	100.7%	3.7%	trans-Permethrin	102.0%	3.3%
Tecnazene	102.7%	5.1%	PCB 101	101.3%	3.7%	Cyfluthrin	99.1%	3.4%
Trifluralin	104.3%	3.8%	alpha-Chlordane	99.5%	4.7%	Cypermethrin	100.6%	3.0%
alpha-HCH	101.6%	2.9%	alpha-Endosulphan	102.3%	3.3%	Fenvalerate	100.6%	4.7%
Hexachlorobenzene	101.7%	4.8%	pp-DDE	101.0%	3.5%	Deltamethrin	98.4%	6.9%
gamma-HCH	101.6%	2.6%	OP-TDE	100.7%	4.0%	delta-HCH	102.0%	2.6%
beta-HCH	101.9%	3.0%	PCB 118	100.9%	3.3%	Triallate	104.1%	3.9%
PCB 28	102.9%	4.4%	PP-TDE	100.8%	4.5%	Parathion-Ethyl	100.7%	3.2%
Chlorothalonil	107.8%	3.6%	Endrin	98.9%	7.2%	Carbophenothion	99.9%	5.6%
Heptachlor	104.7%	6.0%	op-DDT	102.8%	5.4%	Chlorpyrifos-Methyl	101.0%	2.4%
PCB 52	100.8%	5.0%	PCB 153	100.5%	3.6%	Chlorpyrifos-Ethyl	100.7%	2.7%
Fenitrothion	103.5%	3.9%	beta-Endosulphan	103.1%	3.7%	Captan	101.5%	5.4%
Aldrin	104.2%	5.8%	PCB 138	100.5%	3.1%	Phorate	101.1%	2.5%
cis-Heptachlor Epoxide	104.0%	7.1%	pp-DDT	101.1%	2.1%	Disulphoton	102.1%	2.1%

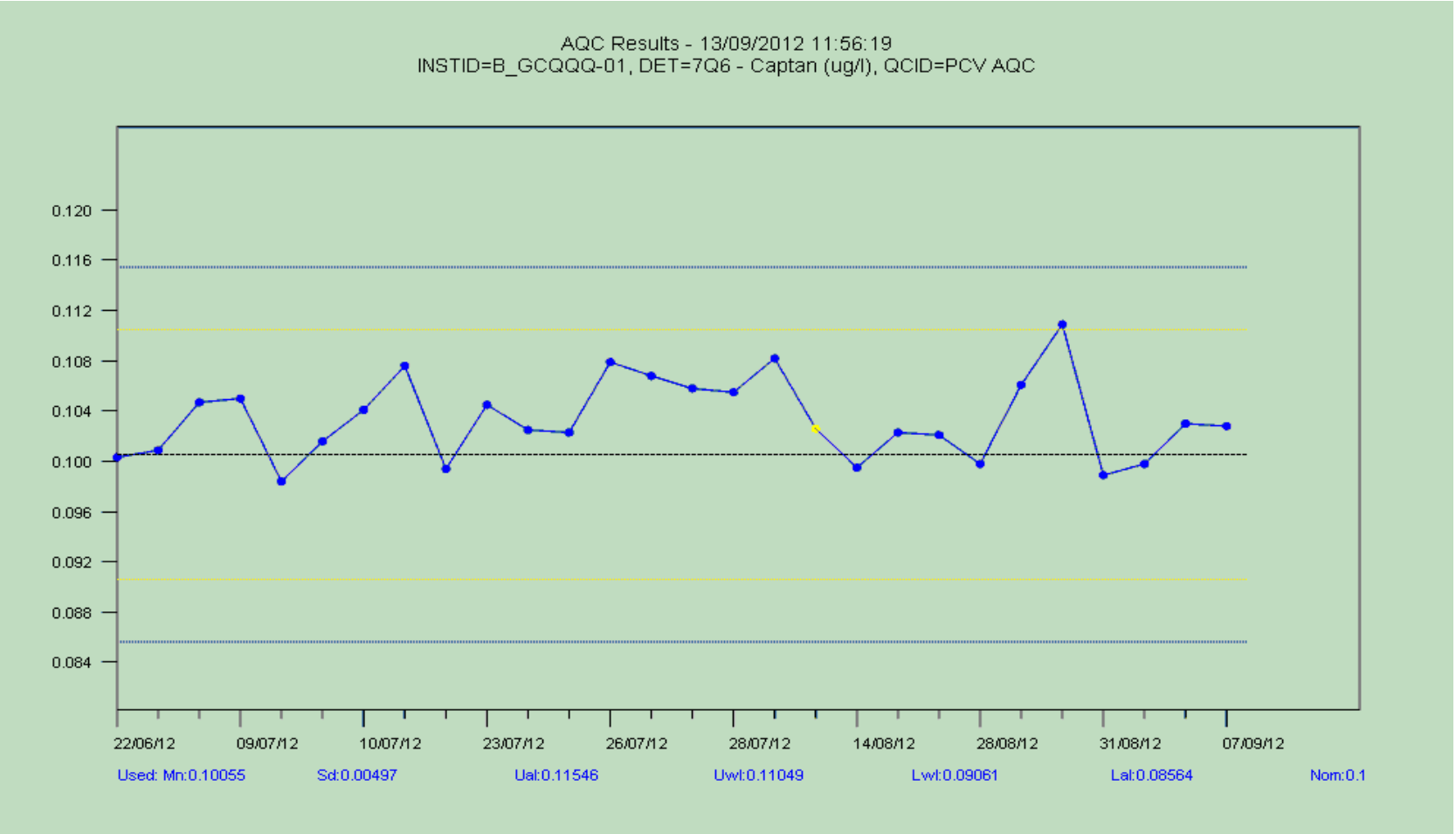
Non-Polars – Routine AQC Performance

- Routine AQC
  - 3 months data
  - RSDs range from 1.6 to 7.4%
  - 43 Compounds <5%
  - 15 Compounds <3%

Routine AQC Chart – delta-HCH



Routine AQC Chart – Captan



Non-Polars in Potable Water - Summary

- Analysis of a suite of non-polar pesticides has been successfully transferred from GC-MSD/ECD to GC-QQQ.

- Method has been accredited by UKAS and is working well in production.

- Advantages over the previous method include:
  - Faster analytical runs.
  - Enhanced sensitivity.
  - Greater robustness.
  - Easier data processing.
  - Better selectivity – 2MRM transitions per compound giving greater confidence in positive results.

Wastewater Analysis

- Compounds
  - PBDEs, PAHs, Diazinon, Cypermethrin
  - Low reporting limits - <0.2ng/L for some compounds
  - Dirty matrices – Crude sewages & trade effluents
  - Sensitivity and selectivity of GC-QQQ essential.

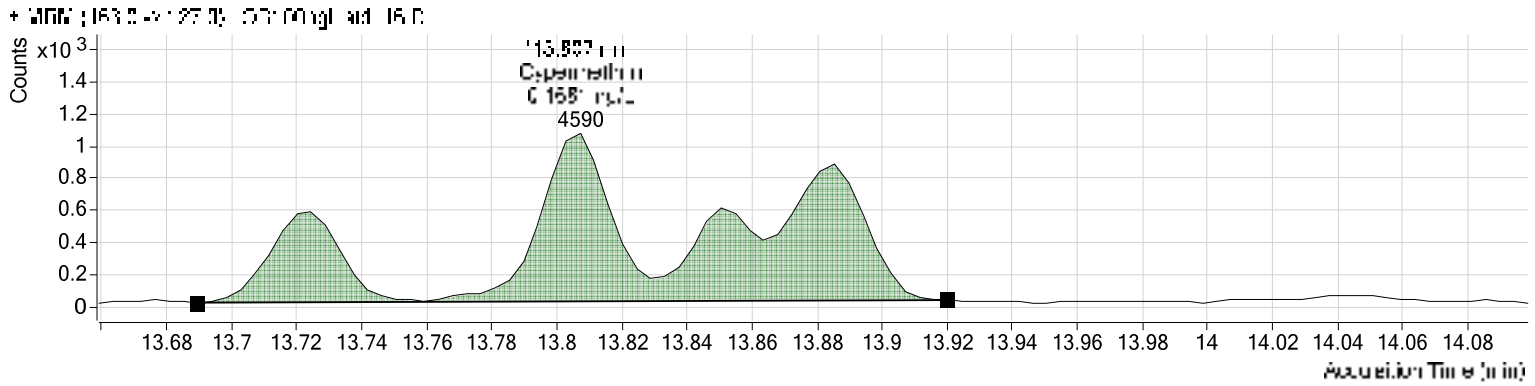
- Sample Preparation
  - 160ml sample with 40ml acetonitrile
  - Extract with 20ml hexane
  - Evaporate 10ml of extract to 1ml
  - Clean-up on NH2 SPE Cartridge
  - Evaporate to 250ul
  - Inject 12.5ul onto GC-QQQ via MMI operated in solvent vent mode

Wastewater Analysis - ctd

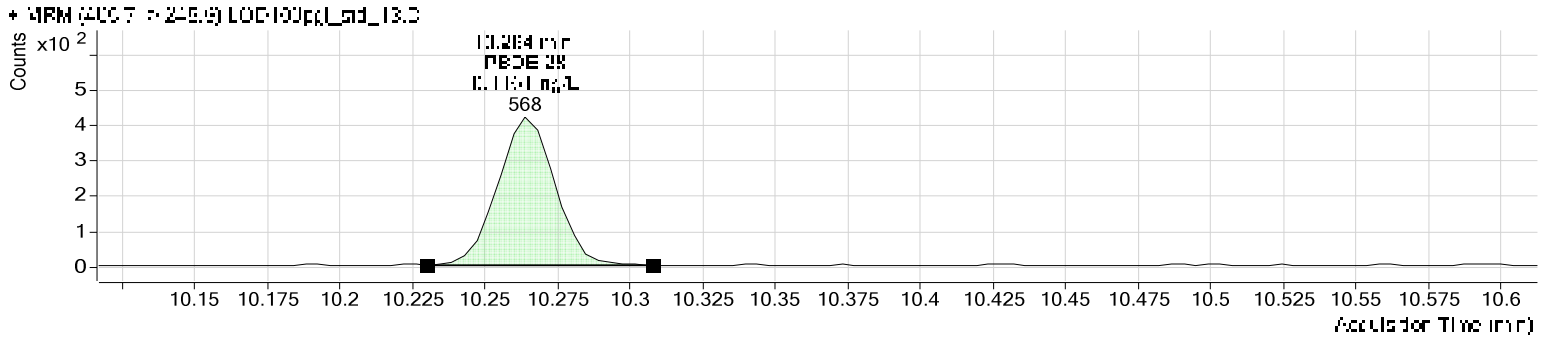
- Instrumental Analysis
  - Inject 12.5ul onto GC-QQQ via MMI operated in solvent vent mode.
  - DB5 column – 17mins run time
  - Initial injector temp – 90^{o}C
  - Initial Oven temp - 60^{o}C
  - Using higher source temperature (300^{o}C) improves performance of less volatile analytes

Sensitivity standard – 0.032pg/ul (equiv. to 0.1ng/L in sample and 0.4pg on-column)

Cypermethrin

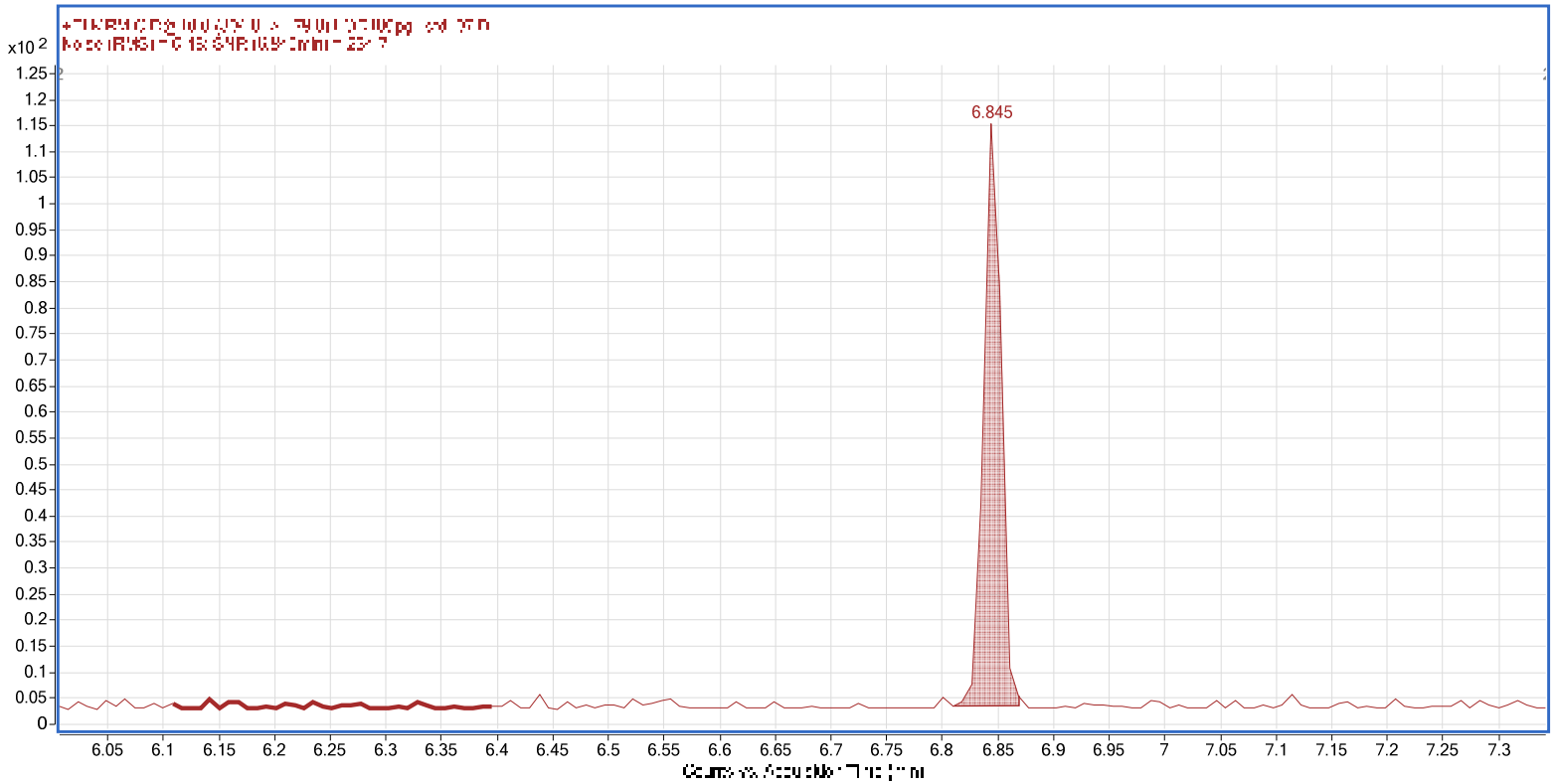


PBDE 28

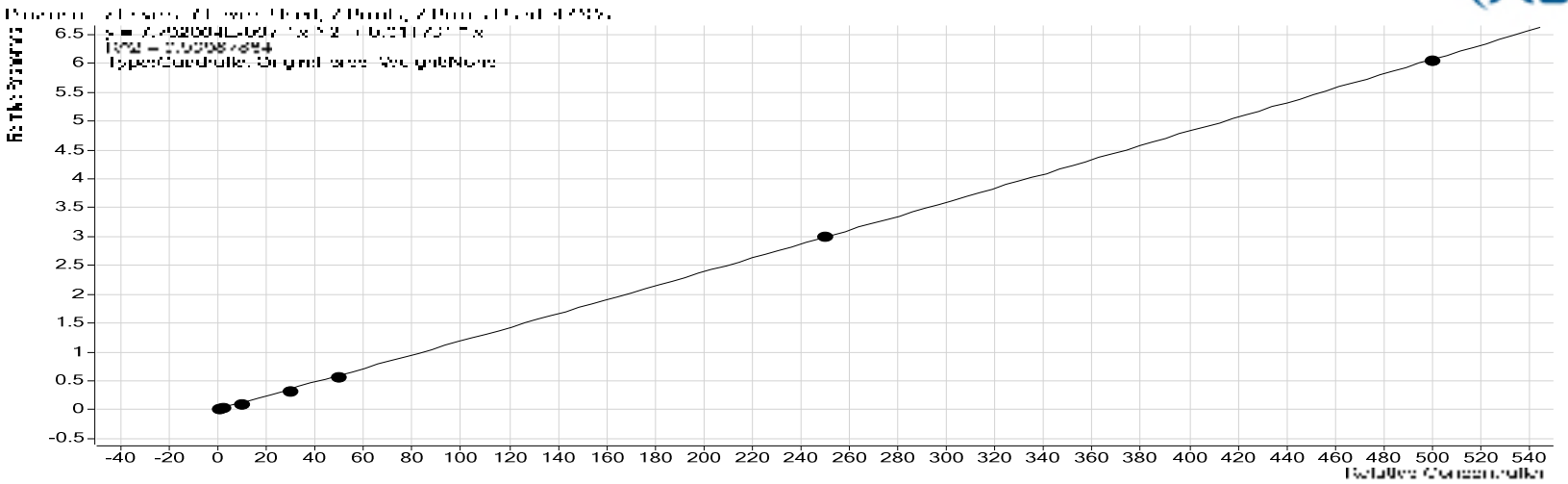


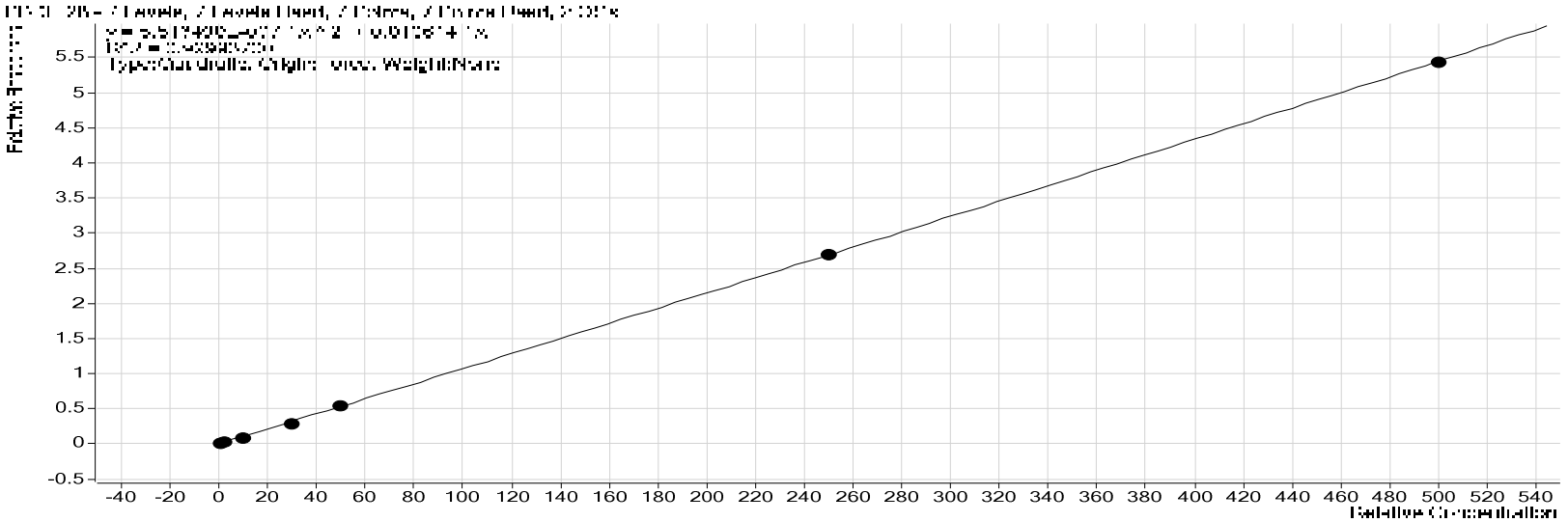
Sensitivity standard – 0.032pg/ul (equiv. to 0.1ng/L in sample and 0.4pg on-column)

Diazinon – RMS S/N ratio 235:1

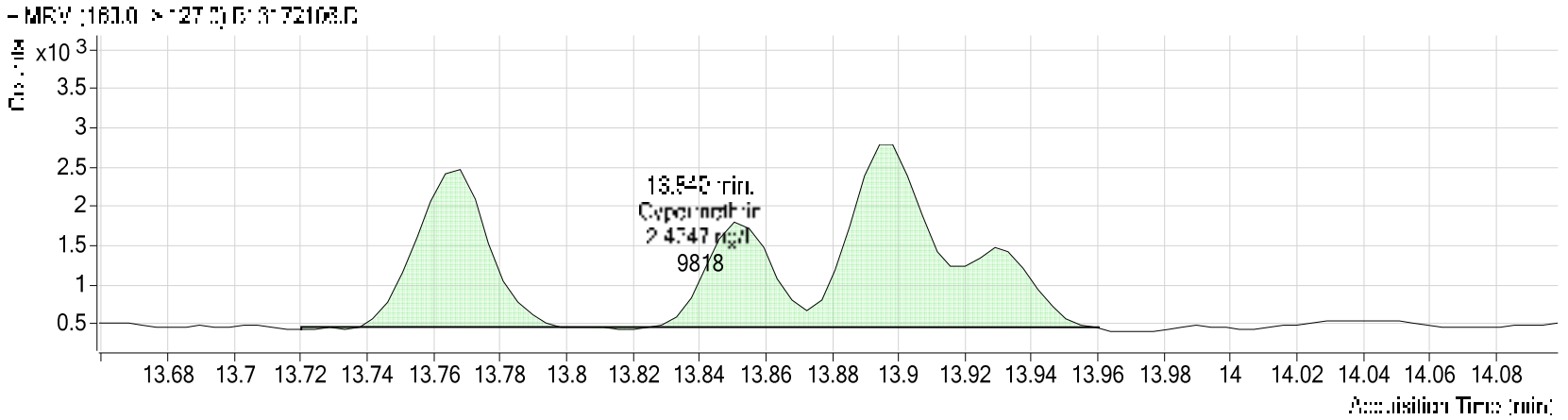


Calibrations – Diazinon / PBDE 28

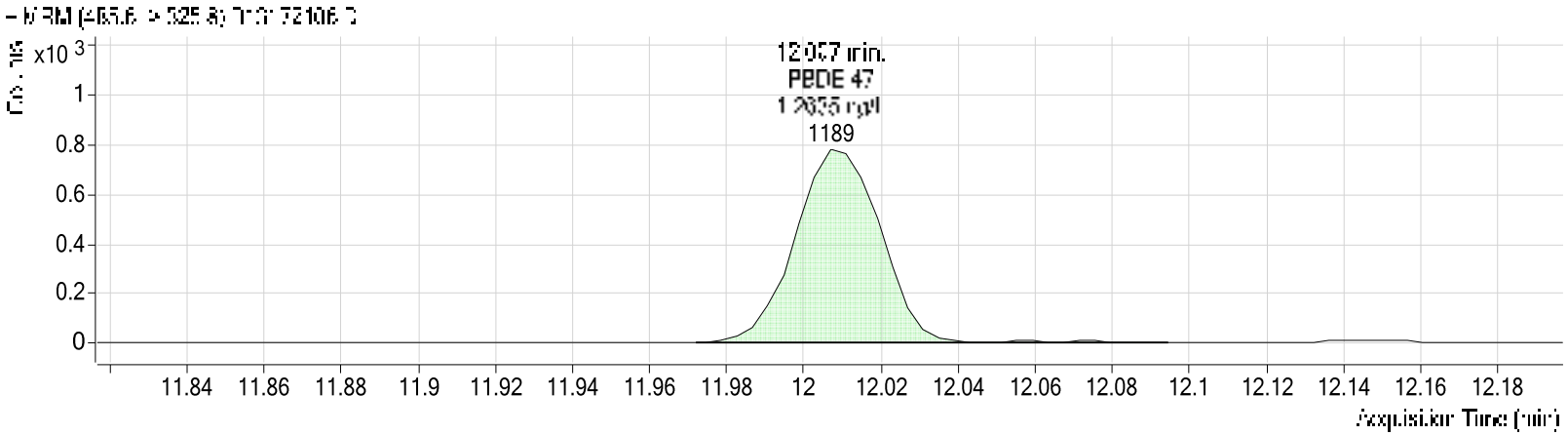




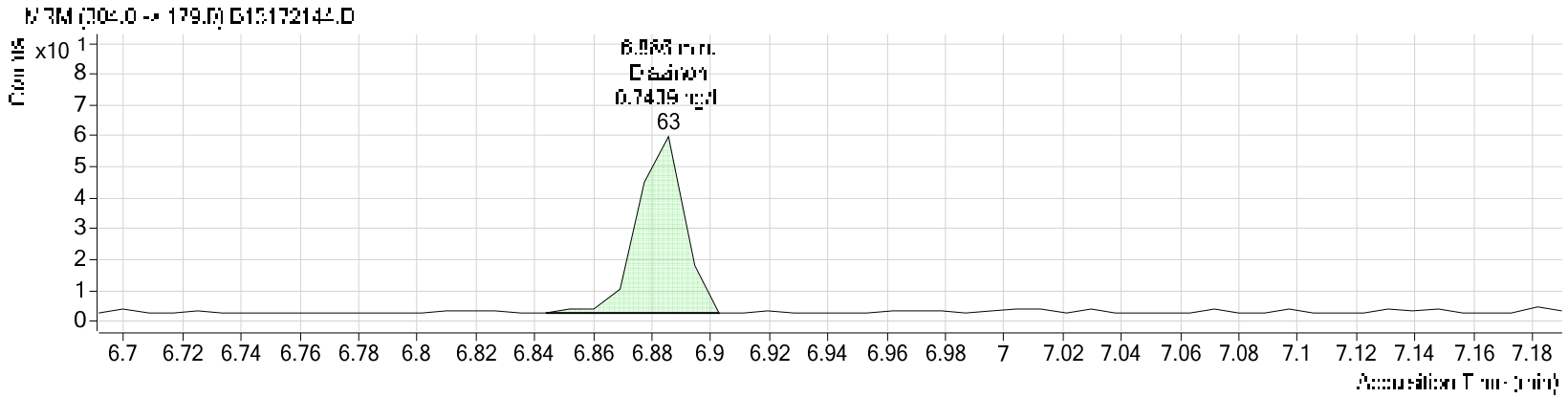
Real Sample – Cypermethrin at 2.5ng/L in Crude Sewage

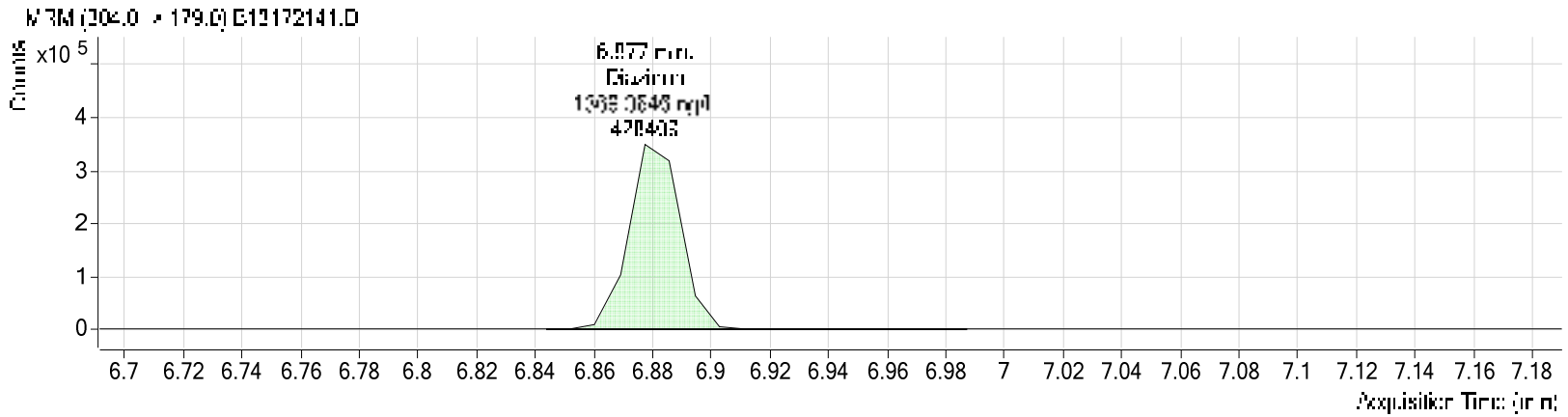


Real Sample – PBDE 47 at 1ng/L in Crude Sewage



Real Samples – Diazinon at 0.7ng/L in landfill leachate and 1300ng/L in dyeing works effluent





Non-Polars in Wastewater - Summary

- GC-QQQ successfully applied to the ultra-trace level analysis of PAHs, PBDEs and some pesticides in a variety of challenging sample matrices.

- 7000 GC-QQQ ideally suited to the task
  - High sensitivity
  - Good selectivity
  - Large dynamic range
  - Robust
  - Easy data processing via Masshunter software

Analysis of NDMA by GC-MSMS

- NDMA – N-nitrosodimethylamine
- Probable carcinogen
- Detected in potable water at low ppt levels – associated with chloramination and considered a disinfection by-product (DBP)
- Analytically difficult
  - Small molecule (MW=74) – selectivity an issue
  - Highly polar (log K_{ow} = -0.57) – difficult to extract
  - Low LODs required – 1ng/L or below
- Increasing interest in the analysis from water utilities
- Objective to upgrade GC-MS method to GC-MSMS avoiding the use of CI if possible.

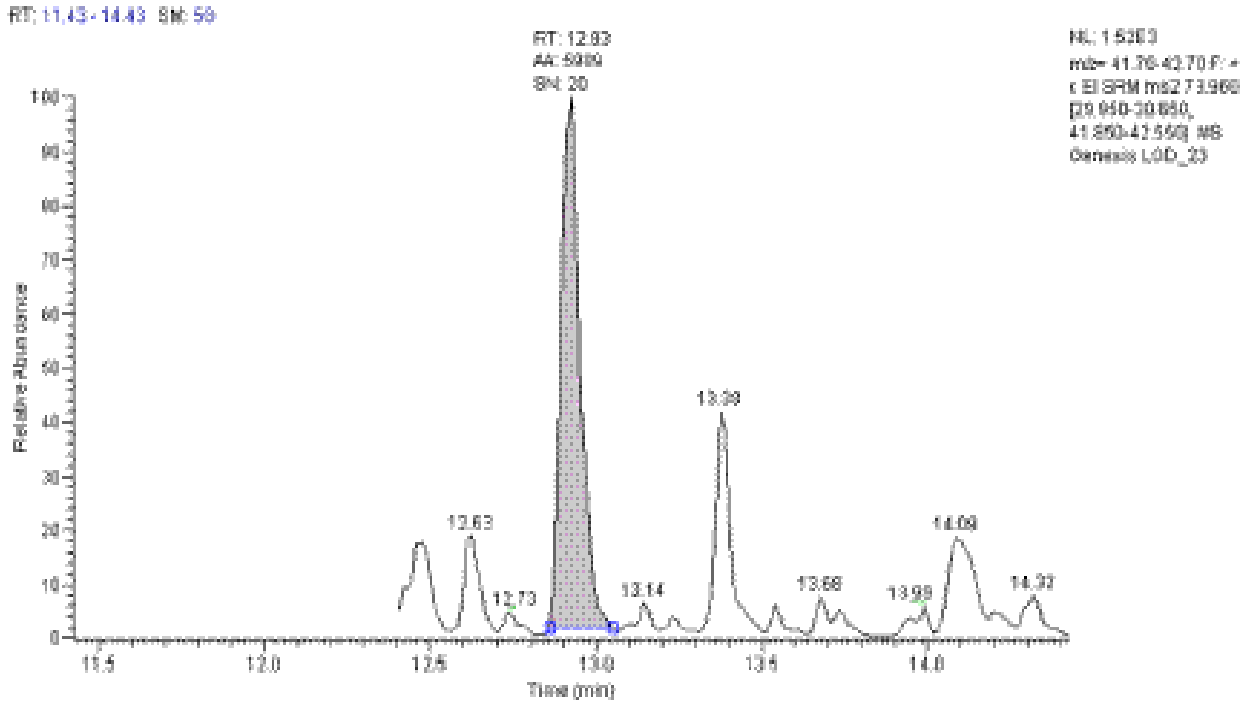
Analysis of NDMA by GC-MSMS

Procedure

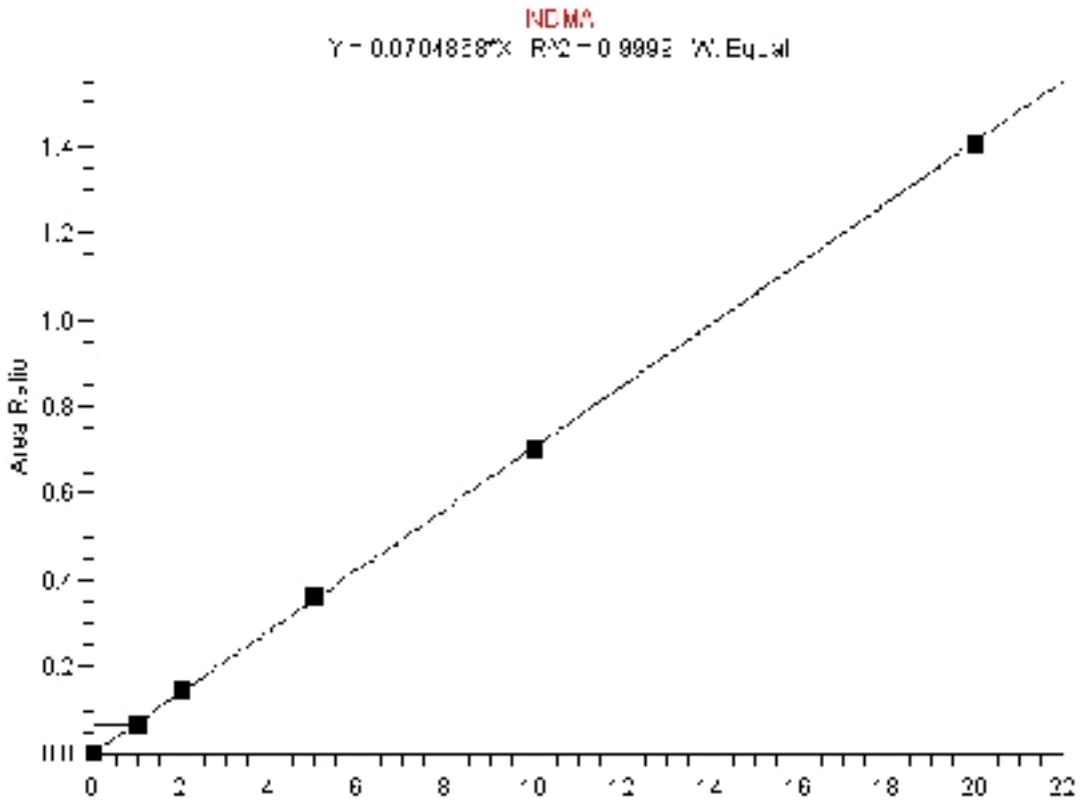
- Extract 1L by SPE (Coconut charcoal cartridge)
- Elute with DCM
- Evaporate to 1ml
- Analyse by GC-MSMS in EI mode
  - 5ul Cold Splitless injection
  - 60m DB624 column
  - d6-NDMA used as IS
  - 2 transitions monitored
    - 74>42 - Quant
    - 74>30 - Qual

NDMA in Potable Water

Chromatogram of 1ng/l Tap water spike



NDMA Calibration (1 – 20ng/L)



NDMA in Potable Water

Method Validation Data

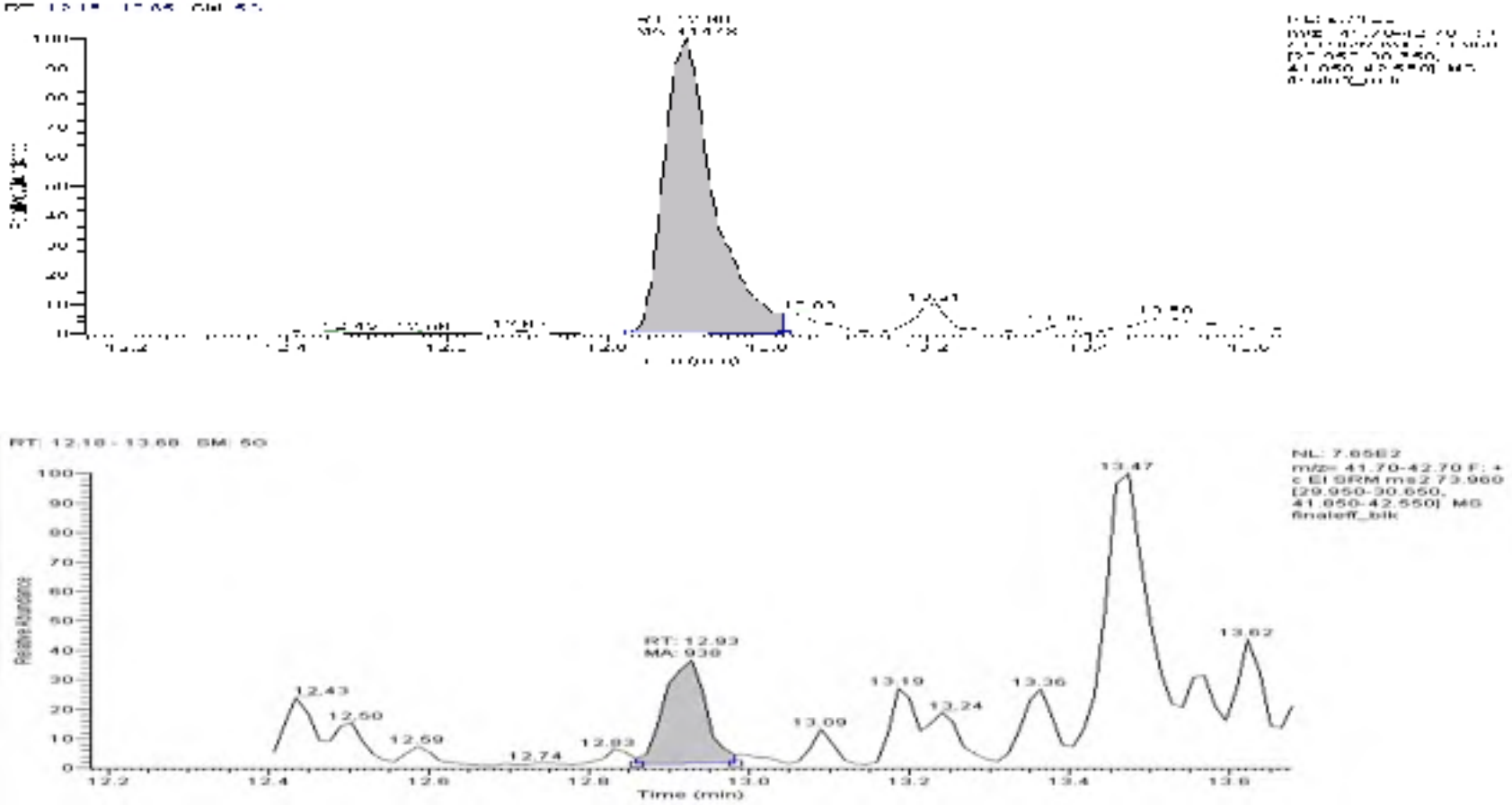
Recovery was determined by spiking a tap water at high, medium and low levels over a period of 11 days. Spike levels were at 16, 4 and 1ng/l of NDMA and analysed in duplicate.

Determinand	LOD (ng/l)	Medium Tap Water				Standard			
		Low Spike		High Spike		Low Std		High Std	
		%RSD	%Rec.	%RSD	%Rec.	%RSD	%Rec.	%RSD	%Rec.
NDMA	0.4288	5.16	101.25	7.86	110.01	11.78	98.42	4.65	101.77

NDMA in Sewage Effluent

Top – Sewage effluent spiked at 10ng/L

Bottom - Unspiked sewage effluent (calculated at 0.2ng/L)



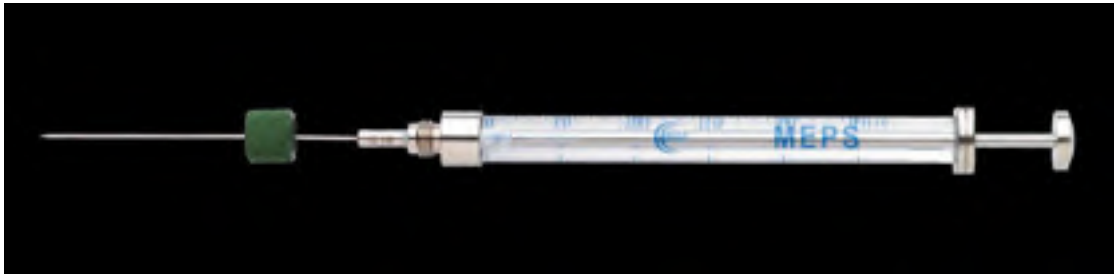
Analysis of NDMA by GC-MSMS

Summary

- Method for the low level analysis of NDMA in potable water by GC-MSMS validated.
- Good precision and bias statistics
- MRL of <0.5ng/L
- 60m GC column used to increase selectivity chromatographically.
- Use of CI reagent gases avoided.
- Method has the potential to be applied to more complex matrices

Automated Micro Extraction on GC-QQQ

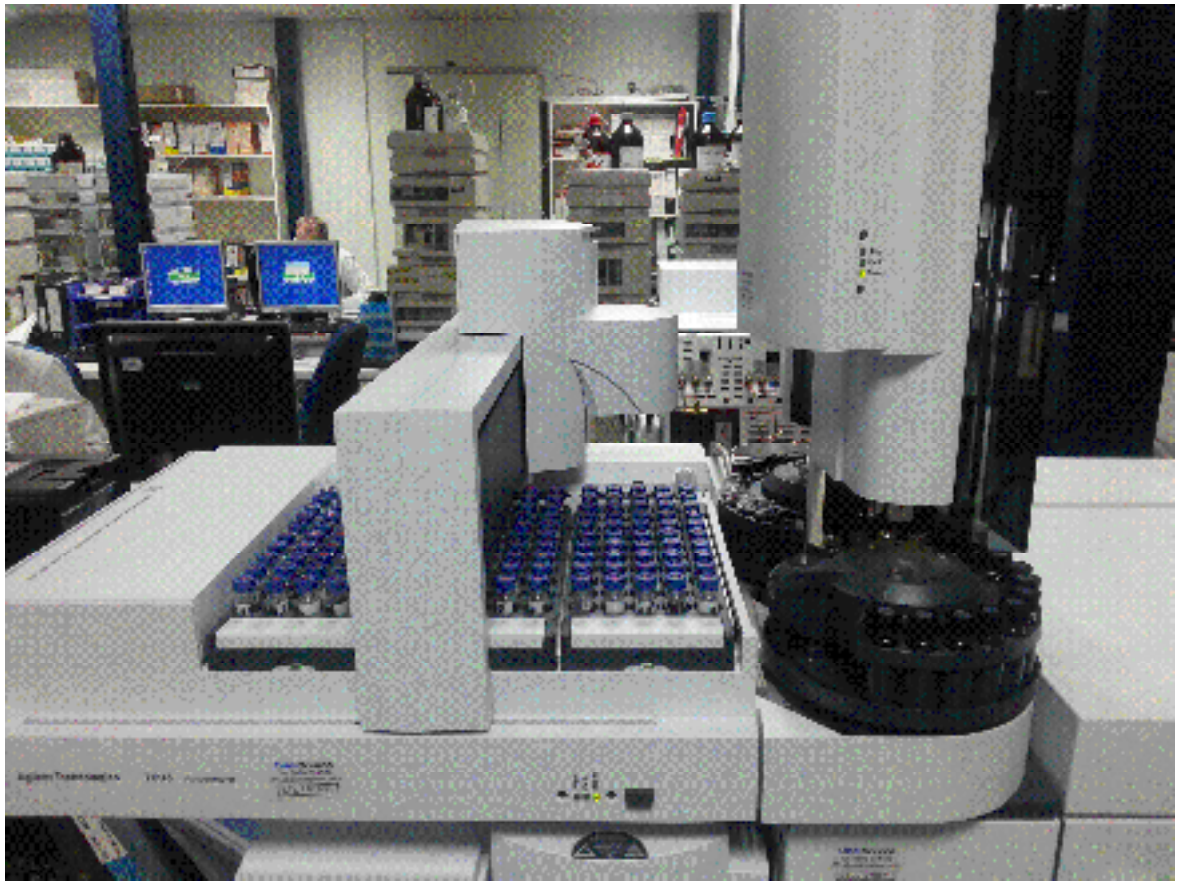
- MEPS – Micro Extraction in Packed Syringe
  - Autosampler syringe with a few mg of SPE sorbent in barrel
  - Entire miniaturised SPE process can be automated on the Agilent 7693 autosampler or Gerstel MPS
  - SPE followed by large volume injection into MMI operated in solvent vent mode
  - Suitable for a screening method??



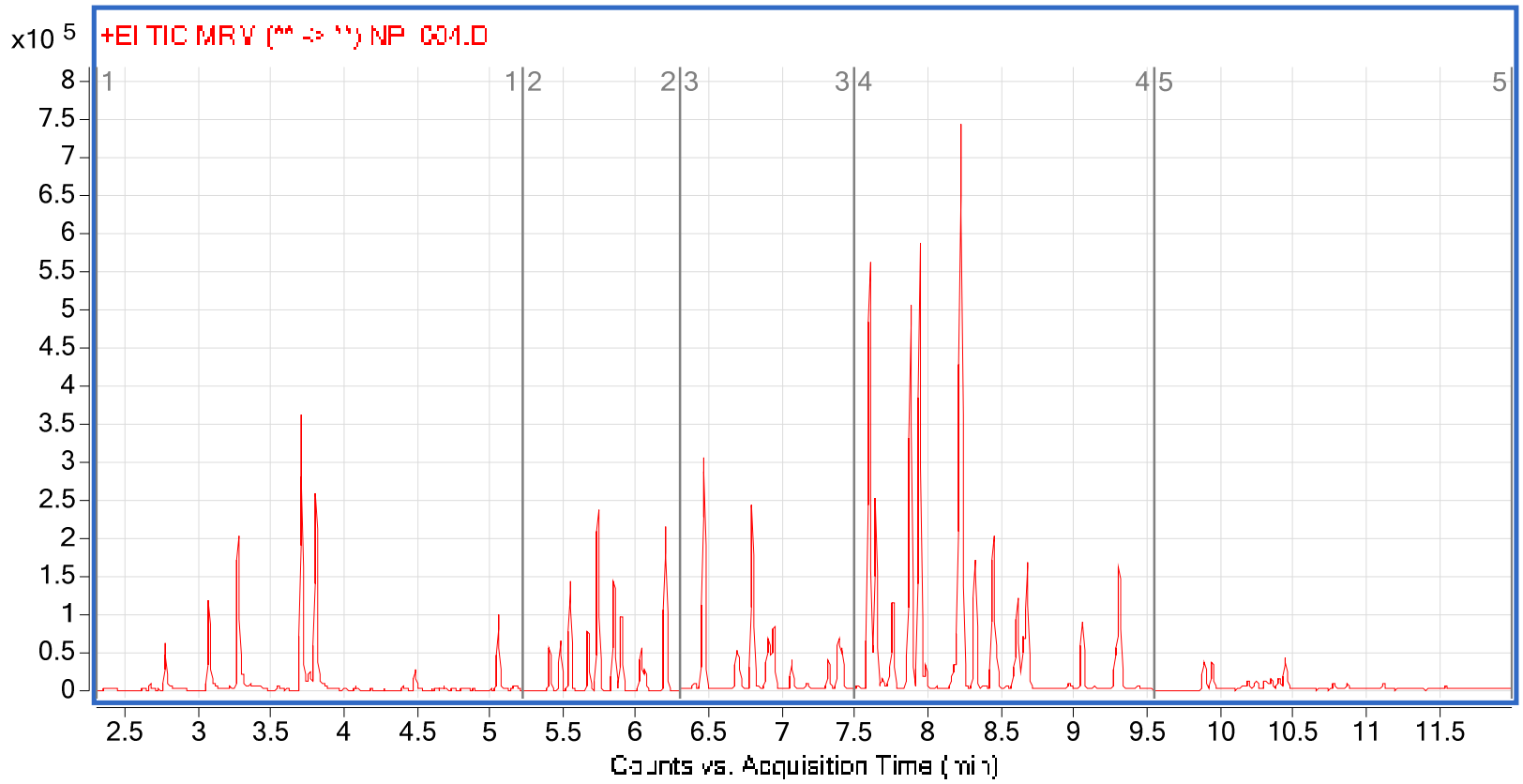
MEPS - Process

- System set-up
  - 100ul MEPS syringe in back tower, 50ul syringe in front tower for 25ul injection onto GC-QQQ.
- SPE
  - MEPS syringe conditioned with Hexane:Et. Ac (1:1)
  - Sample load – 1ml sample in aspirating steps of 100ul at 10ul/sec
  - Sample dry – 5x pumps of air through syringe
  - Elute – 2 x 50ul of Hexane:Et. Ac (1:1) into empty vial
  - Inject 25ul into MMI
  - Sample prep can be overlapped with the analysis of previous sample.

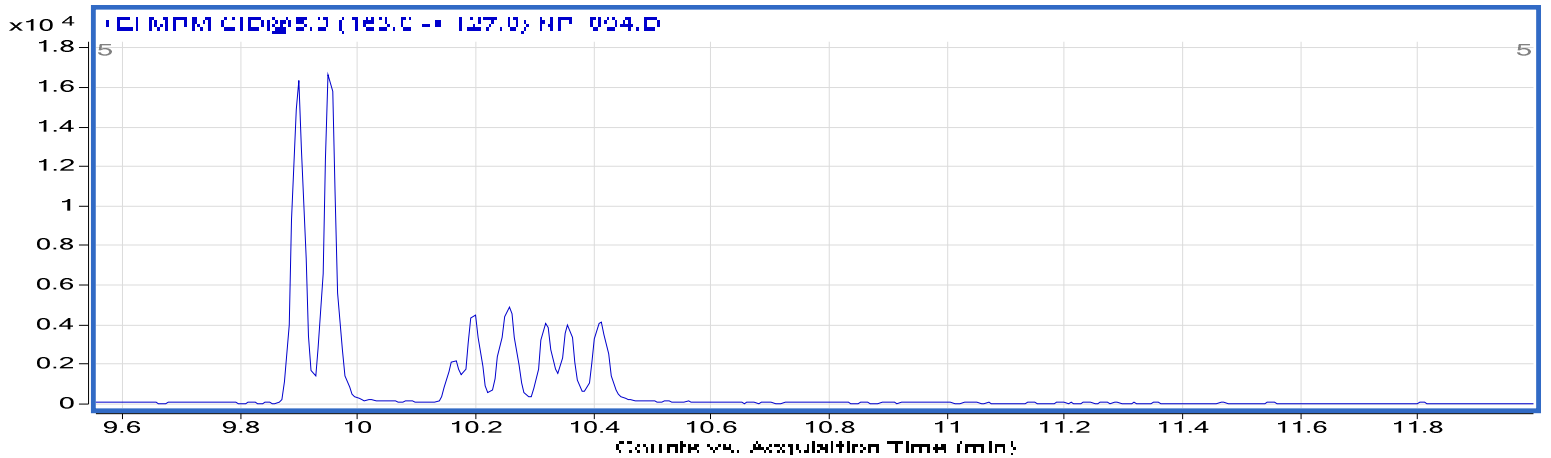
7693 Autosampler

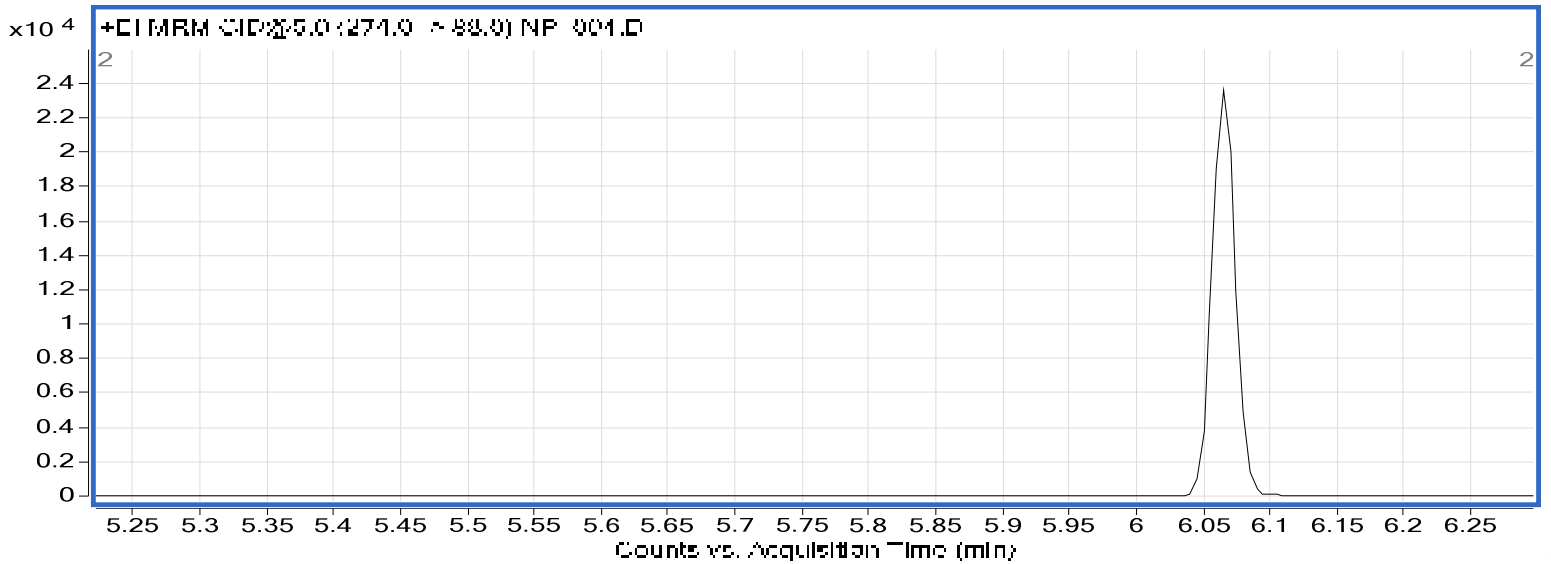


MEPS Chromatogram – 120ng/L

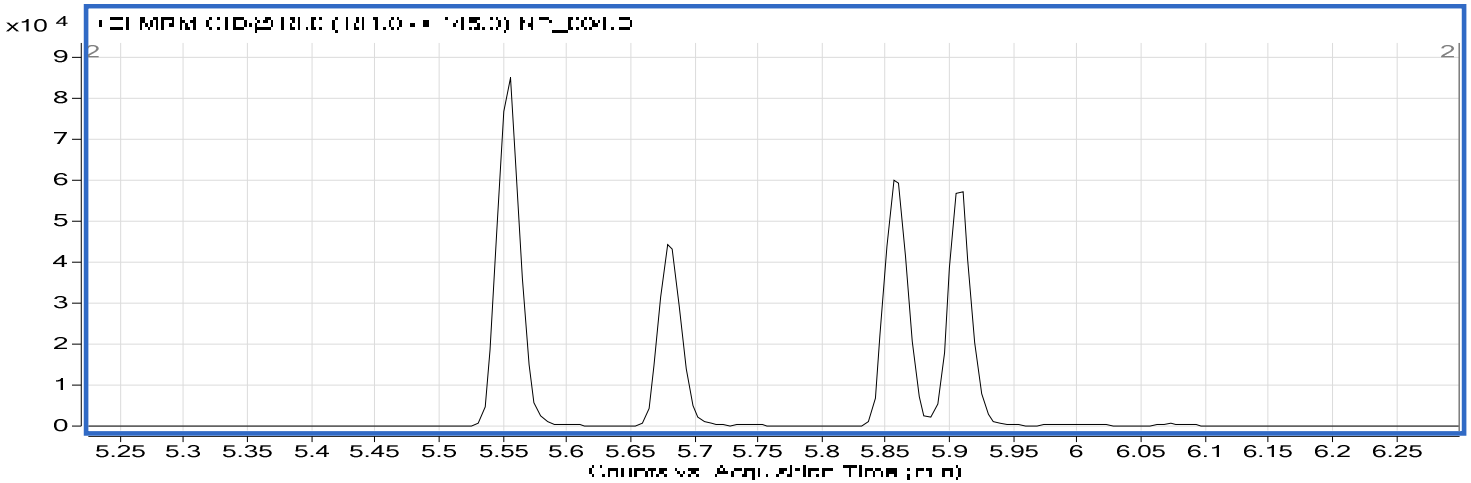


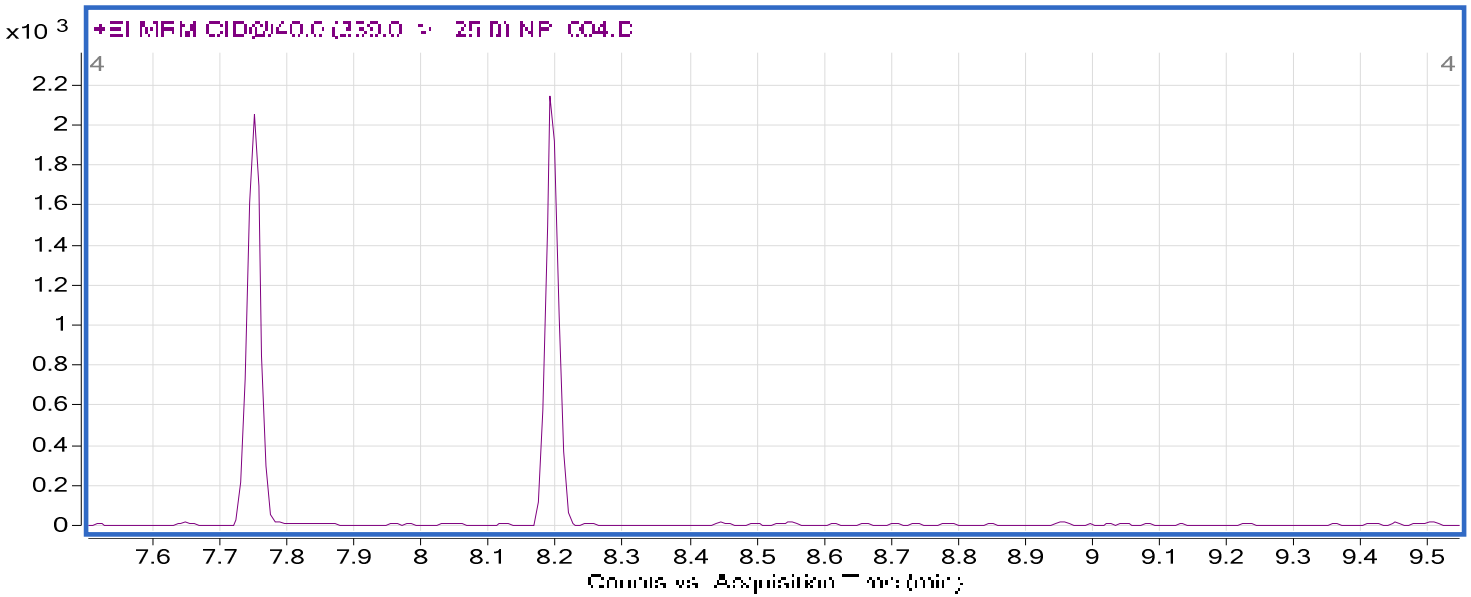
MEPS Pyrethroids/Disulphoton – 120ng/L





MEPS HCHs/Endosulphans – 120ng/L





Summary

- GC-MSMS successfully utilised for the trace level analysis of non-polar organic compounds in a wide variety of matrices across the business.

- Methods being transferred from MSDs to GC-QQQs

- Advantages
  - Reduced analytical run times
  - Greater sensitivity and selectivity
  - Ability to maintain low LODs even in dirty matrices
  - Easier reprocessing

- High sensitivity and selectivity combined with large volume injection and modern autosamplers gives rise to the potential for fully automated methods.

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Thank You!

Any Questions?