


Exploring the advantages automated sample preparation and High Sensitivity GC/MS for SVOC & Pesticide analysis in environmental waters

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5TH SBSE INTERNATIONAL MEETING

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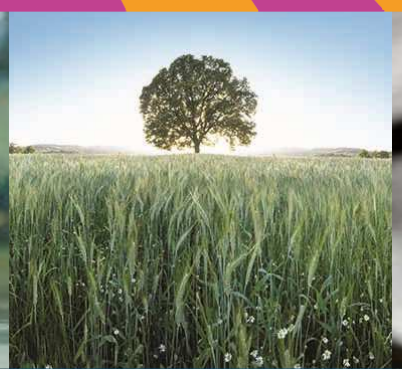
SBSE Technical Meeting


Global locations

50+ Countries

300+ Locations

40+ Years of strong business performance

13,000+ Staff worldwide

20+ million Processed samples per year

$1.2+ billion Global revenues

ALS Environmental - Europe

- Historically based in Eastern Europe & Nordic Region
- Central hub in Prague, Czechia
- Purchased Severn Trent Laboratories in 2013
- Purchased ALcontrol UK businesses in 2016
- UK laboratory sites:
  - Coventry – Wastewater
  - Wakefield – Potable water
  - Hawarden – Contaminated Land
  - Otterbourne – Potable Microbiology

ALS – Background

- ALS Environmental
  - Busy, high throughput commercial environment
  - Efficient, robust methods required

- 2015 – Set of low level methods developed to meet requirements of Chemical Investigation Program (CIP) – part of UK response to the Water Framework Directive (WFD)
  - Ultra-trace level work – low pg/L levels for some compounds
  - Investment in modern instrumentation
  - First automated sample preparation method introduced

- 2016/2017 – CIP methods extended to fully cover WFD suite and matrices
  - Accredited to 17025
  - Now routine

- 2018/2019 – Focus is to apply knowledge gained from CIP/WFD methods to improve efficiency of routine methods
  - A major part of this is a drive to automate sample preparation methods.

Overview – Automated Sample preparation for Organics

- Introduction
  - What developments have made automation possible?
  - Why automate – what are the benefits?
- Case Studies
  - Alkylphenols & Ethoxylates
    - » For CIP/WFD. Hexane extraction and analysis by GC-MSMS in NCI.
    - » Now in routine use for 3 years. Proven robustness.
  - SVOCs/Pesticides
    - » Using Dispersive Liquid/Liquid Microextraction (DLLME)
    - » Currently under development, initial results are very promising – wide range of analytes covered and is very fast!
  - Ultra low level Heptachlors by SPE followed by SBSE and GC-TOF-NCI
    - » SPE of 1 litre sample, extract dilution then SBSE with detection by GC-TOF-NCI
    - » Proof of concept only. Indications are LODs of <1pg/L may be achievable.
- Conclusions

Instrumental Advances

- Mass Spectrometry
  - Big improvements in recent years – sensitivity & selectivity
  - GC-MSMS now routine
  - Agilent HES for 5977B MSD and 7010 GC-MSMS
  - GC-TOF
  - Lower concentration factors required – enables miniaturisation which in turn facilitates automation
  - Nearly all routine methods (MRLs low ng/L) can now be done with sample volumes of 40mls or less.
- Instrument top automation
  - Gerstel MPS – "Lab on a rail" – LLE, SPE, Mixers, Shakers centrifuges etc
- Major improvements in methodologies possible by bringing the above together.

Benefits of Miniaturisation / Automation

- Lower Sample volumes (40mls or less)
  - Reduced sampling, transportation & storage costs
- Analytical cost savings
  - Labour
  - Solvents & other consumables
- Data Quality
  - Improved reproducibility
  - Blank control
- Health & Safety
  - Reduced exposure to solvents & other chemicals

Alkylphenols & Ethoxylates

Automated Extraction and Analysis

GC-MSMS – Alkylphenols & Ethoxylates – for CIP/WFD

- Method set up for CIP in 2015
- 4-Octylphenol, 4-Nonylphenol & 4-Nonylphenol EO1 – EO3
- Analysis by GC-MSMS in NCI mode.
- Simultaneous extraction and derivatisation using Hexane/Pentafluorobenzoyl Chloride.
- Sensitivity of NCI allows process to be miniaturised.
- Fully automated method developed with help from Anatune.
  - Gerstel MPS system
  - Addition of Internal standards
  - LLE / Derivatisation – mVorx
  - Emulsion break
  - Injection onto GC-MSMS
- Method then extended for WFD and re-validated in 2017
  - Centrifuge required to break emulsion for saline samples

WFD Priority Substances – Alkylphenols & APEOs

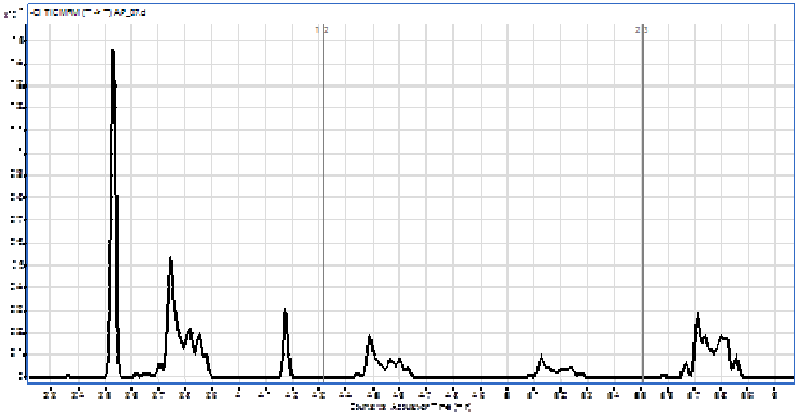
Sample taken in 250ml Glass bottle

- Add NaOH and sub-sample 5.5mls into 10ml vial
- Automated LLE/PFBCl derivatisation performed on Gerstel MPS sampler.
- Sample vials are thermally cleaned to reduce blanks
- Centrifugation step required to break emulsion for saline samples

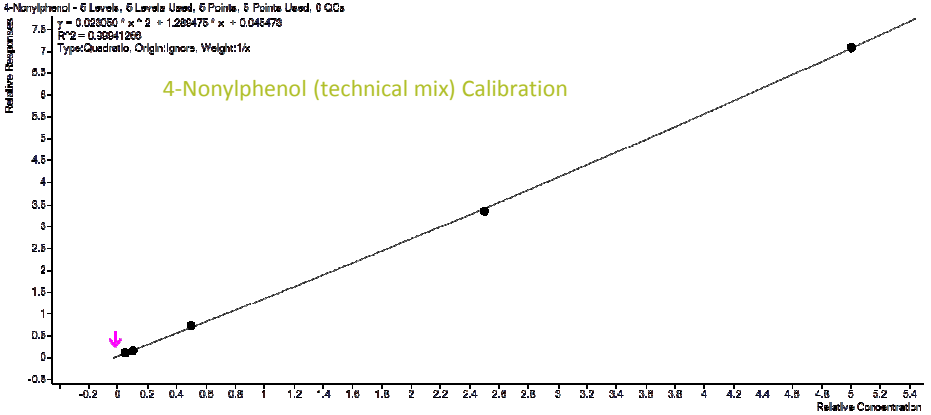
GC-MSMS - NCI

4-Octylphenol
4-Nonylphenol
4-Nonylphenol-1EO
4-Nonylphenol-2EO
4-Nonylphenol-3EO

Alkylphenols & Ethoxylates – GC–MSMS Agilent 7000C (NCI)

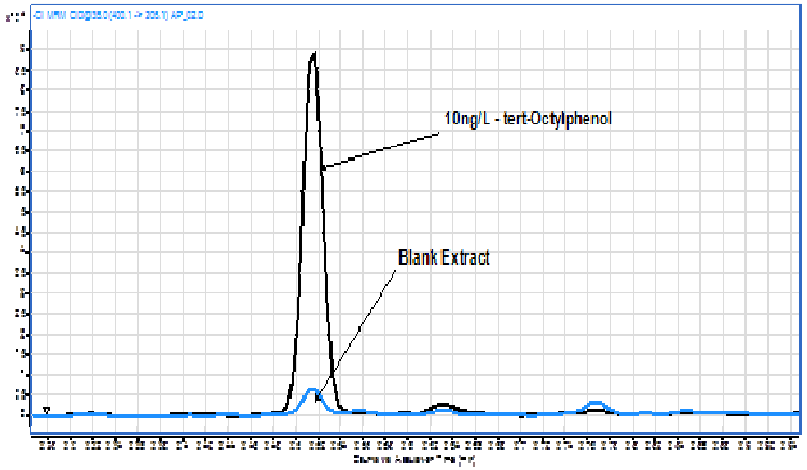


4-tert-OP Sensitivity in Sewage Effluent



4-Nonylphenol (technical mix) Calibration

Performance Statistics



ANALYTE	4-Octylphenol	4-Nonylphenol	4-Nonylphenol - 1EO	4-Nonylphenol - 2EO	4-Nonylphenol - 3EO
UNITS	ug/L	ug/L	ug/L	ug/L	ug/L
Method LOD	0.0043	0.021	0.026	0.029	0.031
Method MRL	0.010	0.040	0.040	0.040	0.040
EFFLUENT					
Spike Recovery	105.6%	103.4%	98.5%	97.5%	101.5%
Spike RSD	6.97%	4.36%	7.38%	8.00%	7.57%
Uncertainty	19.6%	12.1%	16.3%	18.5%	16.7%
RIVERINE					
Spike Recovery	105.5%	102.3%	95.5%	95.0%	102.7%
Spike RSD	6.66%	3.57%	10.36%	8.68%	6.46%
Uncertainty	18.8%	9.4%	25.3%	22.4%	15.7%

Alkylphenols – Conclusions

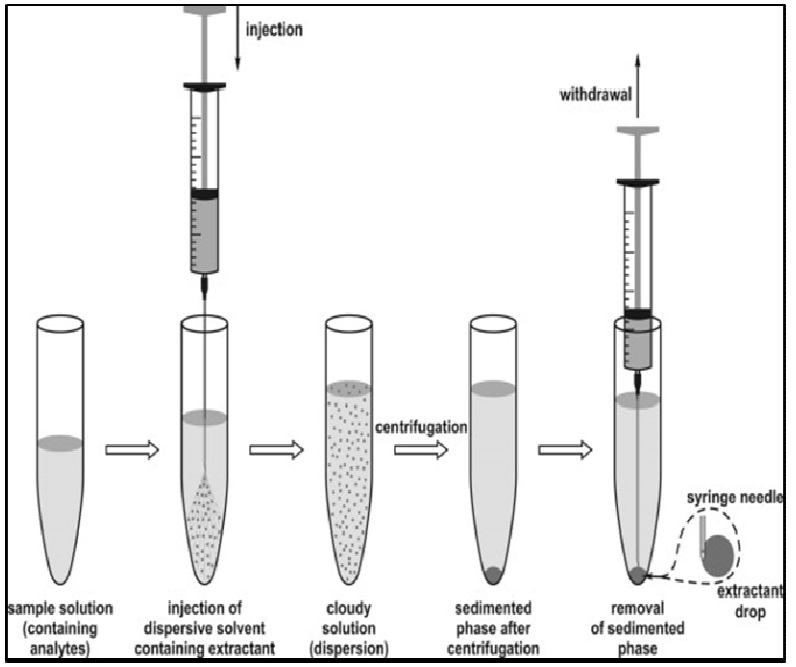
- Method set up in 2015 and the automation has proved robust and reliable.
- Due to high sensitivity of NCI GC-MSMS only a small concentration factor required to meet MRLs in the low-mid ng/L range.
- Method extended in 2017 as part of laboratory project to cover all WFD core determinands and matrices.
- Due to severe emulsion formation for saline samples a centrifugation step was found to be necessary. This was both effective at clearing the emulsion and proved mechanically reliable.
- Current focus of the laboratory is on applying knowledge gained from development of the ultra trace CIP/WFD methods to improve efficiency of routine methods.
- Is it possible to take the work done for alkylphenols and extend it to:
    - Increase the concentration the factor
    - Increase the range of analytes covered
    - Improve the speed of analysis
- Is DLLME a viable option?

SVOCs and Pesticides

Possible method by Dispersive Liquid/Liquid Microextraction (DLLME)

DLLME – Introduction

- Aqueous sample mixed with a dispersive solvent and an extraction solvent
- Dispersive solvent miscible with sample and extraction solvent (Alcohol or MeCN)
- Extraction solvent usually denser than water (e.g DCM)
- After mixing sample is centrifuged to sediment the extraction solvent at the bottom of the vessel.
- Extract then removed with syringe for analysis.



- Significant concentration factor from small volume of sample.
- It is very fast (equilibrium reached in seconds)
- Wide range of amenable target analytes.
- Low usage of solvents and other consumables
- When extracts analysed using modern sensitive instruments low LODs are possible from small sample size.
- Automatable!!

Automated DLLME – Proof of concept

- What range of analytes can be extracted by a DCM based DLLME method?
  - Does the presence of the disperser solvent significantly affect the recovery of polar analytes?
- What concentration factors can be achieved?
- How reproducible is the method?
- Matrix effects?
- How robust is the automation?
- Throughput – samples/day?
- What MRLs are achievable when interfaced to modern instrumentation (with LVI?)
  - Agilent 5977MSD
  - Leco BT
  - Agilent 7200 QTOF

Automated DLLME Procedure

- Sample + 10%IPA in 40ml EPA vial
- Transfer 6 or 9ml to High recovery vial
- Add 300 or 400ul DCM:Pentane 80:20
- On MPS, Vortex 15sec, centrifuge 90sec, transfer 100ul to GC vial. Add acid buffer. Repeat.
- Analysis by GC-TOF (or 5977 with HES)
  MRLs ~ 0.01 – 0.5ug/L

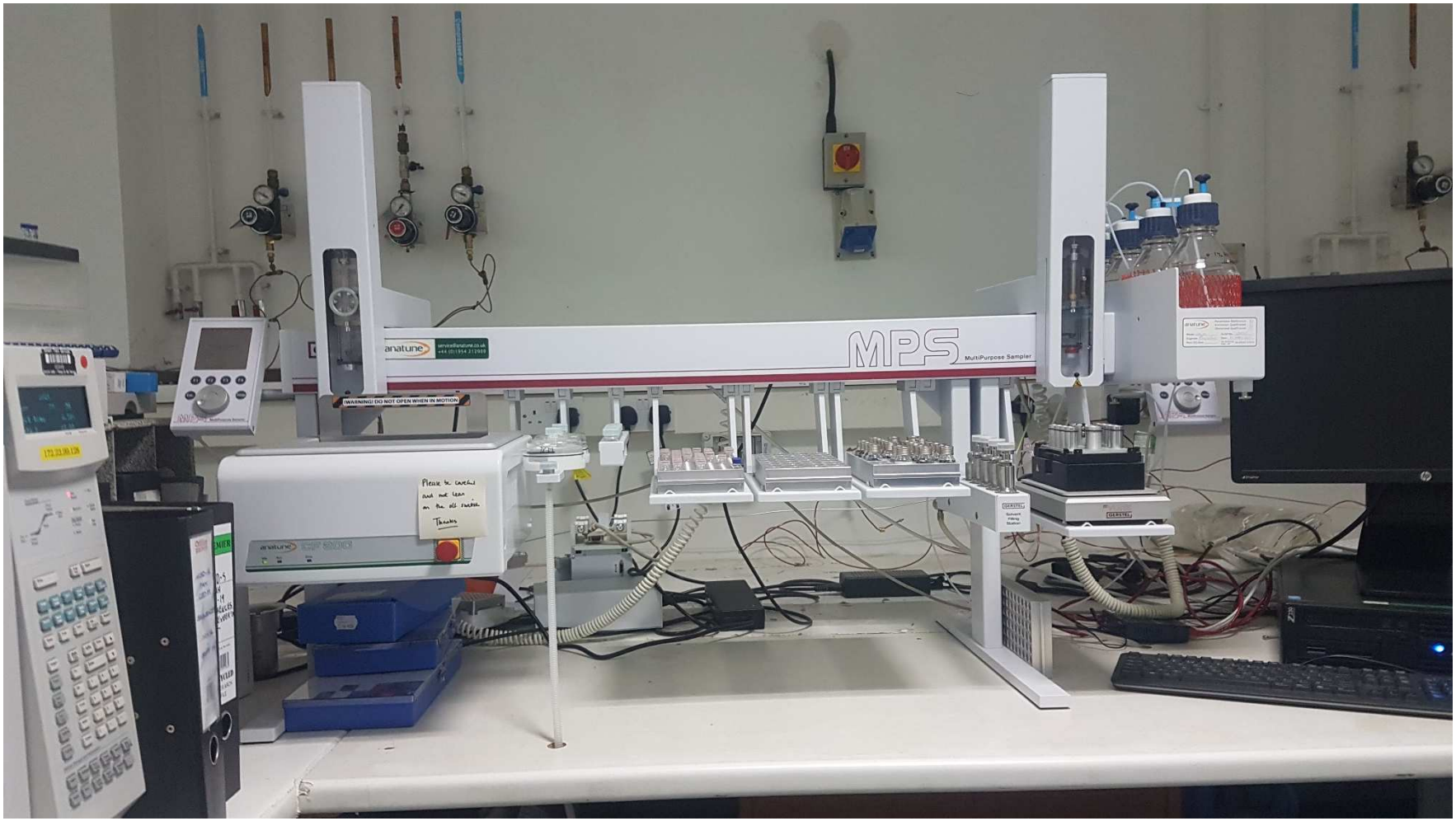
2.5 hours per batch (5mins /sample) – SVOC
1.25 hours per batch (2.5mins/sample) – others
100 Samples/day

Current SVOC Procedure

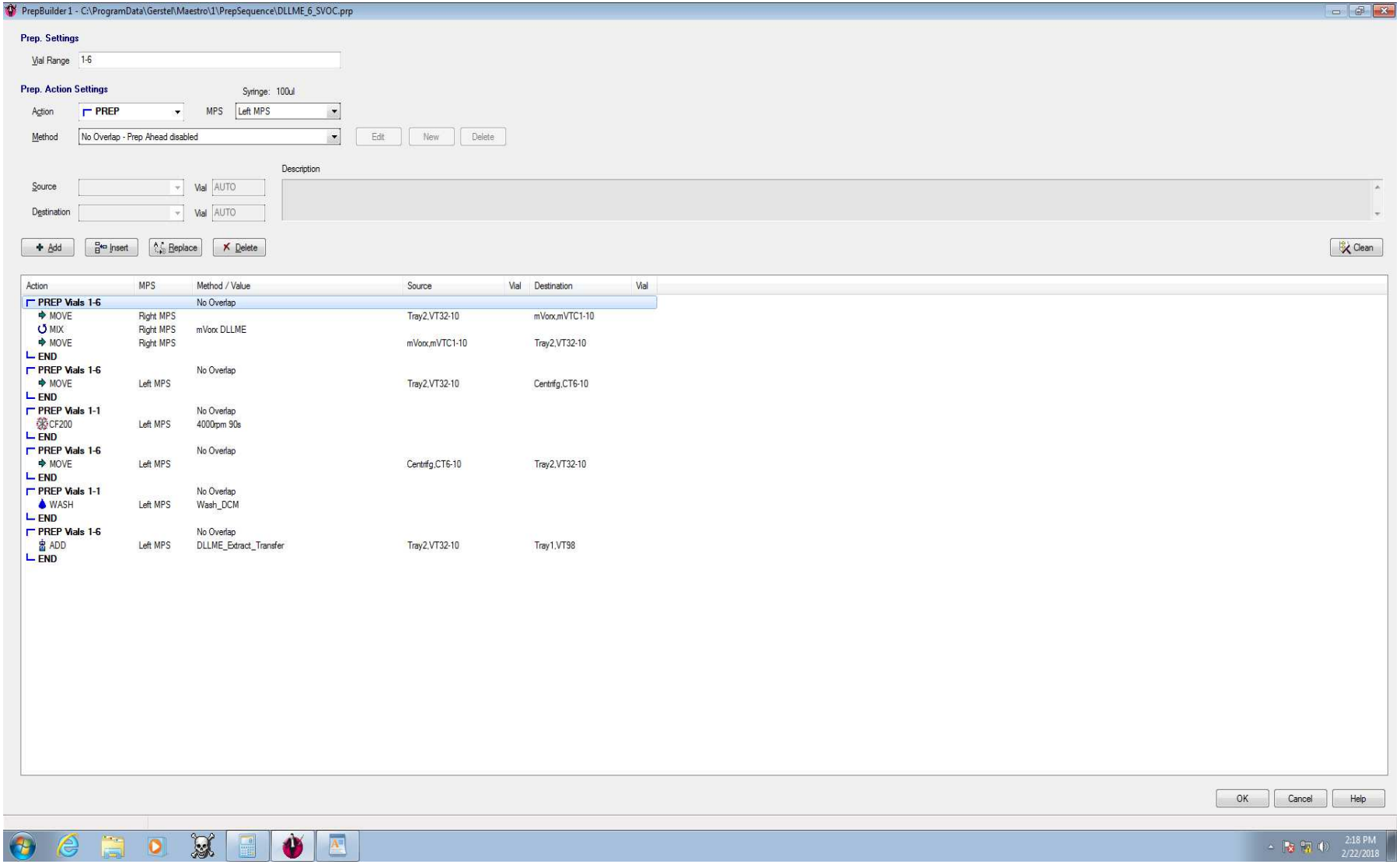
- 200mls sample in 250ml glass bottle
- Extraction 1 – LLE using 20 mls hexane
- Extraction 2 – SPE of 30mls aqueous sample
- Merge SPE extract with 3mls hexane extract and evaporate to 1ml in Turbovap. Transfer to GC vial
- Analysis by GC-MSD (5973) in full scan
  MRLs ~ 1ug/L

1 Extractor 2.5-3 hours / batch
Max 50 samples / day

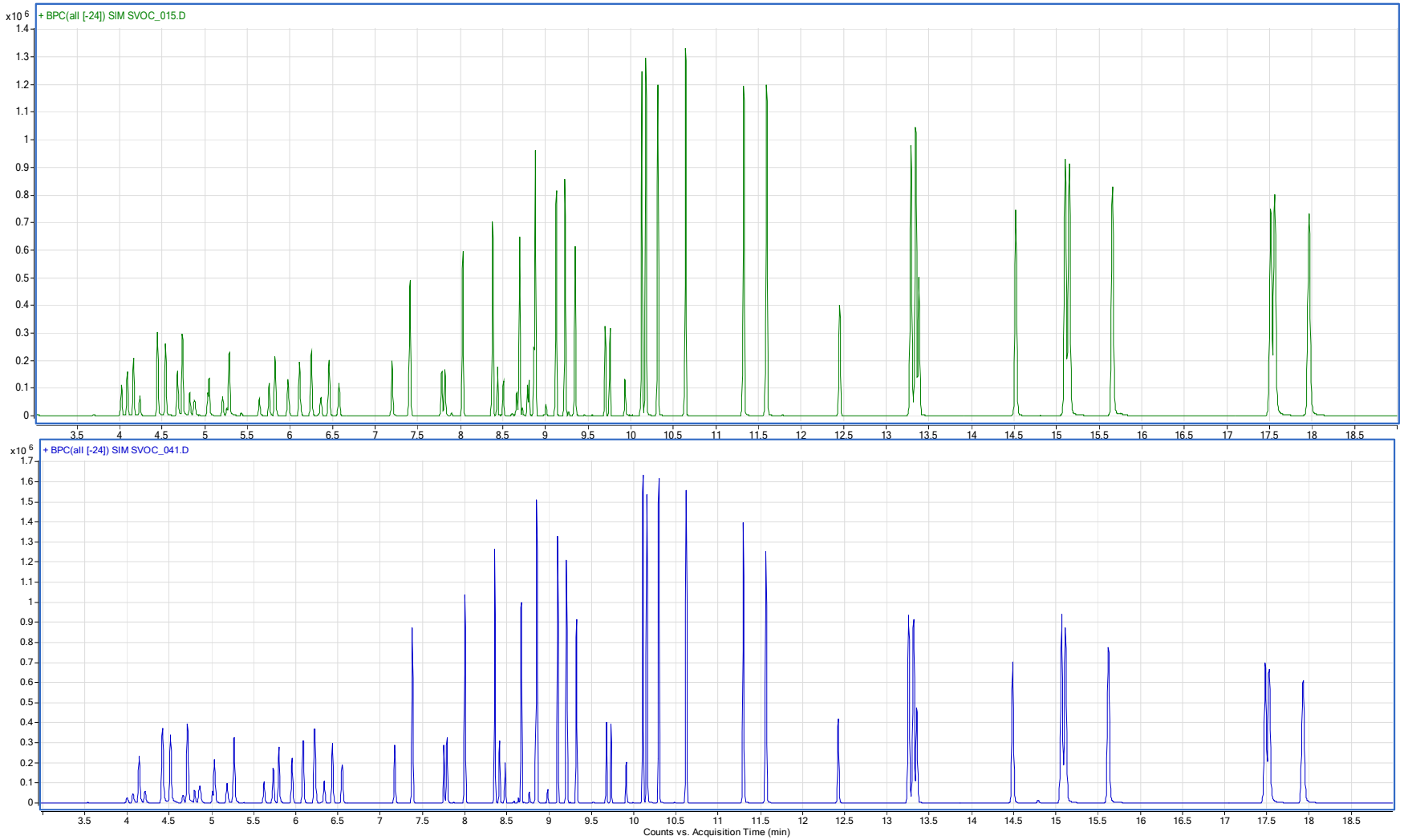
Gerstel MPS



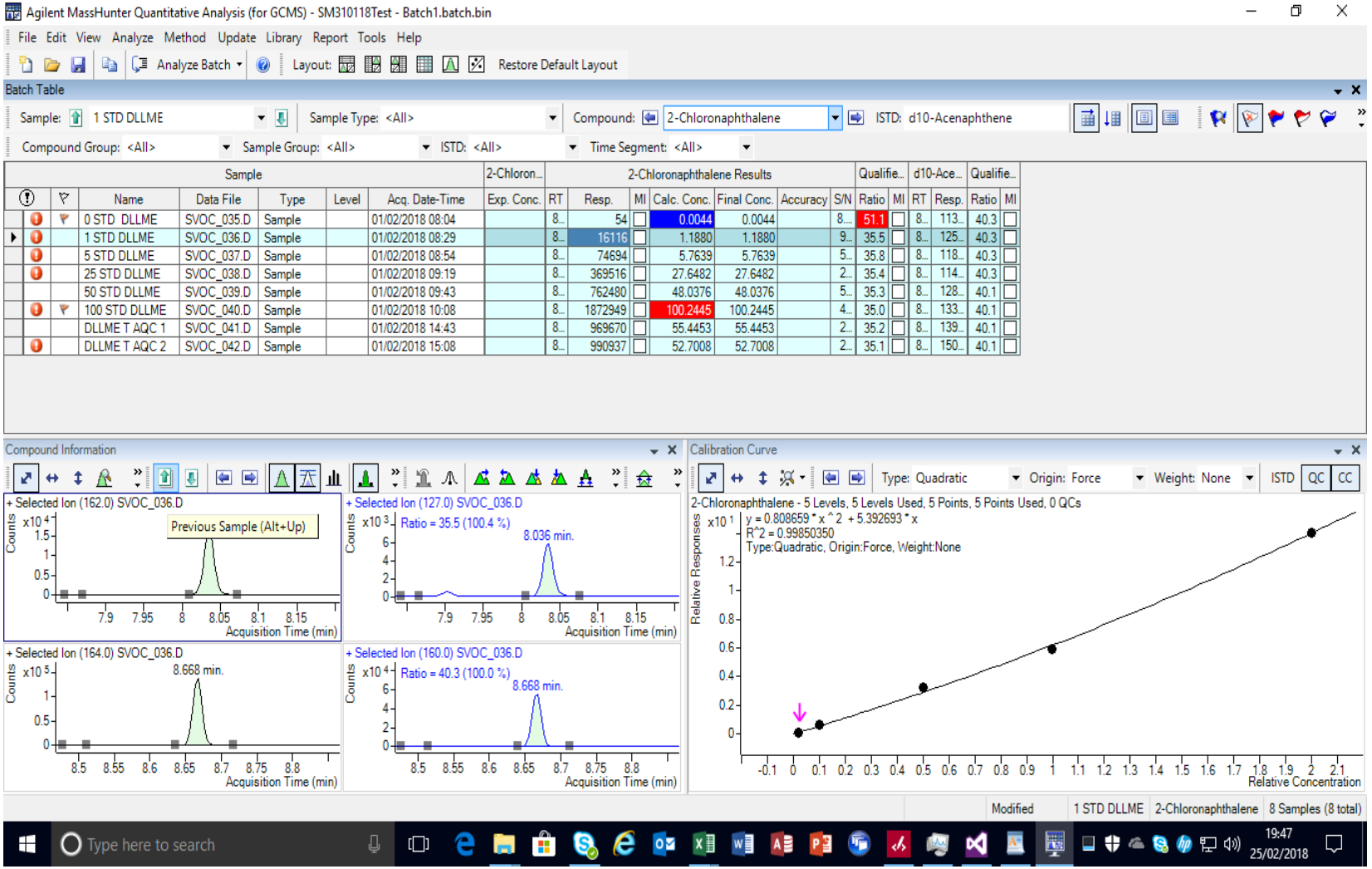
DLLME Extraction on Gerstel MPS Settings



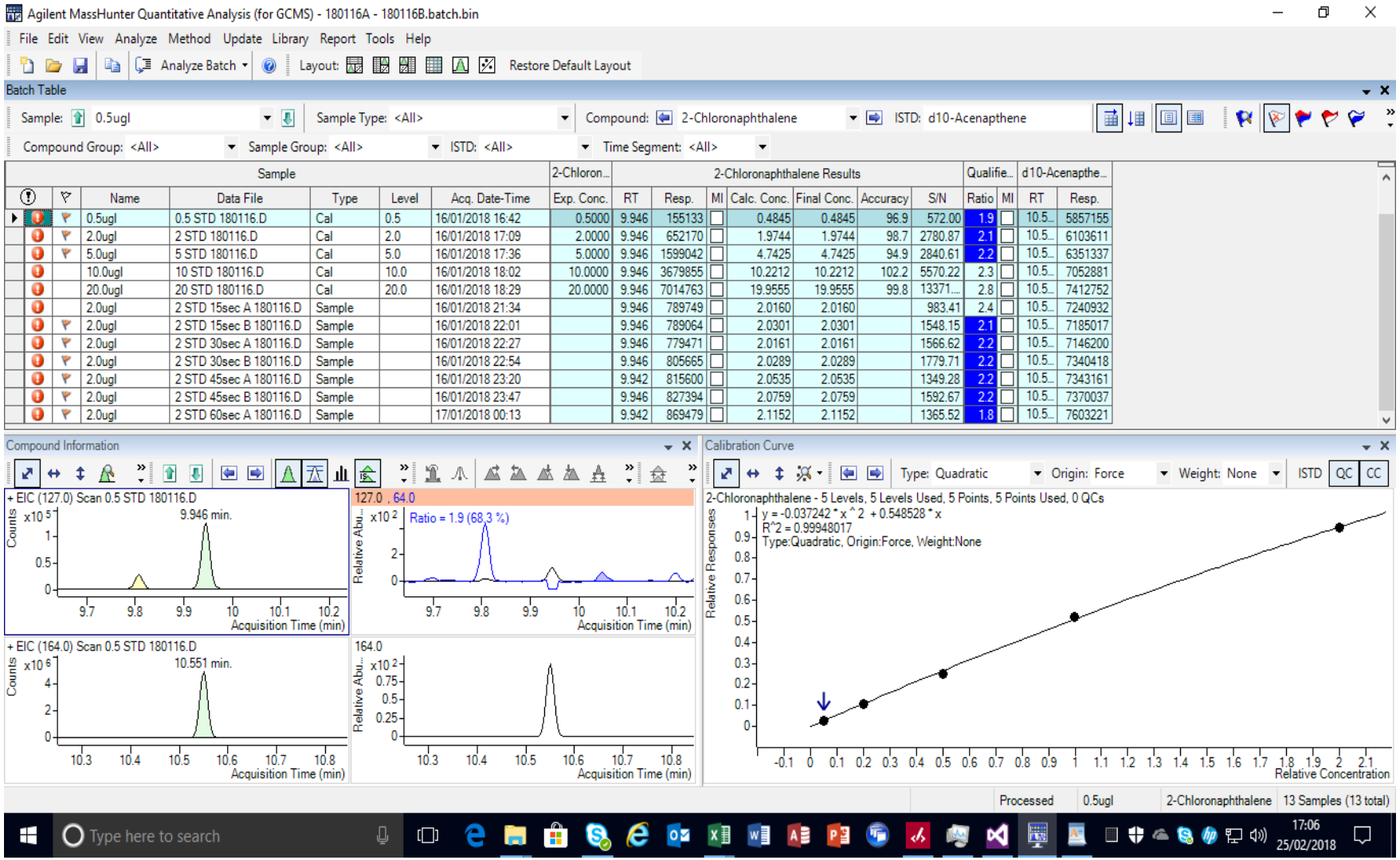
Comparison of SVOC AQC Spikes on 5975MSD
Top trace current method, bottom trace DLLME



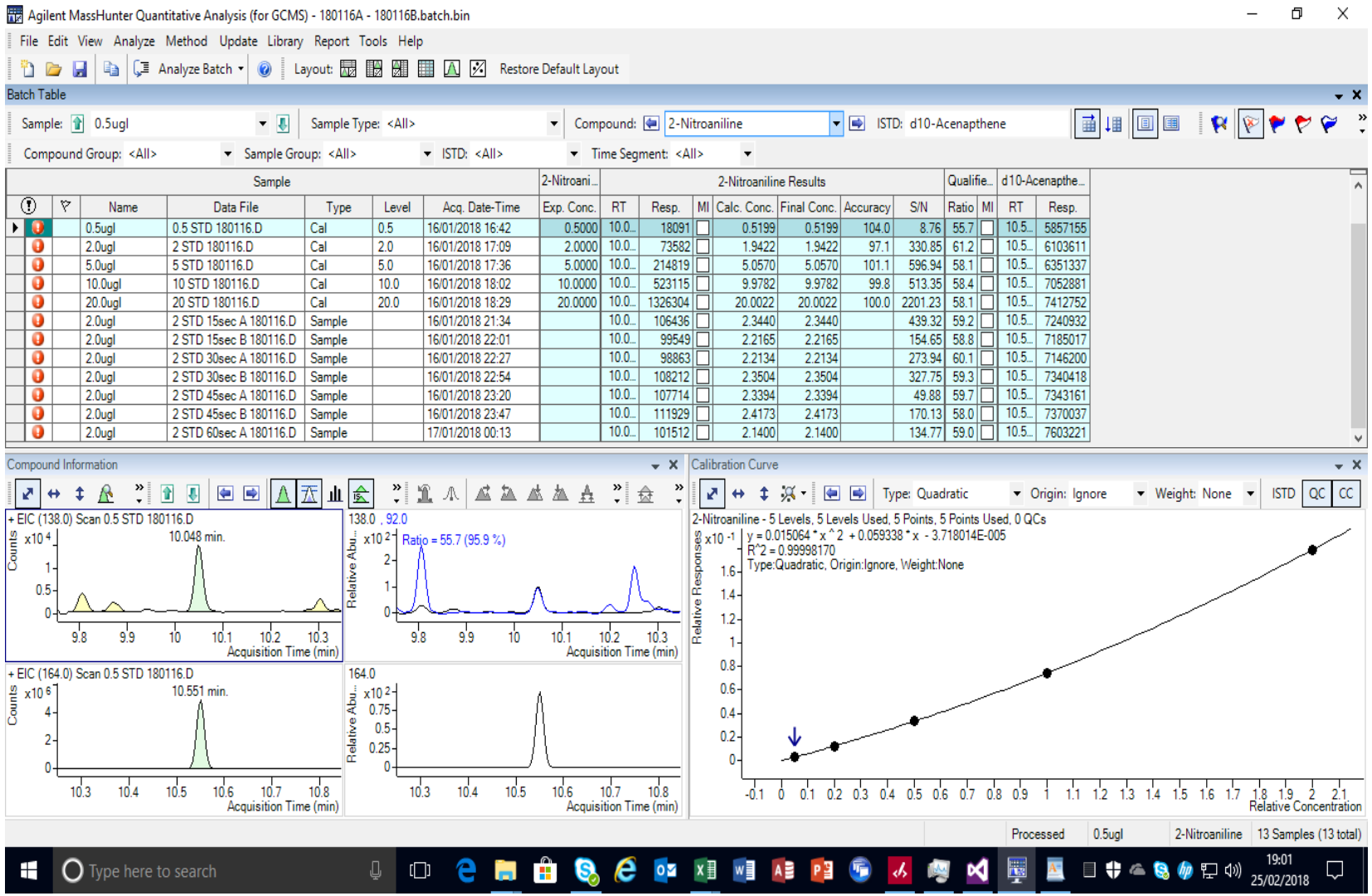
2-Chloronaphthalene on 5975MSD in sim\scan DLLME of 9ml sample & 2ul injection



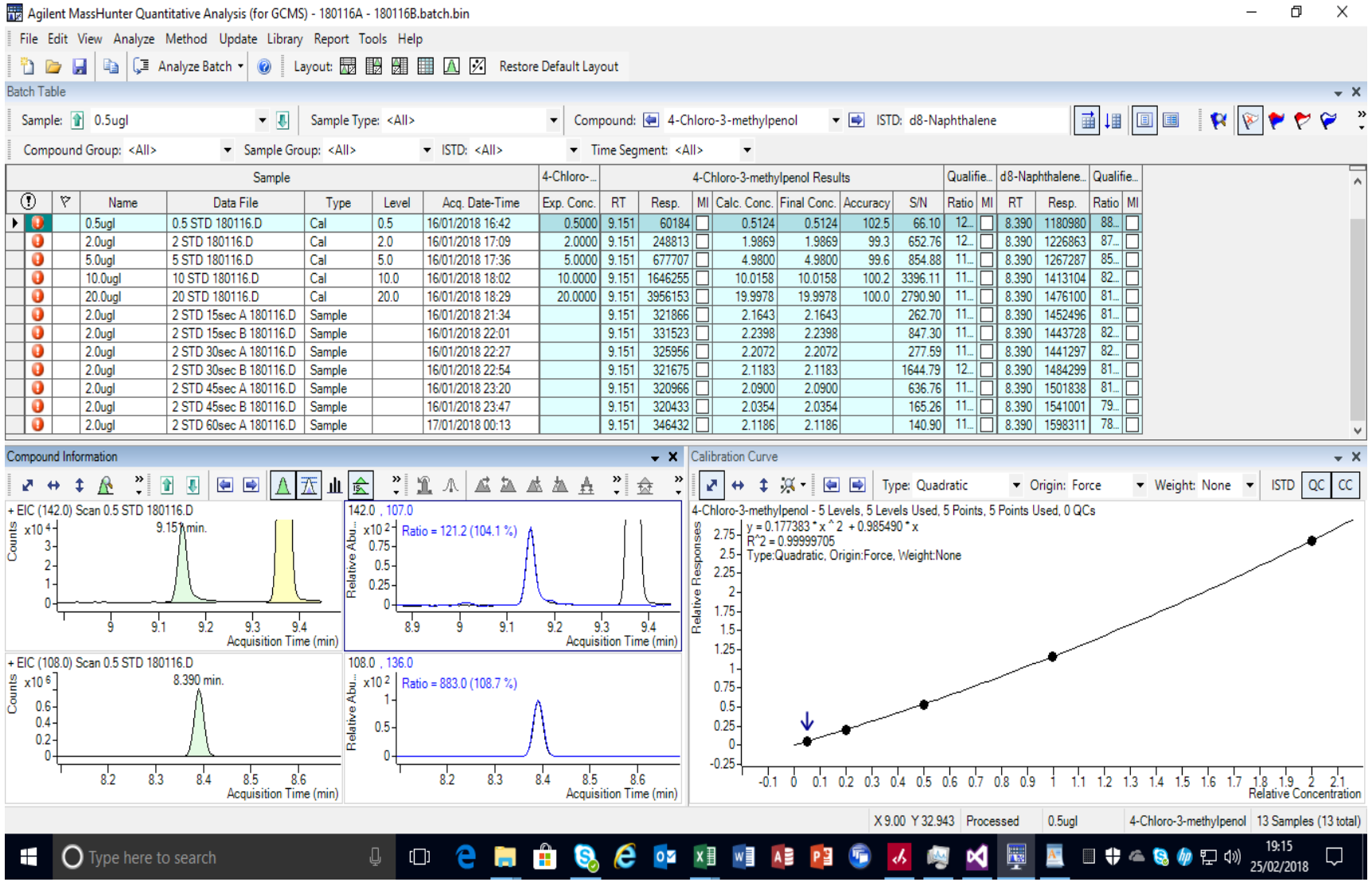
2-Chloronaphthalene on 5977B HES in full scan DLLME of 9ml sample & 1ul injection



2-Nitroaniline on 5977B HES in full scan
DLLME of 9ml sample & 1ul injection



4-Chloro-3-Methylphenol on 5977B HES in full scan DLLME of 9ml sample & 1ul injection



GC-TOF

- Tests undertaken on two systems
  - Leco – Pegasus BT (fast scanning)
  - Agilent 7200 QTOF (high resolution)
- Full scan data with high sensitivity. Capable of analysing very large numbers of compounds simultaneously.
- Low ng/L detection limits possible from just 9mls sample size – screen for Pesticides, PAHs, Phenols & SVOCs from the same GC-MS acquisition method

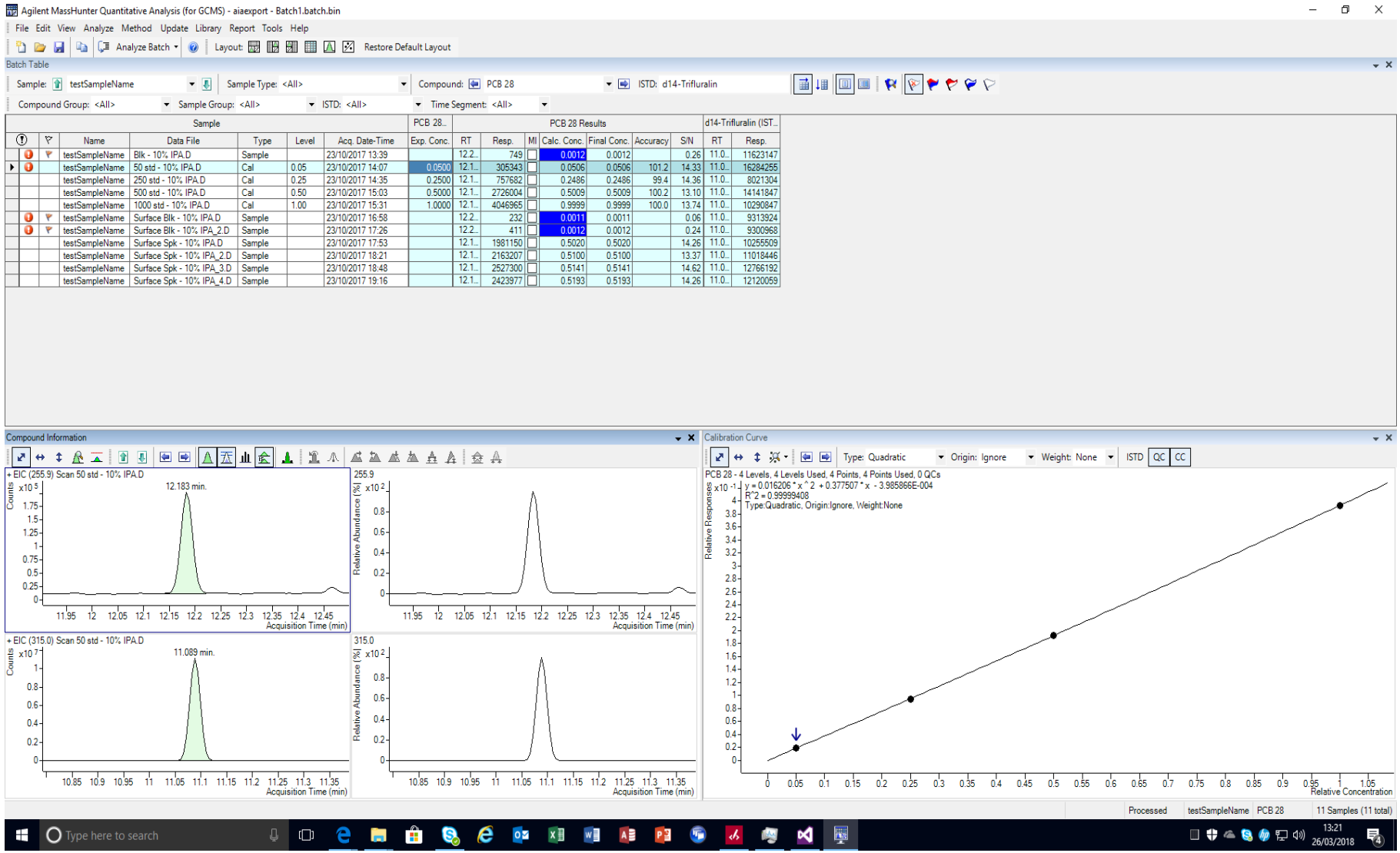
DLLME – GC–TOF Results (SVOC) (71 compounds)

					Surface Water Spike Results					
Compound	**Cal Range (ug/L)**	**R^2 (Quadratic Fit)**	**Est LOD - 2ul Inj (ug/L)**	**Est LOD - 10ul Inj (ug/L)**	**Spike 1**	**Spike 2**	**Spike 3**	**Spike 4**	**Recovery**	**RSD (n=4)**
Phenol	0.5 - 10.0	0.9998	0.50	0.500	9.86	9.80	9.99	10.04	99.2%	1.14%
Aniline	0.5 - 10.0	1.0000	0.20	0.040	10.01	10.04	9.96	9.98	99.9%	0.36%
Bis(2-Chloroethyl)ether	0.5 - 10.0	0.9999	0.05	0.010	10.20	10.57	10.49	10.30	103.9%	1.62%
2-Chlorophenol	0.5 - 10.0	0.9998	0.05	0.010	10.18	10.54	10.51	10.56	104.5%	1.71%
1,3-Dichlorobenzene	0.5 - 10.0	0.9999	0.05	0.010	9.96	9.92	9.93	9.99	99.5%	0.33%
1,4-Dichlorobenzene	0.5 - 10.0	0.9999	0.05	0.010	9.95	9.99	10.01	9.98	99.8%	0.23%
1,2-Dichlorobenzene	0.5 - 10.0	0.9999	0.05	0.010	9.99	10.04	10.04	10.01	100.2%	0.27%
o-Cresol	0.5 - 10.0	1.0000	0.05	0.010	10.09	10.21	10.56	10.53	103.5%	2.24%
Bis(2-chloro-1-methylethyl) ether	0.5 - 10.0	0.9998	0.20	0.040	10.19	10.63	10.58	10.32	104.3%	2.02%
m/p-Cresol	0.5 - 10.0	0.9999	0.05	0.010	10.29	10.59	10.53	10.66	105.1%	1.54%
N-Nitrosodi-n-propylamine	0.5 - 10.0	0.9999	0.20	0.040	10.35	10.75	10.60	10.60	105.7%	1.53%
Hexachloroethane	0.5 - 10.0	1.0000	0.05	0.010	9.94	9.26	9.18	9.79	95.4%	4.00%
Nitrobenzene	0.5 - 10.0	0.9998	0.05	0.010	10.23	10.62	10.48	10.41	104.3%	1.57%
Isophorone	0.5 - 10.0	0.9997	0.05	0.010	10.27	10.35	10.46	10.95	105.1%	2.90%
2-Nitrophenol	0.5 - 10.0	1.0000	0.05	0.010	9.90	9.92	9.58	10.26	99.1%	2.79%
2,4-Dimethylphenol	0.5 - 10.0	0.9998	0.05	0.010	10.39	10.38	10.24	10.81	104.6%	2.32%
Bis(2-Chloroethoxy)methane	0.5 - 10.0	1.0000	0.10	0.020	10.09	10.28	10.04	10.62	102.6%	2.58%
2,4-Dichlorophenol	0.5 - 10.0	0.9998	0.05	0.010	9.99	9.95	9.95	10.47	100.9%	2.53%
1,2,4-Trichlorobenzene	0.5 - 10.0	0.9997	0.01	0.002	10.04	9.63	9.17	9.35	95.5%	4.00%
Naphthalene	0.5 - 10.0	1.0000	0.01	0.010	9.98	10.05	10.06	10.09	100.5%	0.45%
4-Chloroaniline	0.5 - 10.0	1.0000	0.20	0.040	10.20	10.38	10.52	10.97	105.2%	3.11%
Hexachlorobutadiene	0.5 - 10.0	1.0000	0.01	0.002	10.27	9.64	9.66	10.59	100.4%	4.67%
4-Chloro-3-methylpenol	0.5 - 10.0	0.9999	0.05	0.010	10.30	10.34	10.27	10.81	104.3%	2.45%
2-Methylnaphthalene	0.5 - 10.0	0.9999	0.01	0.002	10.11	9.96	10.09	10.51	101.7%	2.35%
1-Methylnaphthalene	0.5 - 10.0	1.0000	0.01	0.002	10.22	10.16	10.26	10.63	103.2%	2.07%
Hexachlorocyclopentadiene	0.5 - 10.0	0.9997	0.01	0.002	10.76	10.00	9.31	10.59	101.7%	6.45%

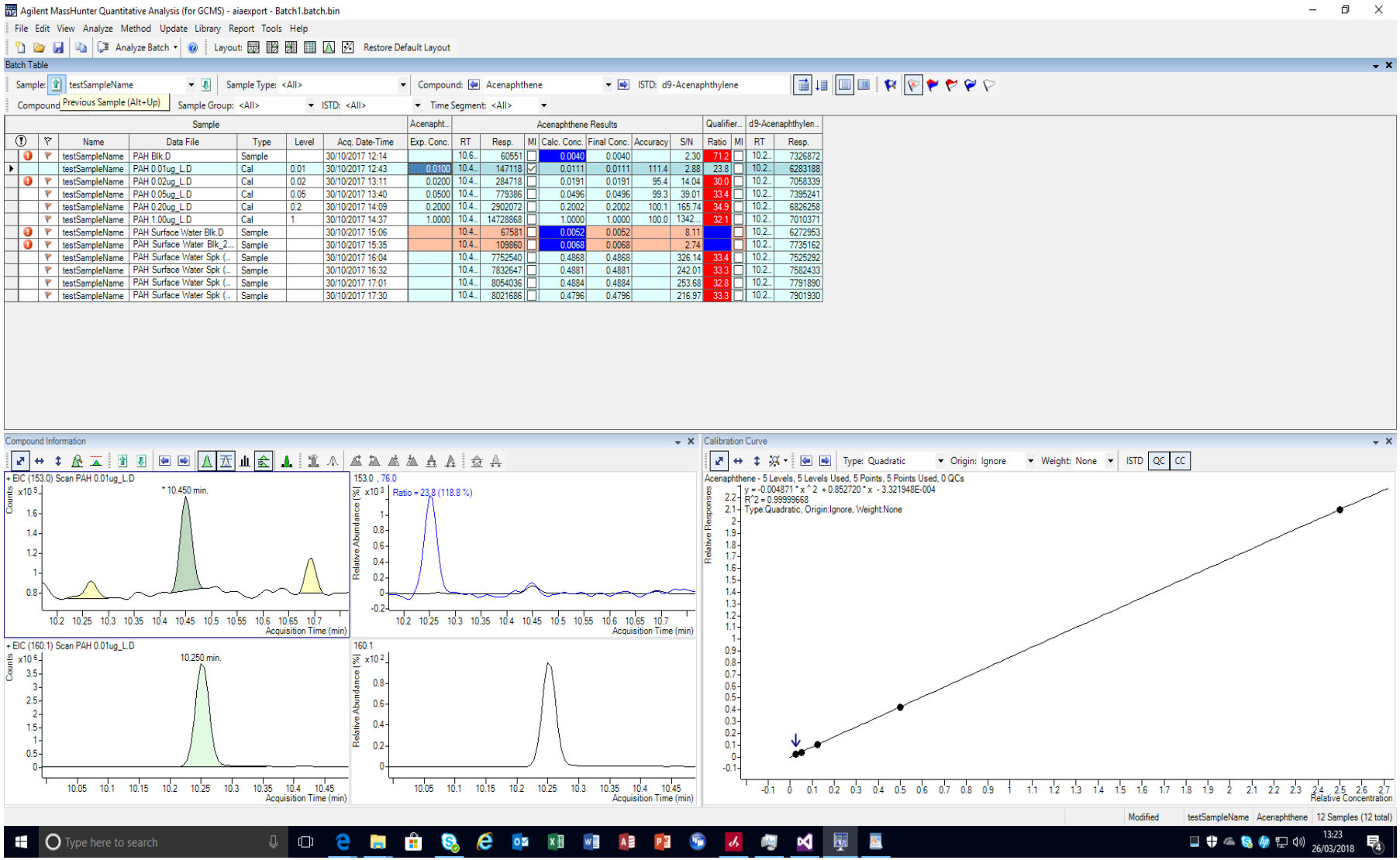
DLLME – GC–TOF Results (Pests) (80 compounds)

					Surface Water Spike Results					
Compound	Cal Range (ug/L)	R^2 (Quadratic Fit)	Est LOD - 1ul Inj (ug/L)	Est LOD - 10ul Inj (ug/L)	Spike 1	Spike 2	Spike 3	Spike 4	Recovery	RSD (n=4)
2,4-D Butyl	0.25 - 5.00	0.9995	0.05	0.01	2.493	2.483	2.479	2.497	99.5%	0.34%
2,4-D Ethyl	0.25 - 5.00	1.0000	0.01	0.002	2.490	2.529	2.513	2.502	100.3%	0.66%
2,4-D Isobutyl	0.25 - 5.00	0.9996	0.05	0.01	2.668	2.743	2.732	2.683	108.3%	1.35%
2,4-D Isopropyl	0.25 - 5.00	0.9998	0.05	0.01	2.502	2.496	2.510	2.494	100.0%	0.29%
2,4-D Methyl	0.25 - 5.00	0.9993	0.05	0.01	2.525	2.468	2.478	2.461	99.3%	1.17%
1,2,3-Trichlorobenzene	0.05 - 1.00	0.9999	0.01	0.002	0.500	0.503	0.505	0.506	100.7%	0.48%
1,2,4-Trichlorobenzene	0.05 - 1.00	1.0000	0.01	0.002	0.504	0.501	0.504	0.509	100.9%	0.68%
1,3,5-Trichlorobenzene	0.05 - 1.00	0.9998	0.01	0.002	0.497	0.495	0.500	0.501	99.6%	0.49%
Aldrin	0.05 - 1.00	1.0000	0.02	0.004	0.493	0.475	0.481	0.479	96.4%	1.66%
alpha-Endosulphan	0.05 - 1.00	1.0000	0.05	0.01	0.450	0.427	0.455	0.421	87.6%	3.79%
alpha-HCH	0.05 - 1.00	1.0000	0.02	0.004	0.497	0.496	0.499	0.500	99.6%	0.34%
beta-Endosulphan	0.05 - 1.00	0.9975	0.05	0.01	0.552	0.572	0.512	0.510	107.3%	5.71%
beta-HCH	0.05 - 1.00	0.9998	0.01	0.002	0.497	0.494	0.498	0.500	99.5%	0.48%
Chlorpropham	0.25 - 5.00	1.0000	0.05	0.01	2.511	2.453	2.474	2.429	98.7%	1.41%
cis-Chlordane	0.05 - 1.00	0.9991	0.01	0.002	0.474	0.460	0.442	0.455	91.5%	2.85%
cis-Permethrin	0.05 - 1.00	0.9983	0.02	0.004	0.513	0.540	0.536	0.504	104.6%	3.32%
Dichlobenil	0.05 - 1.00	0.9999	0.01	0.002	0.483	0.473	0.471	0.466	94.6%	1.47%
Dieldrin	0.05 - 1.00	0.9998	0.02	0.004	0.452	0.472	0.447	0.460	91.5%	2.45%
Endrin	0.05 - 1.00	1.0000	0.05	0.01	0.587	0.538	0.576	0.552	112.7%	3.95%
gamma-HCH	0.05 - 1.00	0.9997	0.02	0.004	0.521	0.512	0.523	0.525	104.0%	1.13%
Heptachlor	0.05 - 1.00	0.9995	0.01	0.002	0.457	0.458	0.458	0.447	91.0%	1.15%
Heptachlor Epoxide	0.05 - 1.00	0.9991	0.01	0.002	0.480	0.494	0.492	0.478	97.2%	1.61%
Hexachlorobenzene	0.05 - 1.00	0.9995	0.01	0.002	0.515	0.509	0.508	0.510	102.1%	0.63%
Hexachlorobutadiene	0.05 - 1.00	0.9991	0.01	0.002	0.491	0.496	0.493	0.490	98.5%	0.53%
Isodrin	0.05 - 1.00	0.9998	0.02	0.004	0.466	0.474	0.459	0.439	91.9%	3.23%
op-DDE	0.05 - 1.00	0.9985	0.01	0.002	0.459	0.470	0.468	0.464	93.0%	1.04%
op-DDT	0.05 - 1.00	0.9993	0.02	0.004	0.491	0.495	0.486	0.495	98.4%	0.90%
op-TDE	0.05 - 1.00	0.9989	0.01	0.002	0.478	0.474	0.467	0.469	94.5%	1.06%
Pentachlorobenzene	0.05 - 1.00	0.9999	0.01	0.002	0.535	0.526	0.524	0.520	105.2%	1.17%
pp-DDE	0.05 - 1.00	0.9999	0.01	0.002	0.494	0.500	0.495	0.502	99.6%	0.74%
pp-DDT	0.05 - 1.00	0.9998	0.02	0.004	0.486	0.482	0.482	0.487	96.9%	0.56%
pp-TDE	0.05 - 1.00	0.9984	0.02	0.004	0.476	0.477	0.460	0.468	94.0%	1.71%
Tecnazene	0.25 - 5.00	1.0000	0.01	0.002	2.527	2.517	2.545	2.539	101.3%	0.50%
trans-Chlordane	0.05 - 1.00	0.9994	0.01	0.002	0.466	0.453	0.443	0.449	90.5%	2.12%
trans-permethrin	0.05 - 1.00	0.9993	0.02	0.004	0.497	0.504	0.514	0.523	101.9%	2.27%

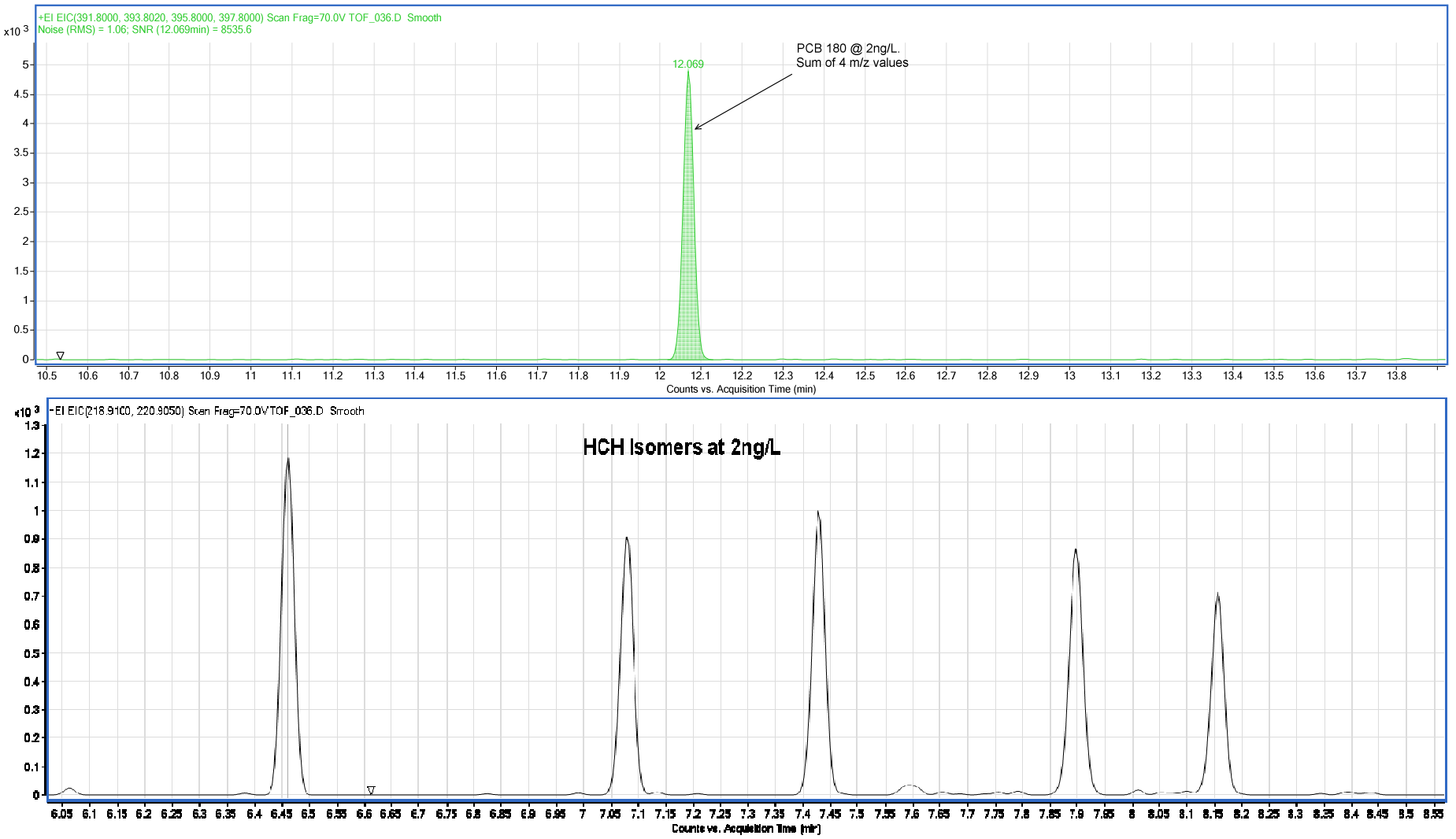
PCB28 on LECO Pegasus BT at 50ng/L
DLLME of 6ml sample & 1ul injection



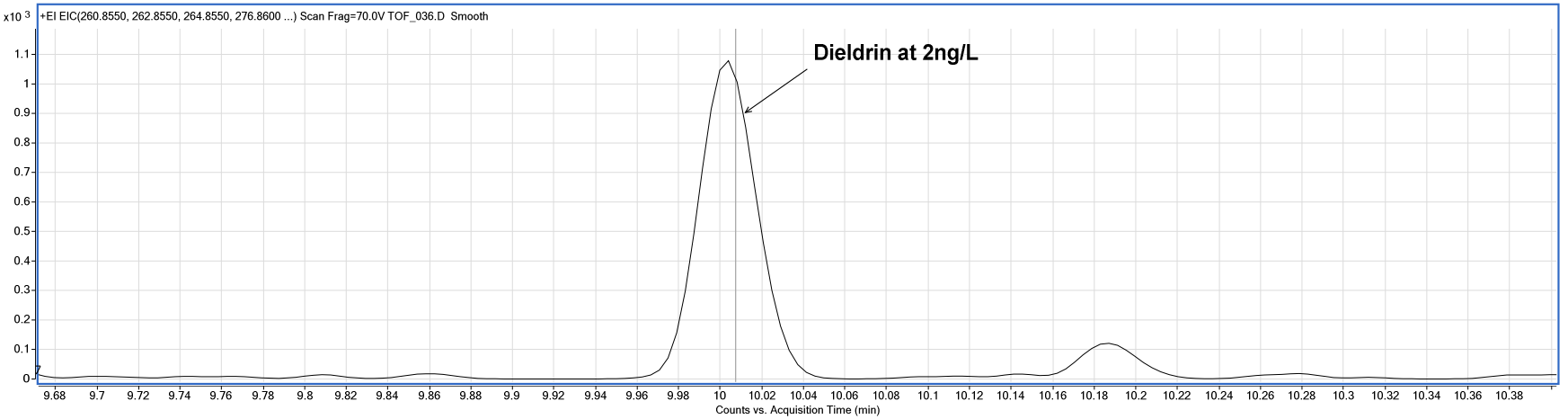
Acenaphthene on LECO Pegasus BT at 10ng/L DLLME of 6ml sample & 1ul injection

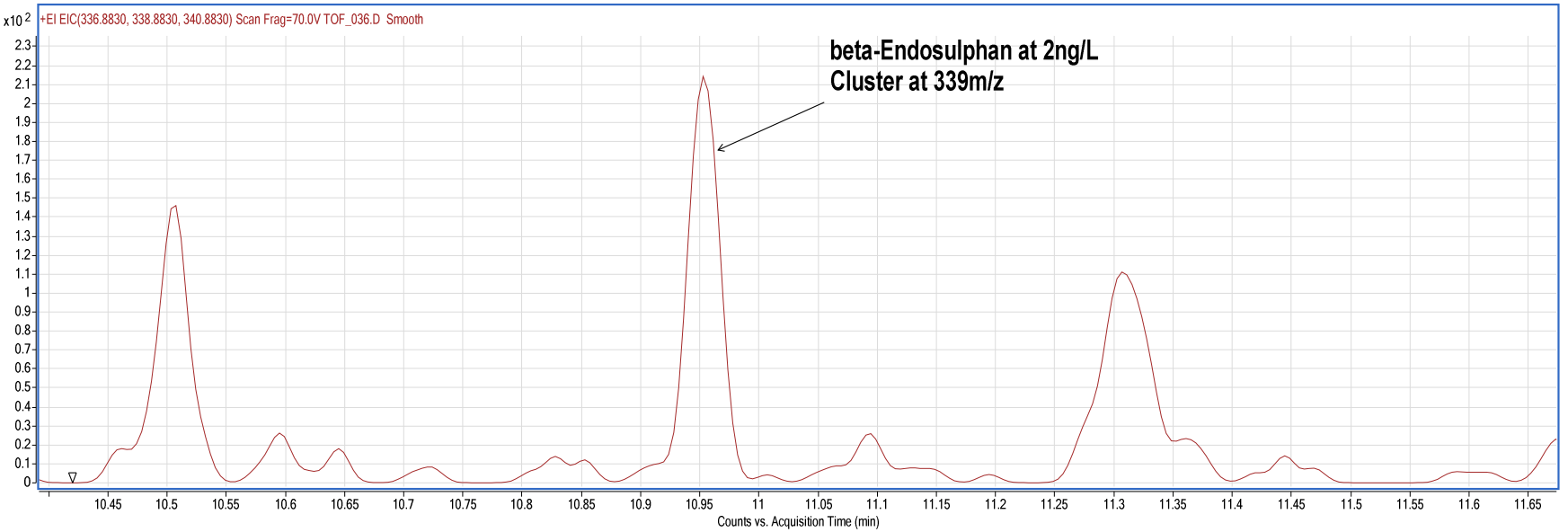


Pesticides by DLLME and Agilent 7200TOF



Pesticides by DLLME and TOF





Pesticides by DLLME GC-QTOF (7200) - Detection Limits

2ng/L	5ng/L	10ng/L	20ng/L		100ng/L	500ng/L
123-Trichlorobenzene	4,4'-Dichlorobenzophenone	2,4-D butyl ester	2,4'-Methoxychlor	Leptophos	Aclonifen	Acrinathrin
124-Trichlorobenzene	Aldrin	2,4-D ethyl ester	4,4'-Methoxychlor olefin	Malathion	Allidochlor	Deltamethrin
135-Trichlorobenzene	alpha-HCH	2,4-D isobutyl ester	Alachlor	Methoxychlor	Azinphos-ethyl	Fenpropathrin
2,3,5,6-Tetrachloroaniline	beta-Endosulphan	2,4-D isopropyl ester	Ametryne	Metolachlor	Azinphos-methyl	lambda-Cyhalothrin
bde 100	beta-HCH	2,4-D methyl ester	Anthraquinone	MGK-264	Bifenox	
bde 153	Bromophos ethyl	2-Phenylphenol	Benzo(k)fluoranthene	Oxadiazon	Chlorfenapyr	
bde 154	Bromophos methyl	3,4-Dichloroaniline	Bifenthrin	Parathion ethyl	Coumaphos	
bde 28	Chloroneb	alpha-Endosulphan	Bromfenvinfos methyl	Parathion methyl	Cyfluthrin	
bde 47	Chlorpyrifos	Anthracene	Bromfenvinphos	Penconazole	Cypermethrin	
bde 99	Chlorpyrifos methyl	Benfluralin	Bromopropylate	Pendimethlin	Fenvalerate	
cis-Chlordane	cis-Heptachlor Epoxide	Benzo(a)pyrene	Bupirimate	Phorate	Flucythrinate	
cis-Nonachlor	DCPA methyl ester	Benzo(b)fluoranthene	Carbophenothion	Phosalone	Fludioxonil	
Dichlobenil	delta-HCH	Benzo(ghi Perylene	Carfentrazone ethyl	Phosmet	Fluquinconazole	
Hexachlorobenzene	Dicofol	Biphenyl	Chlorfenvinphos	Piperonyl butoxide	Lenacil	
Hexachlorobutadiene	Dieldrin	Chlorbenside	Chlorobenzilate	Pirimicarb	Myclobutanil	
op-DDE	epsilon-HCH	Chlorfenson(OVEX)	Chlorpropham	Pirimiphos ethyl	Nitralin	
PCB101	Etridiazole	Chlorothalonil	cis-Permethrin	Pretilachlor	Nitrofen	
PCB118	Fenchlorphos	Chlorthiophos	Cybutryne	Procymidone	Norflurazon	
PCB138	Fipronil	Cyprodinil	Cycloate	Prodiamine	Phenothrin	
PCB153	gamma-HCH	Diallate	Diazinon	Profenofos	Prochloraz	
PCB180	Heptachlor	Dichlorvos	Dichlofluanid	Profluralin	Propargite	
PCB28	Iodofenphos	Diphenylamine	Dichloran	Prometryne	Pyraclofos	
PCB52	Isodrin	Endosulphan ether	Diflufenican	Propachlor	Pyrazaphos	
Pentachloroaniline	Mirex	Endosulphan Sulphate	Dimethachlor	Propanil	Pyridaben	
Pentachlorobenzene	Pentachloroanisole	Endrin aldehyde	Diphenamid	Propazine	Resmethrin	
Pentachlorobenzonitrile	Pentachloronitrobezene	Ethalfluralin	Edifenphos	Propetamphos	Sulprofos	
Pentachlorothioanisole	trans -Heptachlor Epoxide	Fenpropidin	Endrin	Propiconazole	tau-Fluvalinate	
pp-DDE	Trifluralin	Fenthion	Endrin ketone	Propyzamide	Terbuconazole	
Tecnazene		Fluoranthene	EPN	Prothiofos	Tetramethrin	
Trans- Chlordane		Fonofos	EPTC	Pyridaphenthion	Triazophos	
trans-Nonachlor		Indeno (1,2,3-c,d)pyrene	Ethion	Pyrimethanil	Tricyclazole	
		Methacrifos	Ethofumesate	Pyriproxyfen		
		Mevinphos	Ethylan (Perthane)	Quinalphos		
		op-DDT	Etofenprox	Simazine		
		op-TDE	Fenamiphos	Tebufenpyrad		
		Palcobutrazol	Fenarimol	Tefluthrin		
		Pebulate	Fenitrothion	Terbuthylazine		
		Pirimpiphos-methyl	Fenpropimorph	terbutryne		
		PP-DDD(TDE)	Fenson	Tolyfluanid		
		pp-DDT	Fluchloralin	Transfluthrin		
		Quinoxyfen	Fluridone	Trans-Permethrin		
		Sulfotepp	Flusilazole	Triadimenol		
		Terbufos	Flutolanil	Triflumizole		
		Tetrachlorvinphos	Flutriafol	Vinclozolin		
		Tetradifon	Hexazinone			
		Tolclofos-methyl	Isazophos			
		Triallate	Isopropalin			

SVOCs and Pesticides by DLLME – conclusions

- DLLME technique developed to cover a wide range of analytes – acids, base/neutrals with logPs 1 – >6
- Greater concentration factors and wider range of analytes possible than with hexane extracts.
- Extractions can be done at different pH values and the extracts merged
- Good results obtained for >300 compounds so far – EPA 8270 analytes and wide range of organochlorine, organonitrogen and organophosphate pesticides
- IPA was used as disperser solvent and was added to sample prior to transfer to extraction vial to act additionally as an organic modifier – reduce potential adsorption problems.
- Recoveries comparable to current method for vast majority of analytes, some phenols appear a bit lower but less background for phthalates and better coverage of volatile area of chromatogram with DLLME.
- Extraction found to be very quick and very reproducible with good mechanical reliability
- MRLs in the low to mid ng/L range should be easily achievable for many analytes from 9ml sample when interfaced to modern instrumentation.
- Method validated for PAHs on 5977MSD with LODs all <10ng/L. Validation currently underway for EPA8270 on 5977MSD with LODs <0.1ug/L for vast majority of compounds.
- Wide ranging screening method possible in combination with GC-TOF
  - Low ppt detection limit for hundreds of compounds
  - Organohalogen compounds particularly sensitive by HR-TOF
  - Complementary with LC-MS screen.

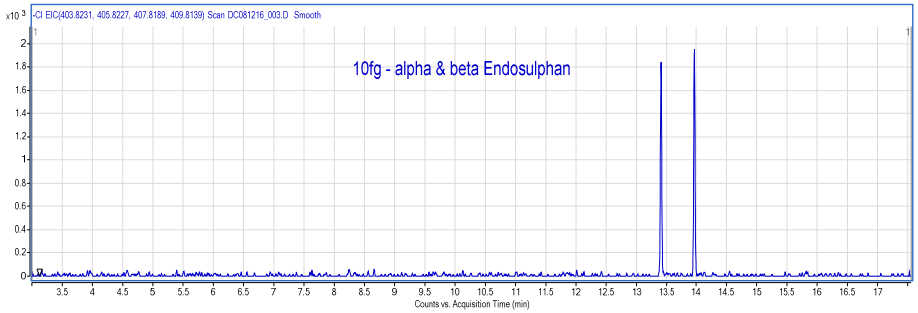
Heptachlors in Surface Water by SPE-SBSE-GC-TOF

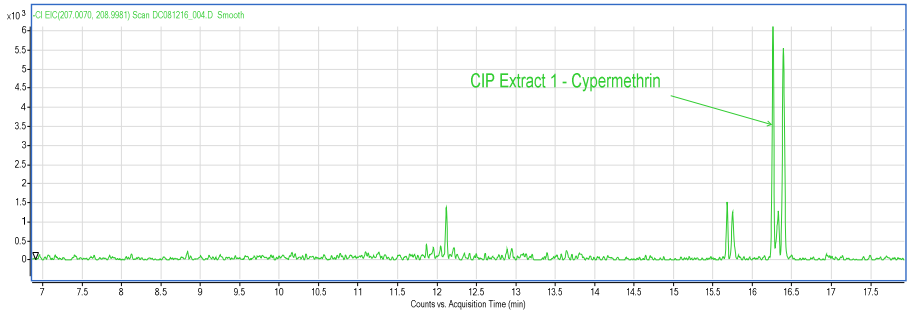
Ultra low-level LODs

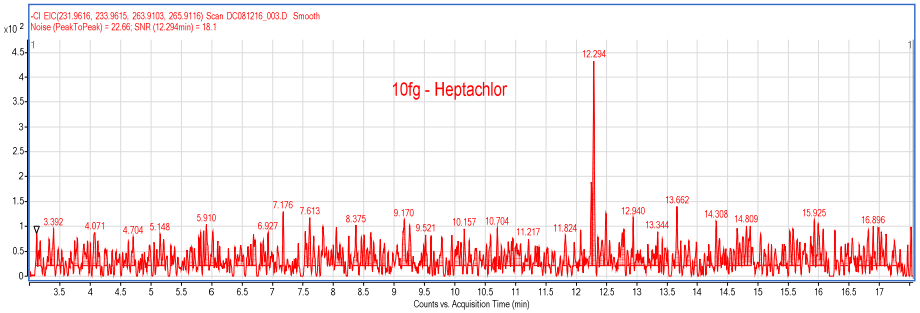
WFD – Heptachlors

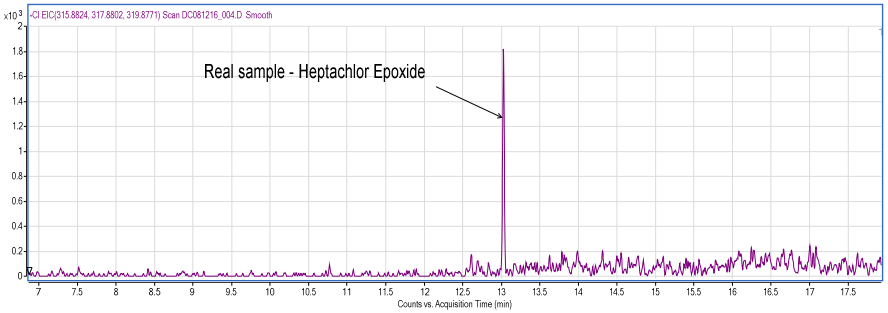
- EQS for inland surface waters $2x10^{-7}$ ug/L (0.2pg/L)
  - Required LODs not currently achievable
  - ALS routine method uses GC-MSMS (EI) with MRLs of 20pg/L.
  - Use GC-MSMS-NCI for Cypermethrin but not good for Heptachlor.
- How low can we go?
  - Most sensitive instrumental technique?
  - How much sample can we get onto the column in a robust fashion?
    - Consider SBSE?

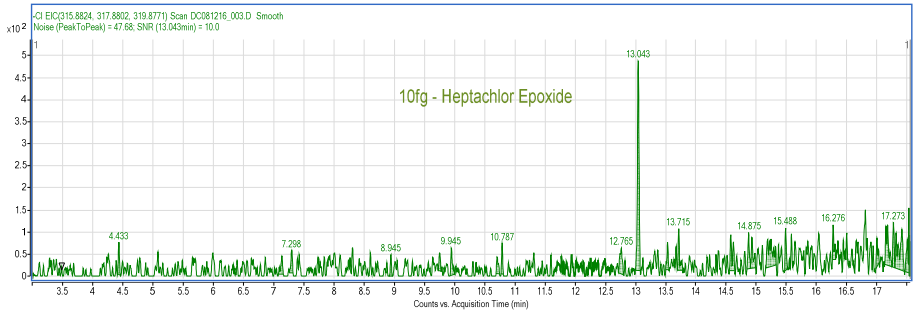
WFD Pesticides – GC-QTOF-NCI (Ammonia)











Better than GC-MSMS EI and GC-MSMS NCI for Heptachlor & Heptachlor Epoxide

Role for SBSE??

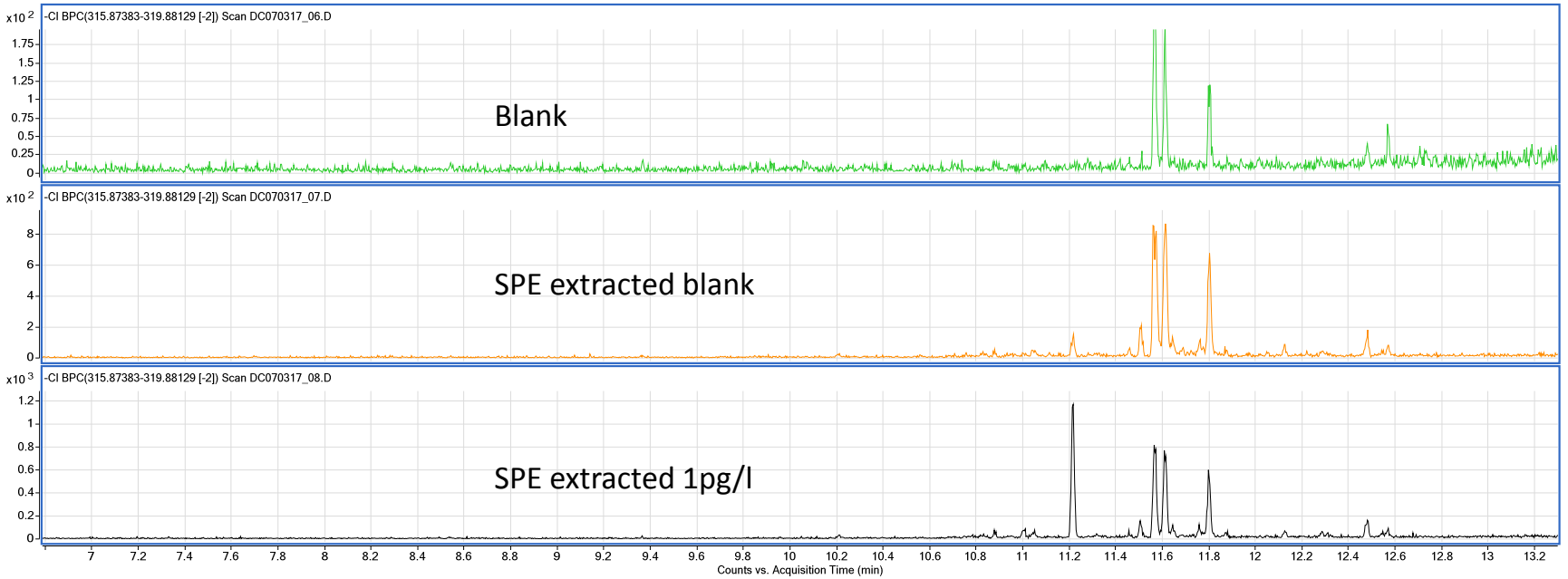
- GC-QTOF-NCI data suggest improvements to limits of detection for Heptachlor and Heptachlor Epoxide possible if enough sample can be transferred to the column.
- Twister an attractive proposition
  - Solvent-less sample introduction – maintain chromatographic integrity.
  - Simple extraction procedure – less scope for blank issues
- But..
  - Large sample volumes required – long equilibration times
  - What about sample particulates??

Heptachlors – Potential SPE/SBSE Method

- Pre-concentration by SPE could potentially be a way forward
  - Extract 1 litre sample by conventional SPE
  - Elute with 1.5mls MeOH or MeCN
  - Make up to about 10mls with DI water
  - SBSE
- Advantages
  - Possible to work with larger initial sample volumes
  - Still relatively simple procedure with very low solvent usage – no evaporation procedure
  - SPE elution solvent acts as co-solvent for SBSE
  - Sample particulates extracted as well
- Disadvantages
  - Additional cost, potential blocking of SPE cartridge with high suspended solids

Initial work on Heptachlor Epoxide – SPE / SBSE extracts

Heptachlor epoxide



Conclusions and final thoughts

- Sensitivity of current GC-MS instrumentation makes it possible to reduce sample sizes to 40mls or below for nearly all “routine” methods – miniaturisation.
- Recent advances in robotics allow us to take advantage of this and automate sample preparation procedures.
    - Automated standard addition, LLE, SPE, derivatization, evaporation, centrifugation and more are all supported.
- Approach complementary to the on-line SPE work done for LC-MS analysis of pesticides in recent years.
    - May allow us to standardise on 40ml vials as sample containers with huge benefits for both laboratories and customers
- DLLME – shows potential for fast, robust, automated extraction of wide range of analytes from aqueous samples.
    - Complementary GC-MS and LC-MS screens now a possibility using low sample volume and fast automated sample prep.
- WFD – Heptachlors
    - Combination of SPE/SBSE with GC-TOF has potential to lower LODs for Heptachlor in surface waters to below 1pg/L if blanks can be controlled.

Acknowledgements

- Pete Stoney – ALS Environmental
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- Dan Carrier – Anatune

Any Questions?