



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

John Quick – ALS Environmental UK

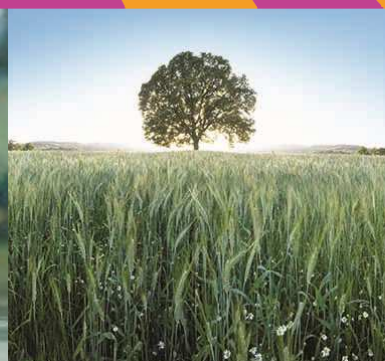


5TH SBSE INTERNATIONAL MEETING

23 & 24 SEPTEMBRE 2019 - NOVOTEL PARIS-SUD

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 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 <1 pg/L may be achievable.
- Conclusions



- 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

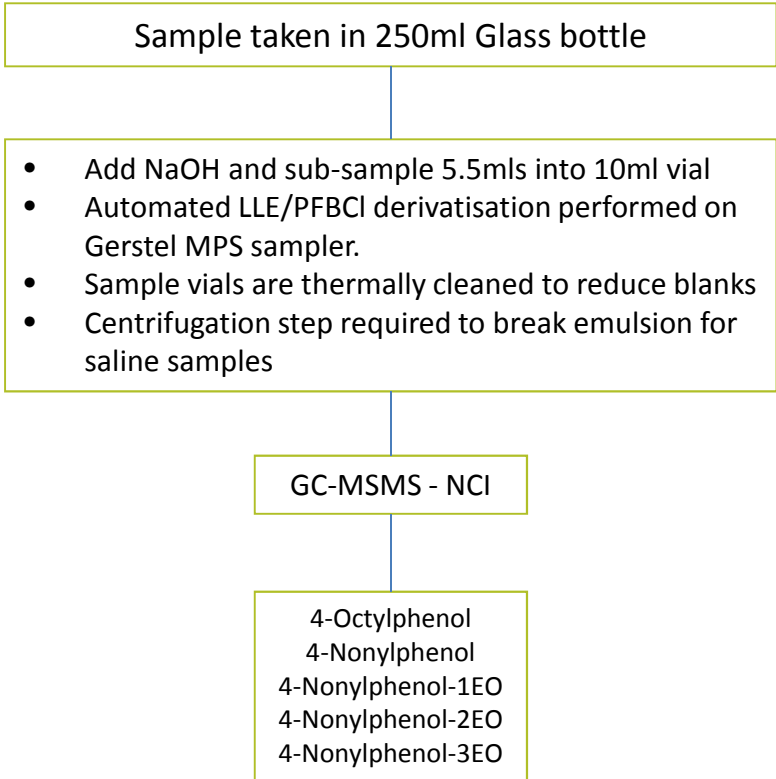
Automated Extraction and Analysis

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

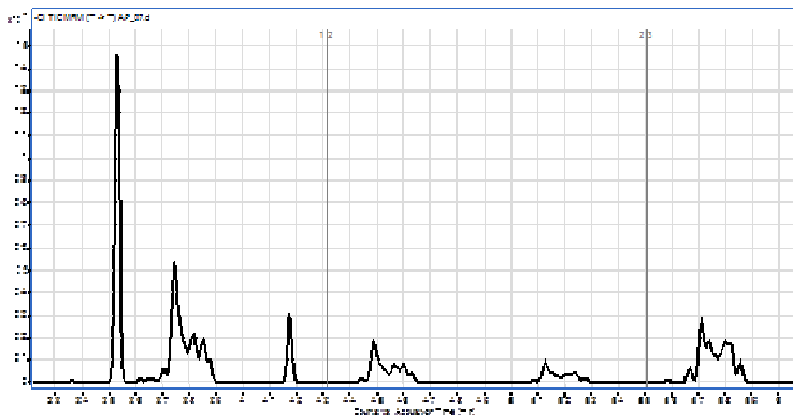


- Method set up for CIP in 2015
- 4-Octylphenol, 4-Nonylphenol & 4-Nonylphenol EO1 – EO3
- Analysis by GC-MSMS in NCI mode.
- Simultaneous extraction and derivatisation using Hexane/Pentafluorobenzoyl Chloride.
- Sensitivity of NCI allows process to be miniaturised.
- Fully automated method developed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

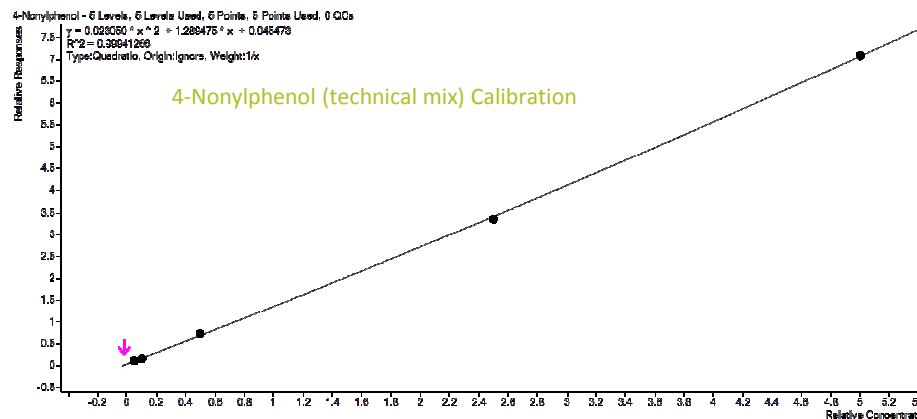
WFD Priority Substances – Alkylphenols & APEOs



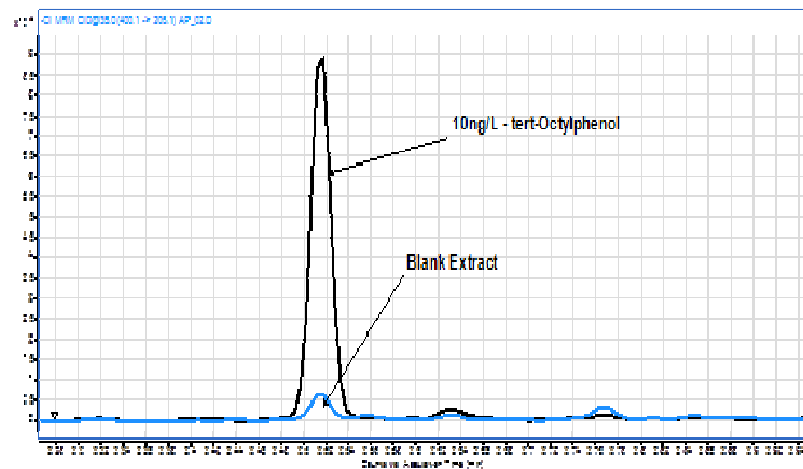
Alkylphenols & Ethoxylates – GC-MSMS Agilent 7000C (NCI)



4-tert-OP Sensitivity in Sewage Effluent



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?



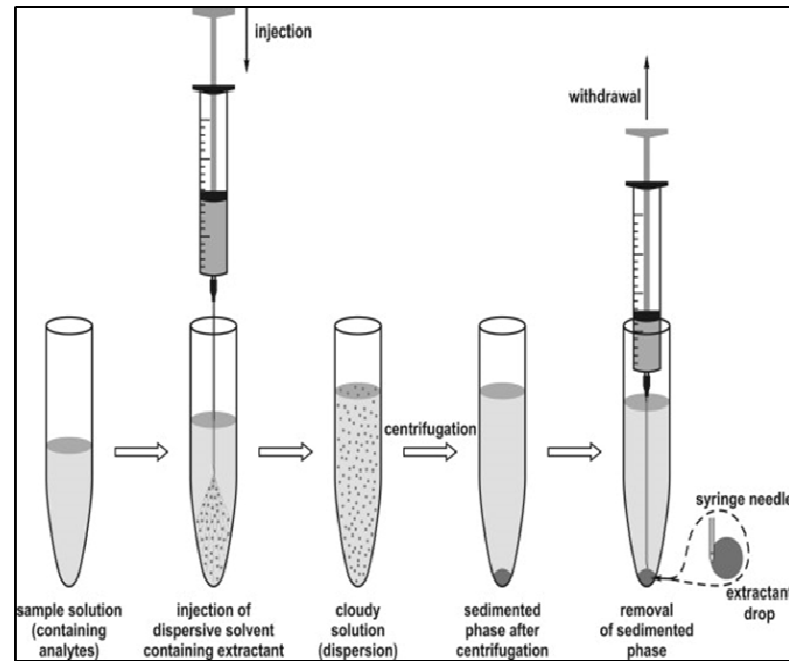
SVOCs and Pesticides

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

Current SVOC 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

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



DLLME Extraction on Gerstel MPS Settings



PrepBuilder 1 - C:\ProgramData\Gerstel\Maestro\1\PrepSequence\DLLME_6_SVOC.prp

Prep. Settings
 Vial Range: 1-6

Prep. Action Settings
 Syringe: 100ul
 Action: PREP MPS Left MPS
 Method: No Overlap - Prep Ahead disabled

Source: [] Vial: AUTO
 Destination: [] Vial: AUTO

Buttons: Add, Insert, Replace, Delete, Clean

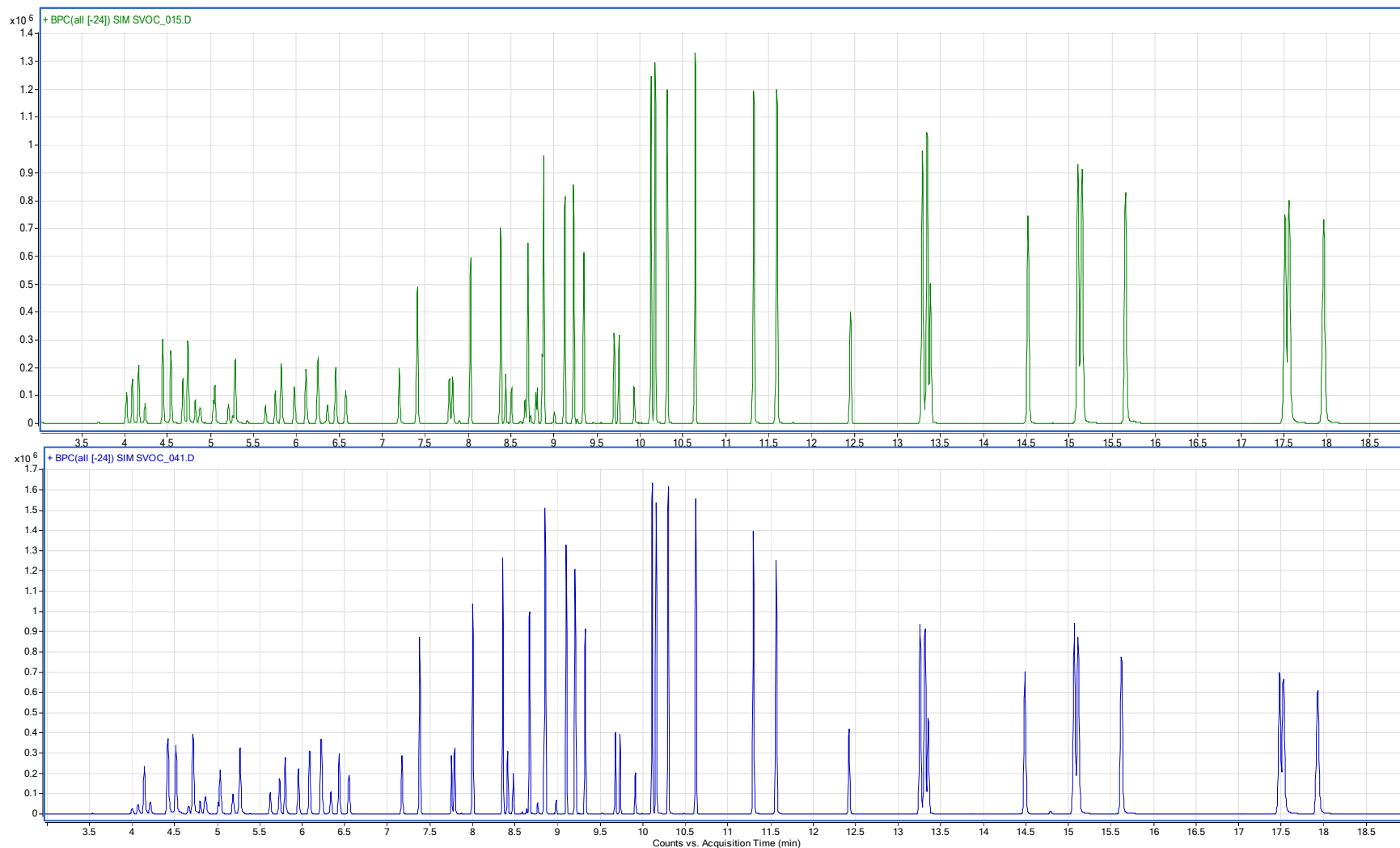
Action	MPS	Method / Value	Source	Vial	Destination	Vial
PREP Vials 1-6		No Overlap				
MOVE	Right MPS		Tray2.VT32-10		mVox.mVTC1-10	
MIX	Right MPS	mVox DLLME				
MOVE	Right MPS		mVox.mVTC1-10		Tray2.VT32-10	
END						
PREP Vials 1-6		No Overlap				
MOVE	Left MPS		Tray2.VT32-10		Centrifg.CT6-10	
END						
PREP Vials 1-1		No Overlap				
CF200	Left MPS	4000rpm 90s				
END						
PREP Vials 1-6		No Overlap				
MOVE	Left MPS		Centrifg.CT6-10		Tray2.VT32-10	
END						
PREP Vials 1-1		No Overlap				
WASH	Left MPS	Wash_DCM				
END						
PREP Vials 1-6		No Overlap				
ADD	Left MPS	DLLME_Extract_Transfer	Tray2.VT32-10		Tray1.VT98	
END						

Buttons: OK, Cancel, Help

Windows Taskbar: 2:18 PM 2/22/2018

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



Agilent MassHunter Quantitative Analysis (for GCMS) - SM310118Test - Batch1.batch.bin

File Edit View Analyze Method Update Library Report Tools Help

Analyze Batch Layout: Restore Default Layout

Batch Table

Sample: 1 STD DLLME Sample Type: <All> Compound: 2-Chloronaphthalene ISTD: d10-Acenaphthene

Compound Group: <All> Sample Group: <All> ISTD: <All> Time Segment: <All>

Sample						2-Chloron...		2-Chloronaphthalene Results					Qualifie..	d10-Ace...	Qualifie..					
?	▼	Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Ratio	MI	RT	Resp.	Ratio	MI
!	▼	0 STD DLLME	SVOC_035.D	Sample		01/02/2018 08:04		8..	54		0.0044	0.0044		8..	51.1		8..	113..	40.3	
!		1 STD DLLME	SVOC_036.D	Sample		01/02/2018 08:29		8..	16116		1.1880	1.1880		9..	35.5		8..	125..	40.3	
!		5 STD DLLME	SVOC_037.D	Sample		01/02/2018 08:54		8..	74694		5.7639	5.7639		5..	35.8		8..	118..	40.3	
!		25 STD DLLME	SVOC_038.D	Sample		01/02/2018 09:19		8..	369516		27.6482	27.6482		2..	35.4		8..	114..	40.3	
!		50 STD DLLME	SVOC_039.D	Sample		01/02/2018 09:43		8..	762480		48.0376	48.0376		5..	35.3		8..	128..	40.1	
!	▼	100 STD DLLME	SVOC_040.D	Sample		01/02/2018 10:08		8..	1872949		100.2445	100.2445		4..	35.0		8..	133..	40.1	
!		DLLME T AQC 1	SVOC_041.D	Sample		01/02/2018 14:43		8..	969670		55.4453	55.4453		2..	35.2		8..	139..	40.1	
!		DLLME T AQC 2	SVOC_042.D	Sample		01/02/2018 15:08		8..	990937		52.7008	52.7008		2..	35.1		8..	150..	40.1	

Compound Information

Selected Ion (162.0) SVOC_036.D

Previous Sample (Alt+Up)

Selected Ion (127.0) SVOC_036.D

Ratio = 35.5 (100.4 %)

8.036 min.

Selected Ion (164.0) SVOC_036.D

8.668 min.

Selected Ion (160.0) SVOC_036.D

Ratio = 40.3 (100.0 %)

8.668 min.

Calibration Curve

Type: Quadratic Origin: Force Weight: None ISTD: QC CC

2-Chloronaphthalene - 5 Levels, 5 Levels Used, 5 Points, 5 Points Used, 0 QCs

$y = 0.808659 \cdot x^2 + 5.392693 \cdot x$

$R^2 = 0.99850350$

Type: Quadratic, Origin: Force, Weight: None

Relative Responses

Relative Concentration

Modified 1 STD DLLME 2-Chloronaphthalene 8 Samples (8 total)

19:47 25/02/2018

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



Agilent MassHunter Quantitative Analysis (for GCMS) - 180116A - 180116B.batch.bin

File Edit View Analyze Method Update Library Report Tools Help

Analyze Batch Layout: Restore Default Layout

Batch Table

Sample: 0.5ugl Sample Type: <All> Compound: 2-Chloronaphthalene ISTD: d10-Acenaphthene

Compound Group: <All> Sample Group: <All> ISTD: <All> Time Segment: <All>

Sample		2-Chloronaphthalene Results											Qualifie...		d10-Acenapthe...	
Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Ratio	MI	RT	Resp.
0.5ugl	0.5 STD 180116.D	Cal	0.5	16/01/2018 16:42	0.5000	9.946	155133		0.4845	0.4845	96.9	572.00	1.9		10.5...	5857155
2.0ugl	2 STD 180116.D	Cal	2.0	16/01/2018 17:09	2.0000	9.946	652170		1.9744	1.9744	98.7	2780.87	2.1		10.5...	6103611
5.0ugl	5 STD 180116.D	Cal	5.0	16/01/2018 17:36	5.0000	9.946	1599042		4.7425	4.7425	94.9	2840.61	2.2		10.5...	6351337
10.0ugl	10 STD 180116.D	Cal	10.0	16/01/2018 18:02	10.0000	9.946	3679855		10.2212	10.2212	102.2	5570.22	2.3		10.5...	7052881
20.0ugl	20 STD 180116.D	Cal	20.0	16/01/2018 18:29	20.0000	9.946	7014763		19.9555	19.9555	99.8	13371...	2.8		10.5...	7412752
2.0ugl	2 STD 15sec A 180116.D	Sample		16/01/2018 21:34		9.946	789749		2.0160	2.0160		983.41	2.4		10.5...	7240932
2.0ugl	2 STD 15sec B 180116.D	Sample		16/01/2018 22:01		9.946	789064		2.0301	2.0301		1548.15	2.1		10.5...	7185017
2.0ugl	2 STD 30sec A 180116.D	Sample		16/01/2018 22:27		9.946	779471		2.0161	2.0161		1566.62	2.2		10.5...	7146200
2.0ugl	2 STD 30sec B 180116.D	Sample		16/01/2018 22:54		9.946	805665		2.0289	2.0289		1779.71	2.2		10.5...	7340418
2.0ugl	2 STD 45sec A 180116.D	Sample		16/01/2018 23:20		9.942	815600		2.0535	2.0535		1349.28	2.2		10.5...	7343161
2.0ugl	2 STD 45sec B 180116.D	Sample		16/01/2018 23:47		9.946	827394		2.0759	2.0759		1592.67	2.2		10.5...	7370037
2.0ugl	2 STD 60sec A 180116.D	Sample		17/01/2018 00:13		9.942	869479		2.1152	2.1152		1365.52	1.8		10.5...	7603221

Compound Information

Calibration Curve

Type: Quadratic Origin: Force Weight: None ISTD QC CC

2-Chloronaphthalene - 5 Levels, 5 Levels Used, 5 Points, 5 Points Used, 0 QCs

$$y = -0.037242 * x^2 + 0.548528 * x$$

$$R^2 = 0.99948017$$

Type: Quadratic, Origin: Force, Weight: None

Processed 0.5ugl 2-Chloronaphthalene 13 Samples (13 total)

17:06 25/02/2018

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



Agilent MassHunter Quantitative Analysis (for GCMS) - 180116A - 180116B.batch.bin

File Edit View Analyze Method Update Library Report Tools Help

Analyze Batch Layout: Restore Default Layout

Batch Table

Sample: 0.5ugl Sample Type: <All> Compound: 2-Nitroaniline ISTD: d10-Acenapthene

Compound Group: <All> Sample Group: <All> ISTD: <All> Time Segment: <All>

Sample				2-Nitroaniline		2-Nitroaniline Results										Qualif..		d10-Acenapth...	
Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Ratio	MI	RT	Resp.			
0.5ugl	0.5 STD 180116.D	Cal	0.5	16/01/2018 16:42	0.5000	10.0	18091		0.5199	0.5199	104.0	8.76	55.7		10.5	5857155			
2.0ugl	2 STD 180116.D	Cal	2.0	16/01/2018 17:09	2.0000	10.0	73582		1.9422	1.9422	97.1	330.85	61.2		10.5	6103611			
5.0ugl	5 STD 180116.D	Cal	5.0	16/01/2018 17:36	5.0000	10.0	214819		5.0570	5.0570	101.1	596.94	58.1		10.5	6351337			
10.0ugl	10 STD 180116.D	Cal	10.0	16/01/2018 18:02	10.0000	10.0	523115		9.9782	9.9782	99.8	513.35	58.4		10.5	7052881			
20.0ugl	20 STD 180116.D	Cal	20.0	16/01/2018 18:29	20.0000	10.0	1326304		20.0022	20.0022	100.0	2201.23	58.1		10.5	7412752			
2.0ugl	2 STD 15sec A 180116.D	Sample		16/01/2018 21:34		10.0	106436		2.3440	2.3440		439.32	59.2		10.5	7240932			
2.0ugl	2 STD 15sec B 180116.D	Sample		16/01/2018 22:01		10.0	99549		2.2165	2.2165		154.65	58.8		10.5	7185017			
2.0ugl	2 STD 30sec A 180116.D	Sample		16/01/2018 22:27		10.0	98863		2.2134	2.2134		273.94	60.1		10.5	7146200			
2.0ugl	2 STD 30sec B 180116.D	Sample		16/01/2018 22:54		10.0	108212		2.3504	2.3504		327.75	59.3		10.5	7340418			
2.0ugl	2 STD 45sec A 180116.D	Sample		16/01/2018 23:20		10.0	107714		2.3394	2.3394		49.88	59.7		10.5	7343161			
2.0ugl	2 STD 45sec B 180116.D	Sample		16/01/2018 23:47		10.0	111929		2.4173	2.4173		170.13	58.0		10.5	7370037			
2.0ugl	2 STD 60sec A 180116.D	Sample		17/01/2018 00:13		10.0	101512		2.1400	2.1400		134.77	59.0		10.5	7603221			

Compound Information

Calibration Curve

Type: Quadratic Origin: Ignore Weight: None ISTD: QC CC

2-Nitroaniline - 5 Levels, 5 Levels Used, 5 Points, 5 Points Used, 0 QCs

$$y = 0.015064 \cdot x^2 + 0.059338 \cdot x - 3.718014E-005$$

$$R^2 = 0.99998170$$

Type: Quadratic, Origin: Ignore, Weight: None

Processed 0.5ugl 2-Nitroaniline 13 Samples (13 total)

19:01 25/02/2018

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



Agilent MassHunter Quantitative Analysis (for GCMS) - 180116A - 180116B.batch.bin

File Edit View Analyze Method Update Library Report Tools Help

Analyze Batch Layout: Restore Default Layout

Batch Table

Sample: 0.5ugl Sample Type: <All> Compound: 4-Chloro-3-methylpenol ISTD: d8-Naphthalene

Compound Group: <All> Sample Group: <All> ISTD: <All> Time Segment: <All>

Sample						4-Chloro-3-methylpenol Results								Qualifie..		d8-Naphthalene..		Qualifie..		
?	▼	Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Ratio	MI	RT	Resp.	Ratio	MI
▶	!	0.5ugl	0.5 STD 180116.D	Cal	0.5	16/01/2018 16:42	0.5000	9.151	60184		0.5124	0.5124	102.5	66.10	12...		8.390	1180980	88...	
	!	2.0ugl	2 STD 180116.D	Cal	2.0	16/01/2018 17:09	2.0000	9.151	248813		1.9869	1.9869	99.3	652.76	12...		8.390	1226863	87...	
	!	5.0ugl	5 STD 180116.D	Cal	5.0	16/01/2018 17:36	5.0000	9.151	677707		4.9800	4.9800	99.6	854.88	11...		8.390	1267287	85...	
	!	10.0ugl	10 STD 180116.D	Cal	10.0	16/01/2018 18:02	10.0000	9.151	1646255		10.0158	10.0158	100.2	3396.11	11...		8.390	1413104	82...	
	!	20.0ugl	20 STD 180116.D	Cal	20.0	16/01/2018 18:29	20.0000	9.151	3956153		19.9978	19.9978	100.0	2790.90	11...		8.390	1476100	81...	
	!	2.0ugl	2 STD 15sec A 180116.D	Sample		16/01/2018 21:34		9.151	321866		2.1643	2.1643		262.70	11...		8.390	1452496	81...	
	!	2.0ugl	2 STD 15sec B 180116.D	Sample		16/01/2018 22:01		9.151	331523		2.2398	2.2398		847.30	11...		8.390	1443728	82...	
	!	2.0ugl	2 STD 30sec A 180116.D	Sample		16/01/2018 22:27		9.151	325956		2.2072	2.2072		277.59	11...		8.390	1441297	82...	
	!	2.0ugl	2 STD 30sec B 180116.D	Sample		16/01/2018 22:54		9.151	321675		2.1183	2.1183		1644.79	12...		8.390	1484299	81...	
	!	2.0ugl	2 STD 45sec A 180116.D	Sample		16/01/2018 23:20		9.151	320966		2.0900	2.0900		636.76	11...		8.390	1501838	81...	
	!	2.0ugl	2 STD 45sec B 180116.D	Sample		16/01/2018 23:47		9.151	320433		2.0354	2.0354		165.26	11...		8.390	1541001	79...	
	!	2.0ugl	2 STD 60sec A 180116.D	Sample		17/01/2018 00:13		9.151	346432		2.1186	2.1186		140.90	11...		8.390	1598311	78...	

Compound Information

Calibration Curve

Type: Quadratic Origin: Force Weight: None ISTD: QC CC

4-Chloro-3-methylpenol - 5 Levels, 5 Levels Used, 5 Points, 5 Points Used, 0 QCs

$$y = 0.177383 \cdot x^2 + 0.985490 \cdot x$$

$$R^2 = 0.99999705$$

Type: Quadratic, Origin: Force, Weight: None

X 9.00 Y 32.943 Processed 0.5ugl 4-Chloro-3-methylpenol 13 Samples (13 total)

19:15 25/02/2018



- 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)



Compound	Cal Range (ug/L)	R ² (Quadratic Fit)	Est LOD - 2ul Inj (ug/L)	Est LOD - 10ul Inj (ug/L)	Surface Water Spike Results					
					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-methylphenol	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)



Compound	Cal Range (ug/L)	R ² (Quadratic Fit)	Est LOD - 1ul Inj (ug/L)	Est LOD - 10ul Inj (ug/L)	Surface Water Spike Results					
					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



Agilent MassHunter Quantitative Analysis (for GCMS) - aiexport - Batch1.batch.bin

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Analyze Batch Layout: Restore Default Layout

Batch Table

Sample: testSampleName Sample Type: <All> Compound: PCB 28 ISTD: d14-Triflurain

Compound Group: <All> Sample Group: <All> ISTD: <All> Time Segment: <All>

Name	Data File	Type	Level	Acq. Date-Time	PCB 28_					d14-Triflurain (IST_				
					Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	RT	Resp.
testSampleName	Blk - 10% IPA.D	Sample		23/10/2017 13:39	12.2	749			0.0012	0.0012	0.26	11.0	11623147	
testSampleName	50 std - 10% IPA.D	Cal	0.05	23/10/2017 14:07	0.0500	12.1	305343		0.0506	0.0506	101.2	14.33	16284255	
testSampleName	250 std - 10% IPA.D	Cal	0.25	23/10/2017 14:35	0.2500	12.1	757682		0.2486	0.2486	99.4	14.36	8021304	
testSampleName	500 std - 10% IPA.D	Cal	0.50	23/10/2017 15:03	0.5000	12.1	2726004		0.5009	0.5009	100.2	13.10	14141847	
testSampleName	1000 std - 10% IPA.D	Cal	1.00	23/10/2017 15:31	1.0000	12.1	4046965		0.9999	0.9999	100.0	13.74	10290847	
testSampleName	Surface Blk - 10% IPA.D	Sample		23/10/2017 16:58	12.2	232			0.0011	0.0011	0.06	11.0	9313924	
testSampleName	Surface Blk - 10% IPA_2.D	Sample		23/10/2017 17:26	12.2	411			0.0012	0.0012	0.24	11.0	9300968	
testSampleName	Surface Spk - 10% IPA.D	Sample		23/10/2017 17:53	12.1	1981150			0.5020	0.5020	14.26	11.0	10255509	
testSampleName	Surface Spk - 10% IPA_2.D	Sample		23/10/2017 18:21	12.1	2163207			0.5100	0.5100	13.37	11.0	11018446	
testSampleName	Surface Spk - 10% IPA_3.D	Sample		23/10/2017 18:48	12.1	2527300			0.5141	0.5141	14.62	11.0	12766192	
testSampleName	Surface Spk - 10% IPA_4.D	Sample		23/10/2017 19:16	12.1	2423977			0.5193	0.5193	14.26	11.0	12120059	

Compound Information

Calibration Curve

Type: Quadratic Origin: Ignore Weight: None ISTD: QC CC

PCB 28 - 4 Levels, 4 Levels Used, 4 Points, 4 Points Used, 0 QCs

$$y = 0.016206 \cdot x^2 + 0.377507 \cdot x - 3.985866E-004$$

$$R^2 = 0.99999408$$

Type: Quadratic, Origin: Ignore, Weight: None

Processed testSampleName PCB 28 11 Samples (11 total)

13:21 26/03/2018

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



Agilent MassHunter Quantitative Analysis (for GCMS) - aiaexport - Batch1.batch.bin

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Analyze Batch Layout: Restore Default Layout

Batch Table

Sample: testSampleName Sample Type: <All> Compound: Acenaphthene ISTD: d9-Acenaphthylene

Compound: Previous Sample (Alt+Up) Sample Group: <All> ISTD: <All> Time Segment: <All>

Name	Data File	Type	Level	Acq. Date-Time	Acenaphthene				Acenaphthene Results				Qualifier...		d9-Acenaphthylene	
					Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Ratio	MI	RT	Resp.
testSampleName PAH Blk. D		Sample		30/10/2017 12:14		10.6	60551		0.0040	0.0040		2.30	71.2		10.2	7326872
testSampleName PAH 0.01ug_L.D		Cal	0.01	30/10/2017 12:43	0.0100	10.4	147118		0.0111	0.0111	111.4	2.88	23.8		10.2	6283188
testSampleName PAH 0.02ug_L.D		Cal	0.02	30/10/2017 13:11	0.0200	10.4	284718		0.0191	0.0191	95.4	14.04	30.0		10.2	7058339
testSampleName PAH 0.05ug_L.D		Cal	0.05	30/10/2017 13:40	0.0500	10.4	779386		0.0496	0.0496	99.3	39.01	33.4		10.2	7395241
testSampleName PAH 0.20ug_L.D		Cal	0.2	30/10/2017 14:09	0.2000	10.4	2902072		0.2002	0.2002	100.1	165.74	34.9		10.2	6826258
testSampleName PAH 1.00ug_L.D		Cal	1	30/10/2017 14:37	1.0000	10.4	14728868		1.0000	1.0000	100.0	1342.	32.1		10.2	7010371
testSampleName PAH Surface Water Blk. D		Sample		30/10/2017 15:06		10.4	67581		0.0052	0.0052		8.11			10.2	6272953
testSampleName PAH Surface Water Blk. 2		Sample		30/10/2017 15:35		10.4	109860		0.0068	0.0068		2.74			10.2	7735162
testSampleName PAH Surface Water Spk (...)		Sample		30/10/2017 16:04		10.4	7752540		0.4868	0.4868		326.14	33.4		10.2	7525292
testSampleName PAH Surface Water Spk (...)		Sample		30/10/2017 16:32		10.4	7832647		0.4881	0.4881		242.01	33.3		10.2	7582433
testSampleName PAH Surface Water Spk (...)		Sample		30/10/2017 17:01		10.4	8054036		0.4884	0.4884		253.68	32.8		10.2	7791890
testSampleName PAH Surface Water Spk (...)		Sample		30/10/2017 17:30		10.4	8021686		0.4796	0.4796		216.97	33.3		10.2	7901930

Compound Information

Calibration Curve

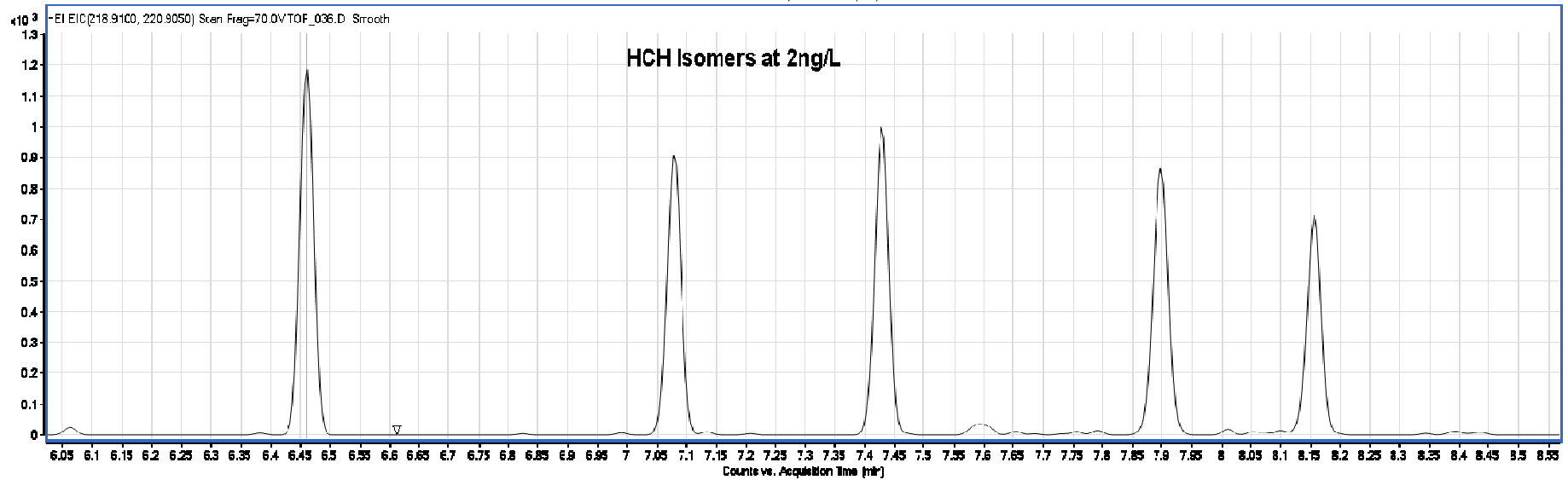
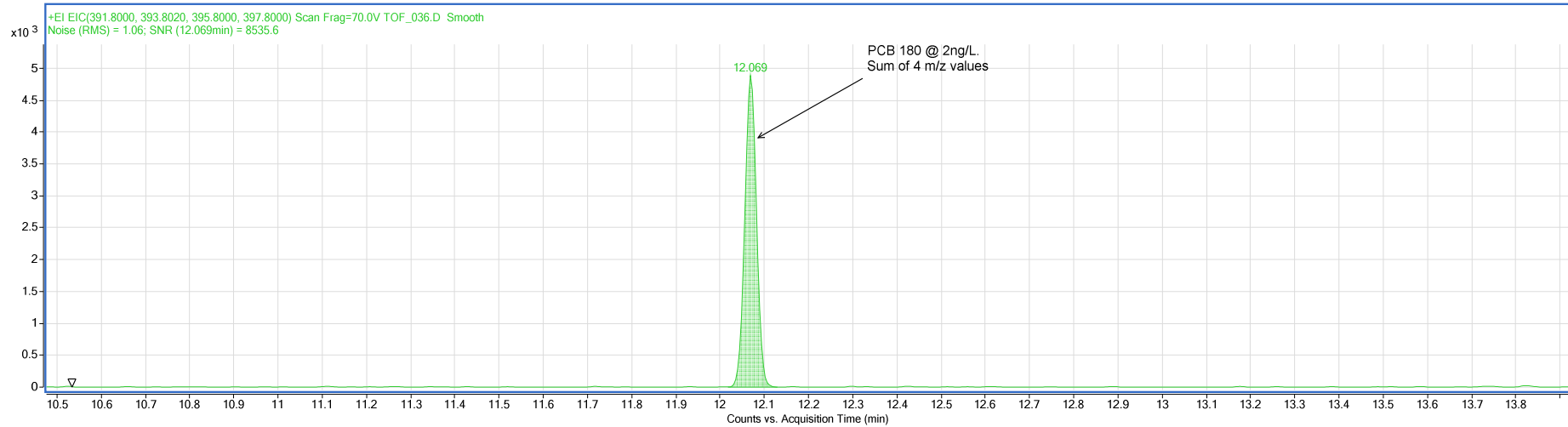
Type: Quadratic Origin: Ignore Weight: None ISTD: QC CC

Acenaphthene - 5 Levels, 5 Levels Used, 5 Points, 5 Points Used, 0 QCs
 $y = -0.004871 \cdot x^2 + 0.852720 \cdot x - 3.321948E-004$
 $R^2 = 0.99999668$
 Type: Quadratic, Origin: Ignore, Weight: None

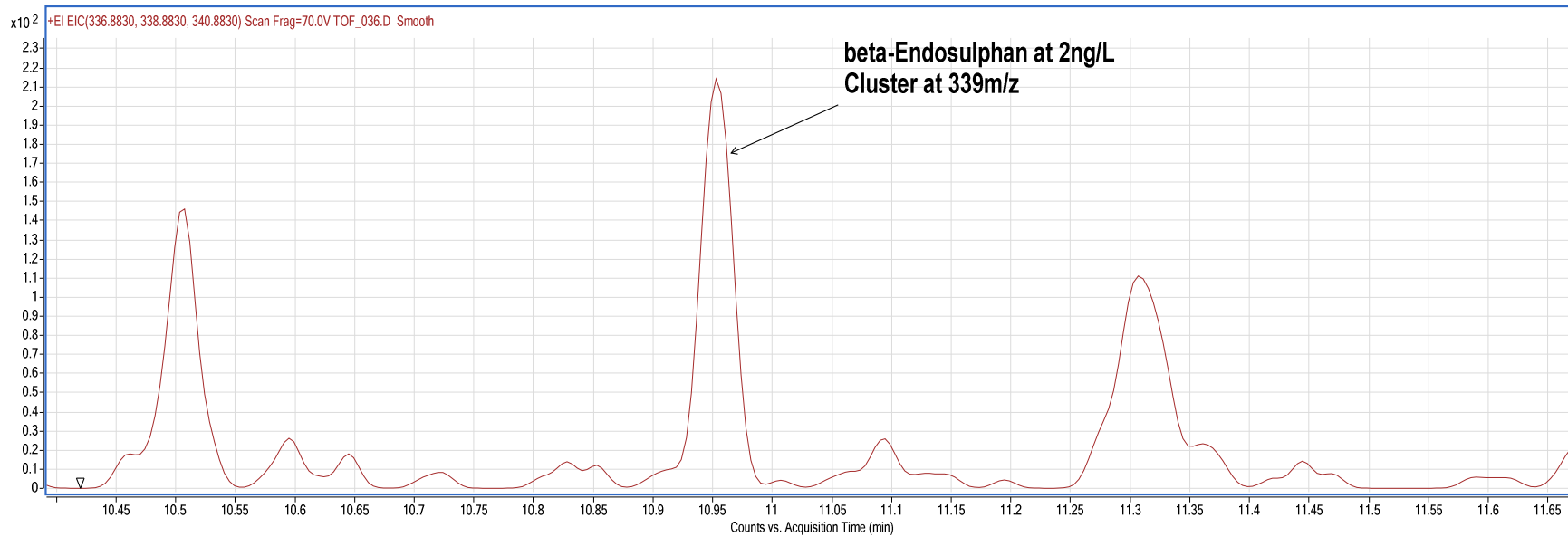
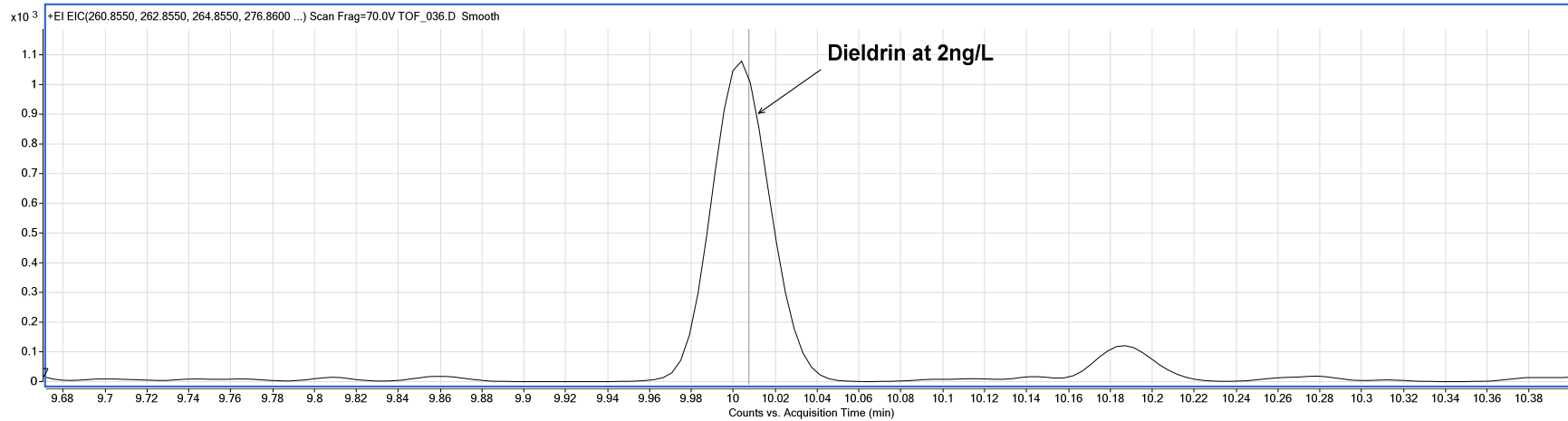
Modified: testSampleName Acenaphthene 12 Samples (12 total)

13:23 26/03/2018

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	Acronifen
124-Trichlorobenzene	Aldrin	2,4-D ethyl ester	4,4'-Methoxychlor olefin	Malathion	Allidochlor
135-Trichlorobenzene	alpha-HCH	2,4-D isobutyl ester	Alachlor	Methoxychlor	Azinphos-ethyl
2,3,5,6-Tetrachloroaniline	beta-Endosulphan	2,4-D isopropyl ester	Ametryne	Metolachlor	Azinphos-methyl
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	Bromfeninfos methyl	Parathion methyl	Cyfluthrin
bde 47	Chlorpyrifos	Anthracene	Bromfeninfos	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	Chlorfeninfos	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	Pyraclufos
PCB52	Isodrin	Endosulphan ether	Diflufenican	Propachlor	Pyrazaphos
Pentachloroaniline	Mirex	Endosulphan Sulphate	Dimethachlor	Propanil	Pyridaben
Pentachlorobenzene	Pentachloroanisole	Endrin aldehyde	Diphenamid	Propazine	Resmethrin
Pentachlorobenzonitrile	Pentachloronitrobenzene	Ethalfuralin	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	
		Quinoxifen	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.



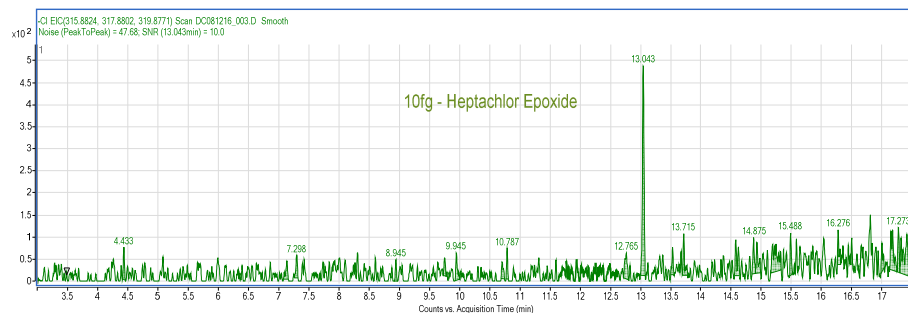
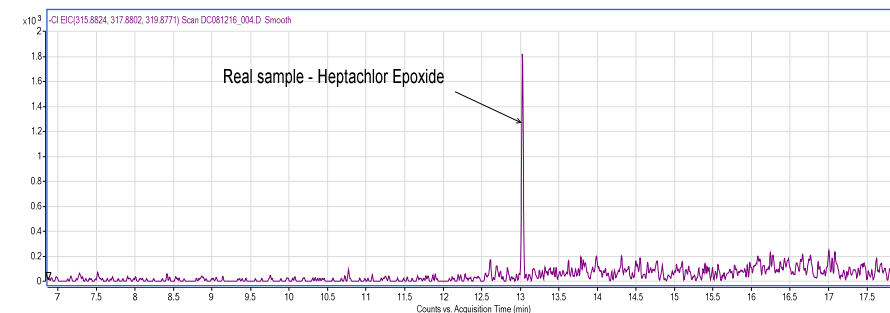
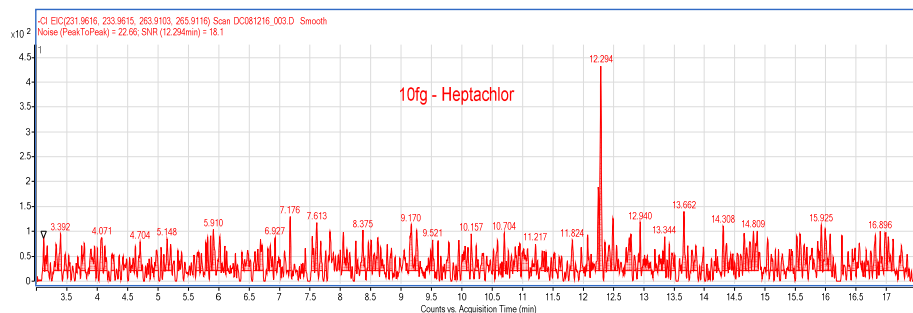
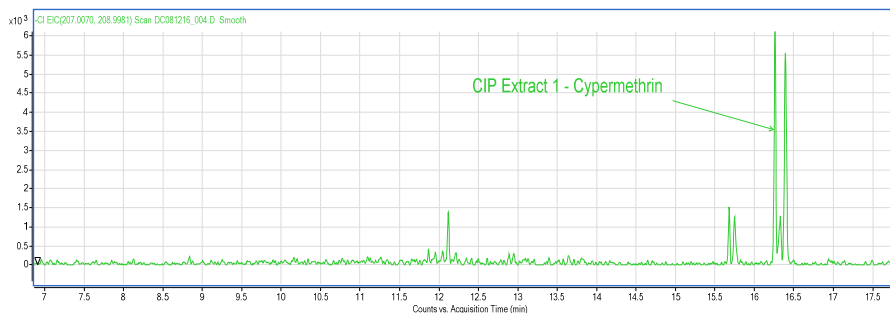
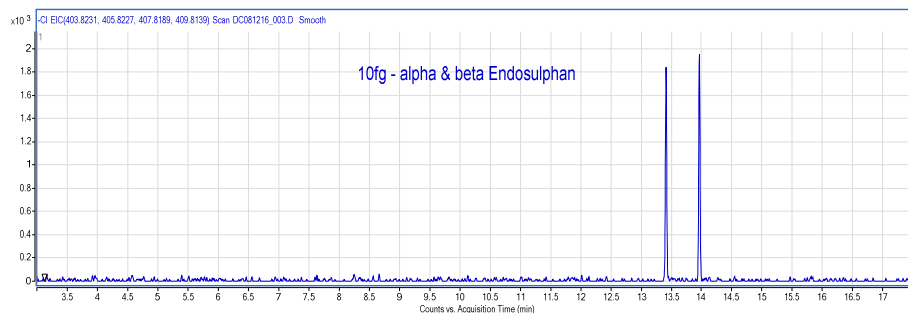
Heptachlors in Surface Water by SPE-SBSE-GC-TOF

Ultra low-level LODs



- EQS for inland surface waters 2×10^{-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

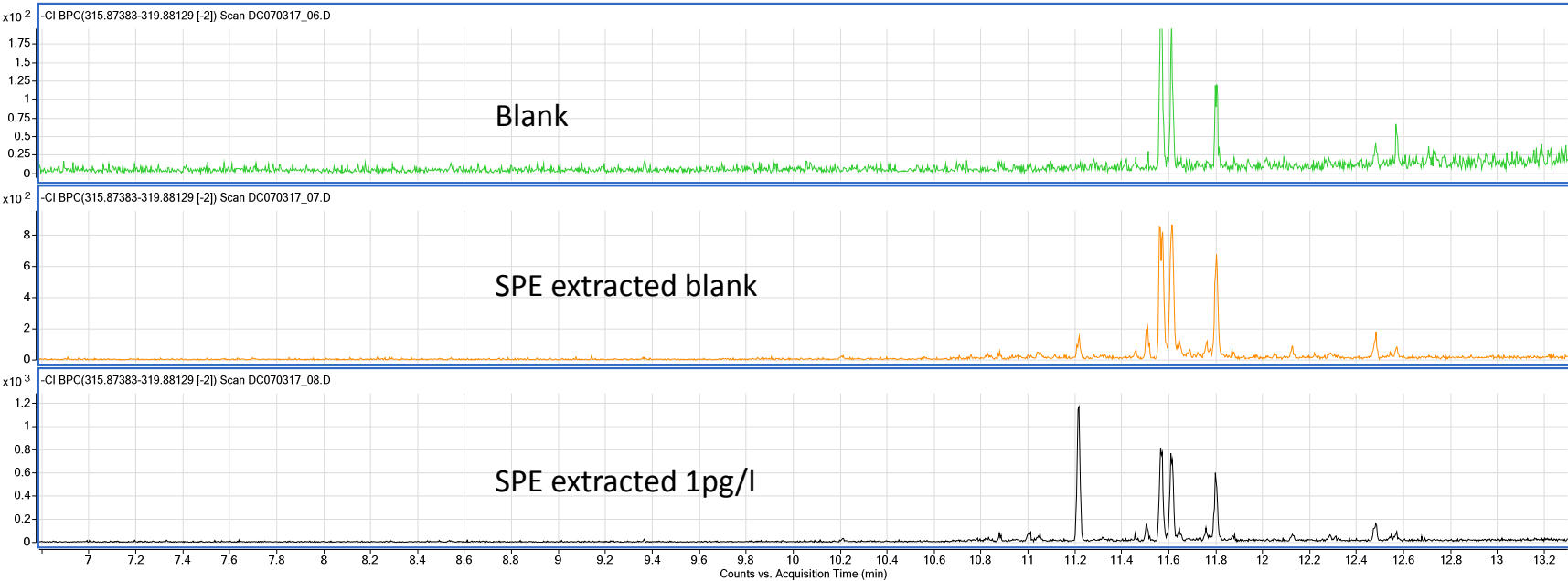


- Pre-concentration by SPE could potentially be a way forward
 - Extract 1 litre sample by conventional SPE
 - Elute with 1.5mls MeOH or MeCN
 - Make up to about 10mls with DI water
 - SBSE
- Advantages
 - Possible to work with larger initial sample volumes
 - Still relatively simple procedure with very 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 1 pg/L if blanks can be controlled.

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Any Questions?