Analysis of Semi Volatiles method by GC/MS/MS with liquid-liquid extractions using ePrep Full Automation for EPA 3511

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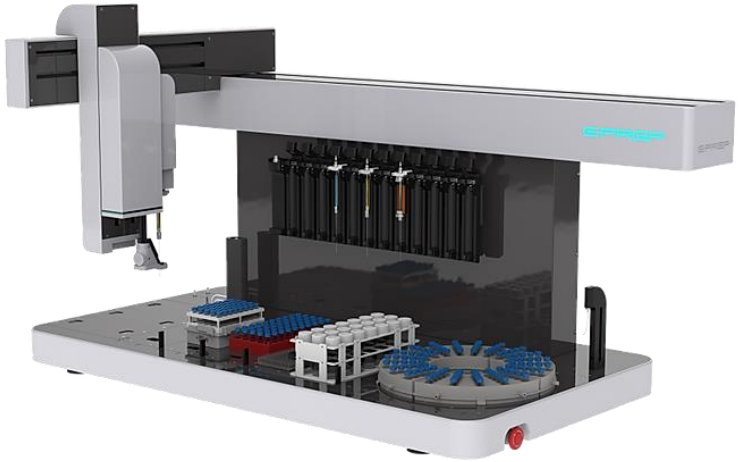

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Trusted Answers

ePrep

DE12290342

Introduction slide/background info/reason for project

- Semi-volatiles and Volatiles monitoring is critical for the integrity of our water supply. We need Reliable Data for Sound Decision Making.
- Automated micro extractions and GCMSMS are the right tools for reliable data.

- Historic preparation of wastewater samples for semi volatiles has been done by using a 1L sample of liquid-liquid extraction (EPA 3510C).
- Customers are looking to reduce sample volume due to expense in shipping, time in preparation, consumption of solvent, etc.
- 1L sample extracts have been analyzed by GCMS single quad to date, with sufficient detection limits.
- Customers are now looking to move to micro-extractions, this leads to needing instrumentation that has move sensitivity due to loss of the concentration factor
- Coupling automated sample prep of EPA 3511 with 8270E on GC/MS/MS is the perfect pairing for a busy environmental lab.

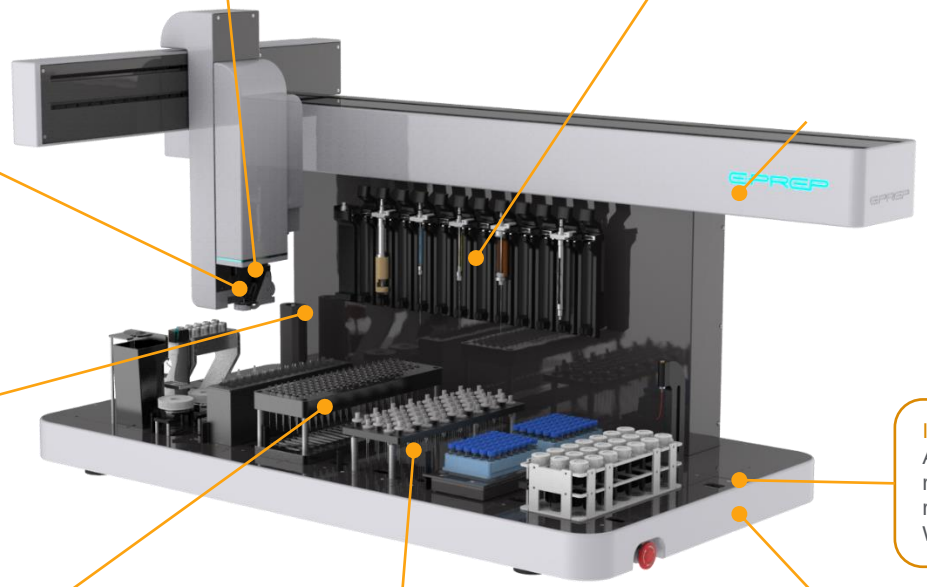
ePrep Product Features

SAMPLE AND TOOL RECORDING
Reporting all liquid movements and tool usage is essential to Chain of Custody applications

ROTATING FOOT
Enabling tool exchange, senor operation and mechanical push-pull of cartridges and filters

ROBOTIC TOOL CHANGE (XCHANGE®)
Enabling efficient and automated exchange of syringes and tools during procedures

CONTROL SOFTWARE
Touch Screen Bases
Enabling creation of new Workflows within minutes independent of user ability



INBUILT FOOT SENSORS
Detecting vial dimensions, allowing for diversity of vial types used on the deck

SYRINGE WASH STATION
Syringe washing is essential to syringe priming, carryover control, clean sample processing and waste disposal

WORKFLOW ELEMENTS
Preparation procedures can include sealed vials, µSPEed cartridges, filters, needle syringes and other sample preparation elements

ACCESSORIES AND CONSUMABLES
A diverse range of accessories allows the ePrep to be customised to the needs of individual users

INTERCHANGEABLE DECK
Allowing rapid configuration of vial racks, accessories and elements required for a sample preparation Workflow

INDEPENDENT OPERATION
A single ePrep instrument can feed multiple analytical instruments uninterrupted, maximising efficiency

Summary ePrep's Full Automation of 8270 Semi Volatiles in Water

Suitable for **Drinking** and **Waste** Water Samples

Uses ePrep Analytical syringe to effect micro Liquid-Liquid Extraction by solvent nebulization

2mL DCM extraction solvent

Salt added using high ionic strength brine.

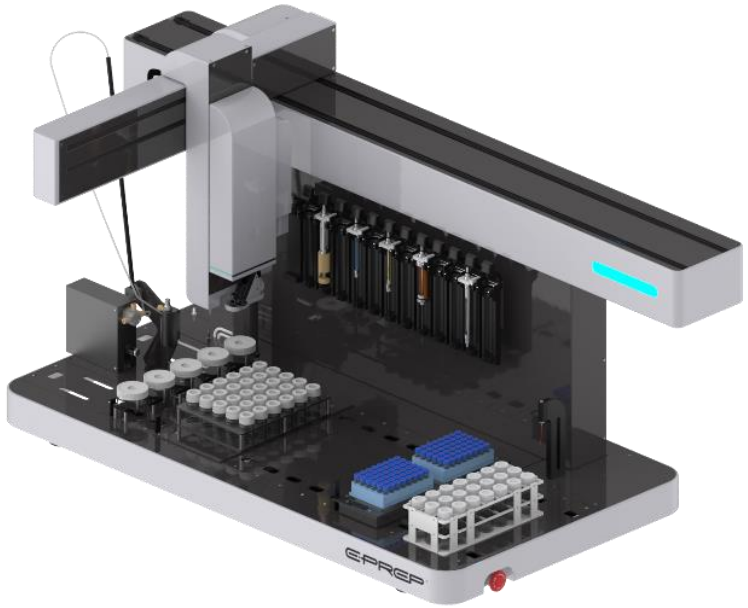
Acidic and base pH adjusted & confirmed

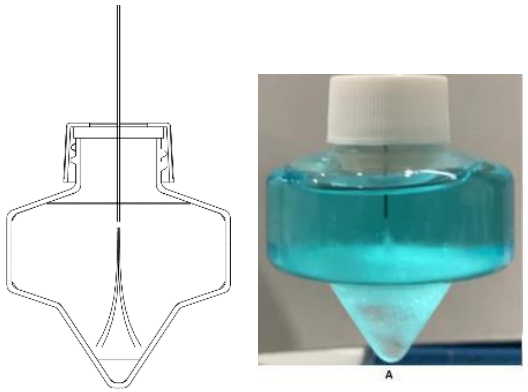
High-speed vortexing and syringe purge used to enhance DCM homogenization, precipitation and break "dirty samples" emulsion

500µL extraction DCM sodium sulphate dried, for acid reduction

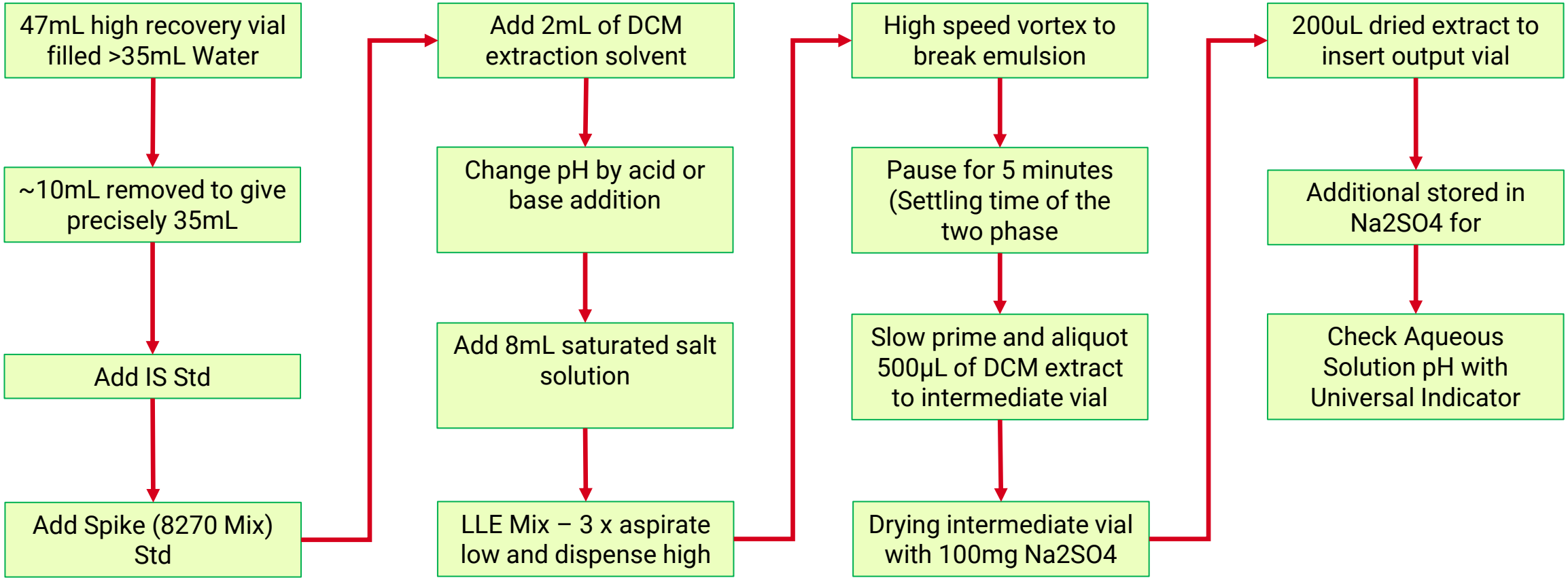
200uL dried extract aliquoted to final autosampler vial.

Results by isotope dilution normalisation or external standard quantitation





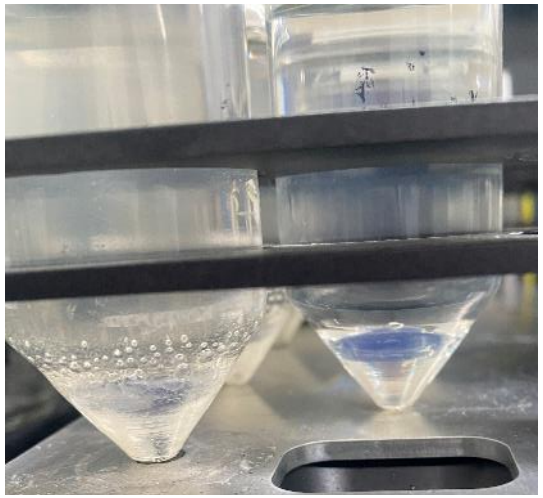
ePrep 3511 Step by Step Workflow Schematic



Images of setup and samples

ePrep Deck layout

7 different syringes required



DCM at bottom of the HR vial after vortex mixing

(Left) Dirty Water, (Right) Tap Water

Indicator addition at the end of the workflow to check pH

Experimental - Instrument and Standards

- An Agilent Technologies 8890 GC was coupled to a 7000E Triple Quad MS
- Base, neutral and acid calibration standard (EPA 8270) part number US-201-1 from Agilent
- PAH Deuterated Std in Methylene Chloride @ 4000ppm (4000ug/mL) from Chemservice PN – PPHC8X12-1ML

  Acenaphthene-d10

  Chrysene-d12

  1,4-Dichorobenzene-d4

  Naphthalene-d8

  Perylene-d12

  Phenanthrene-d10
- Phenol Deuterated Std in Methanol @ 2000ppm (2000ug/mL) from Chemservice PN – S-13001M51ML-1ML
- Synthetic Waste-Water (ASTM D5905, 625 Round Robin Study 2017)

  0.4g flour

  2g Ocean Salt

  0.08g Kalolin

  0.024g Triton X-100 surfactant

  120mL Beer

  Dilute to 2L with reagent grade water

Experimental - High Recovery Vial

Specifications: 47mL (Ø ≈ 36mm) High Recovery Glass flat bottom. Designed to be transportable.

Fill: Neck filled 45mL and to brim 47mL

Analysis: at 35mL

Availability: Vial manufacturer to ePrep design. Vials can be supplied with conformance certificate.

Labeling: Label can be affixed to diameter.

Concentration Factor: Approximately 17.5 (35mL final volume to 2mLs DCM

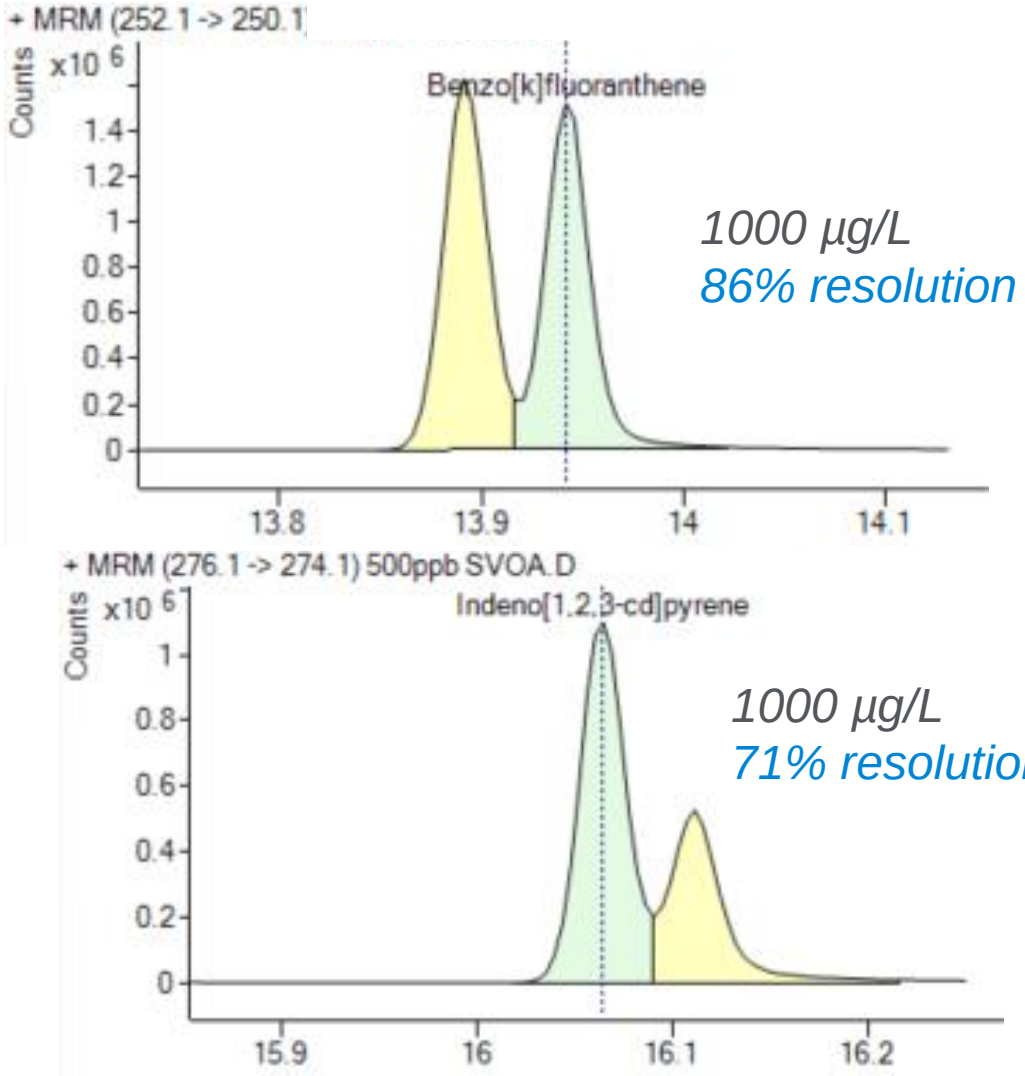
EPA 8270E List of Compounds Analyzed

Acenaphthene (83-32-9)
Acenaphthylene (208-96-8)
Aniline (62-53-3)
Anthracene (120-12-7)
Azobenzene (103-33-3)*
Benz[a]anthracene (56-55-3)
Benzo[a]pyrene (50-32-8)
Benzo[b]fluoranthene (205-99-2)
Benzo[g,h,i]perylene (191-24-2)
Benzo[k]fluoranthene (207-08-9)
Benzyl alcohol (100-51-6)
Benzyl butyl phthalate (85-68-7)
Bis(2-chloroethoxy)methane (111-91-1)
Bis(2-chloroethyl)ether (111-44-4)
Bis(2-ethylhexyl)adipate (103-23-1)
Bis(2-ethylhexyl)phthalate (117-81-7)
4-Bromophenyl phenyl ether (101-55-3)
Carbazole (86-74-8)
4-Chloroaniline (106-47-8)
4-Chloro-3-methylphenol (59-50-7)
2-Chloronaphthalene (91-58-7)
2-Chlorophenol (95-57-8)
4-Chlorophenyl phenyl ether (7005-72-3)
Chrysene (218-01-9)
Dibenz[a,h]anthracene (53-70-3)
Dibenzofuran (132-64-9)
1,2-Dichlorobenzene (95-50-1)
1,3-Dichlorobenzene (541-73-1)
1,4-Dichlorobenzene (106-46-7)
2,4-Dichlorophenol (120-83-2)
Diethylphthalate (84-66-2)
2,4-Dimethylphenol (105-67-9)
Dimethylphthalate (131-11-3)
Di-*n*-butyl phthalate (84-74-2)
1,2-Dinitrobenzene (528-29-0)
1,3-Dinitrobenzene (99-65-0)
1,4-Dinitrobenzene (100-25-4)
4,6-Dinitro-2-methylphenol (Dinitro-*o*-cresol) (534-52-1)
2,4-Dinitrophenol (51-28-5)
2,4-Dinitrotoluene (121-14-2)
2,6-Dinitrotoluene (606-20-2)
Di-*n*-octyl phthalate (117-84-0)
Diphenylamine (122-39-4)†
Fluoranthene (206-44-0)
Fluorene (86-73-7)
Hexachlorobenzene (118-74-1)
Hexachlorobutadiene (87-68-3)
Hexachlorocyclopentadiene (77-47-4)
Hexachloroethane (67-72-1)
Indeno[1,2,3-cd]pyrene (193-39-5)
Isophorone (78-59-1)
1-Methylnaphthalene (90-12-0)
2-Methylnaphthalene (91-57-6)
2-Methylphenol (*o*-cresol) (95-48-7)
3-Methylphenol (*m*-cresol) (108-39-4)
4-Methylphenol (*p*-cresol) (106-44-5)
Naphthalene (91-20-3)
2-Nitroaniline (88-74-4)
3-Nitroaniline (99-09-2)
4-Nitroaniline (100-01-6)
Nitrobenzene (98-95-3)
2-Nitrophenol (88-75-5)
4-Nitrophenol (100-02-7)
N-Nitrosodimethylamine (62-75-9)
N-Nitroso-di-*n*-propylamine (621-64-7)
2,2'-Oxybis(1-chloropropane) (108-60-1)
Pentachlorophenol (87-86-5)
Phenanthrene (85-01-8)
Phenol (108-95-2)
Pyrene (129-00-0)
Pyridine (110-86-1)
2,3,4,6-Tetrachlorophenol (58-90-2)
2,3,5,6-Tetrachlorophenol (935-95-5)
1,2,4-Trichlorobenzene (120-82-1)
2,4,5-Trichlorophenol (95-95-4)
2,4,6-Trichlorophenol (88-06-2)

Method parameters: 8890/7000E GC/TQ

<18-minute method

Parameter	Value
Injection Volume	1µL
Inlet	SSL @ 260°C or 280°C pulsed splitless mode 30 psi pulse until 0.6 min Purge 15mL/min at 0.75 min
Liner	Agilent Ultra Inert bottom frit liner
Column	DB-UI 8270D Column 30m x 250µm, 0.25mm
Carrier gas	Helium @ ~1.2mL/min constant flow Retention time locked to Acenaphthene-*d10* @7.08 min
Oven	40°C hold 0.5 Ramp 25°C/min → 260 Ramp 5°C/min → 280 Ramp 25°C/min → 320, hold 3 min
MSD Transfer Line	320°C



Why GC MS/MS?

Facilitates selective quantitation of target analytes in high chemical background samples

Better S/N in complex matrices when compared to single quad approaches

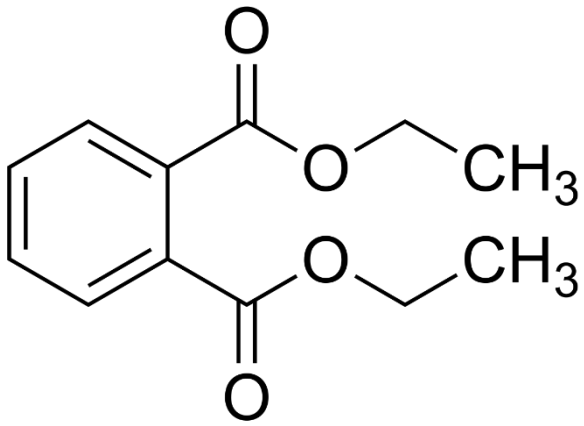
Femtogram levels of detection and quantification

Ability to meet stricter regulations regarding sample analytical limits for certain applications

What is MRM?

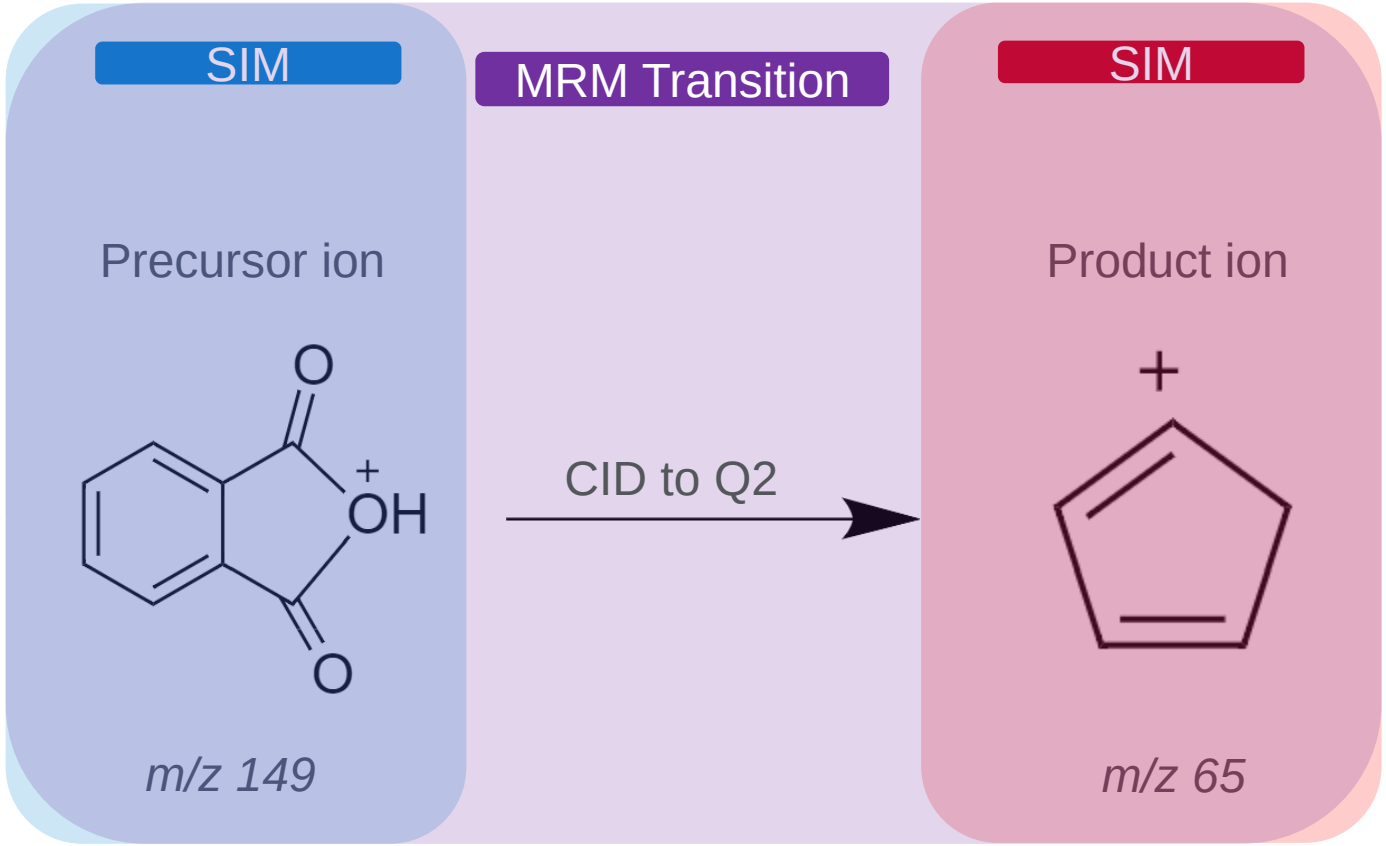
Multiple **R**eaction **M**onitoring

Diethyl phthalate

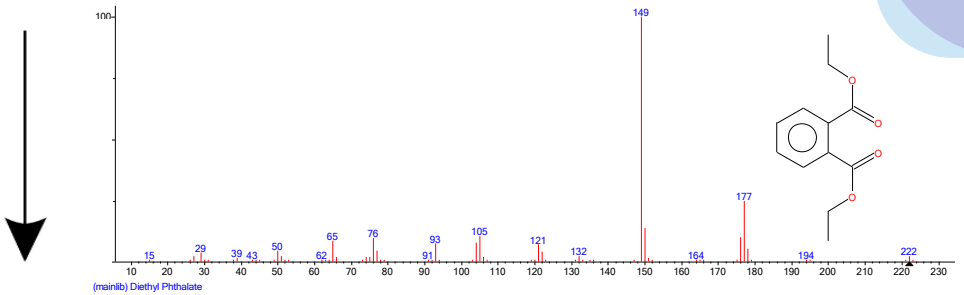


EI to Q1

Q1 only lets *m/z* *149* pass



CID to Q2



Other fragments

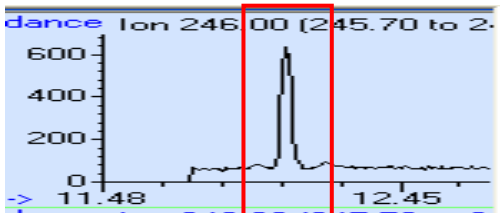
Comparison of GC/SQ SIM to GC/TQ MRM in Various Matrices

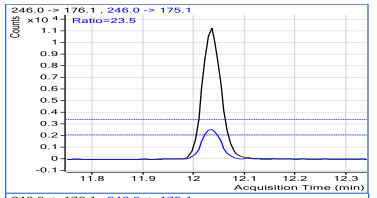
1 µL injection of p,p'-DDE at 10 ppb

SIM (246)

MRM

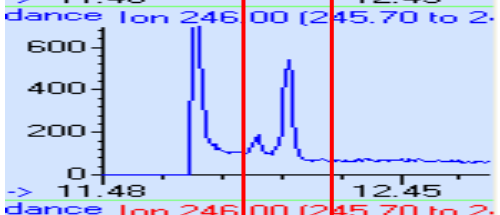
Apple

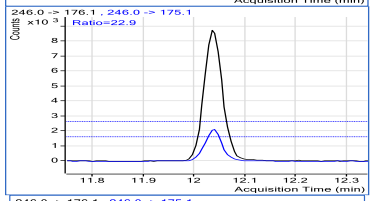




S/N = 448

Cabbage





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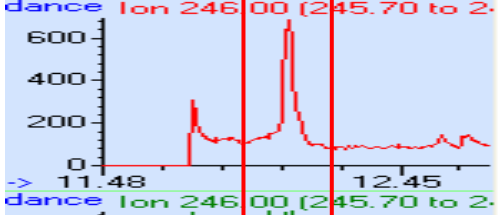
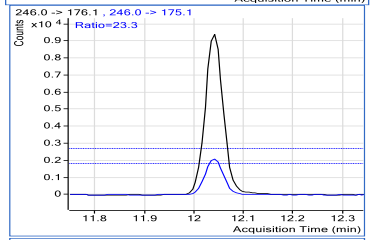
Ginseng





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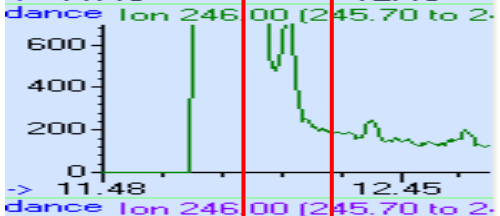
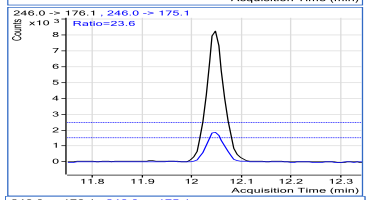
Orange





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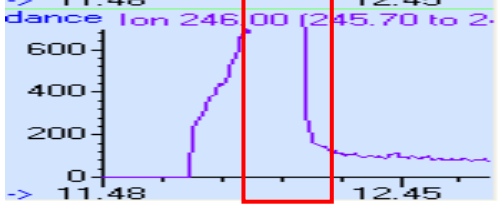
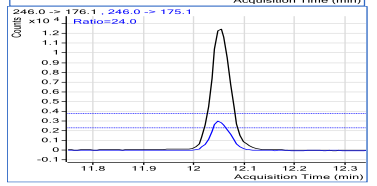
Spinach





S/N = 260

Increased Sensitivity and Selectivity Come with a Few Considerations

DFTPP Tuning

DFTPP tune checks no longer required for operation in MRM mode (8270E)

RTL

TQ methods containing long lists of analytes are best operated while retention time locked to maintain proper transition windows

MassHunter DA

MRM data cannot be processed by MSD ChemStation

- MH is superior software, faster processing than older MSD ChemStation software.

Automated Calibration Results for Standards

	Compounds	Transition	Retention Time	Cal range (ug/L)	LOD (ug/L)	Fit Type	R^2	Avg RF RSD	RSE %
1	NDMA	74.0 -> 44.0	1.99	2.0-1000	2.0	Avg RF		9.6	9.6
2	Pyridine	79.0 -> 51.0	2.07	100-1000	100	Quadratic	0.9994	30.3	6.1
3	Phenol	94.0 -> 66.1	3.80	1.0-1000	0.5	Avg RF		12.8	12.8
4	Aniline	93.0 -> 66.0	3.84	1.0-1000	0.5	Avg RF		18.3	18.3
5	bis(2-Chloroethyl)ether	93.1 -> 63.0	3.88	0.5-1000	0.5	Avg RF		7.3	7.3
6	2-Chlorophenol	128.0 -> 64.0	3.94	0.5-1000	0.5	Avg RF		11.7	11.7
7	1,3-Dichlorobenzene	146.0 -> 111.0	4.06	0.5-1000	0.5	Avg RF		4.0	4.0
8	1,4-Dichlorobenzene	146.0 -> 111.0	4.13	0.5-1000	0.5	Avg RF		2.8	2.8
9	1,2-Dichlorobenzene	146.0 -> 111.0	4.26	0.5-1000	0.5	Avg RF		4.2	4.2
10	2-Methylphenol	107.0 -> 77.0	4.32	1.0-1000	0.5	Avg RF		13.1	13.1
11	3+4-Methylphenol	108.0 -> 107.1	4.45	1.0-1000	0.5	Avg RF		8.9	8.9
12	Benzyl alcohol	108.0 -> 79.0	4.45	1.0-1000	1.0	Avg RF		14.3	14.3
13	4-chloro-3-methylphenol	107.0 -> 77.0	4.45	0.5-1000	0.5	Avg RF		8.3	8.3
14	N-Nitrosodi-n-propylamine	113.1 -> 71.0	4.46	0.5-1000	0.5	Avg RF		9.2	9.2
15	Hexachloroethane	200.9 -> 165.9	4.56	0.5-1000	0.5	Avg RF		4.8	4.8
16	Nitrobenzene	77.0 -> 51.0	4.61	1.0-1000	1.0	Avg RF		6.0	6.0
17	Isophorone	82.0 -> 54.0	4.83	0.5-1000	0.5	Avg RF		10.9	10.9
18	2-Nitrophenol	138.9 -> 81.0	4.90	0.5-1000	0.5	Avg RF		13.3	13.3
19	2,2'-oxybis[1-chloropropane]	121.0 -> 77.0	4.94	1.0-1000	1.0	Quadratic	0.9996	25.5	14.1
20	2,4-Dimethylphenol	107.1 -> 77.1	4.94	2.0-1000	1.0	Quadratic	0.9996	25.9	14.6
21	bis(2-Chloroethoxy)methane	93.0 -> 63.0	5.03	0.5-1000	0.5	Avg RF		5.5	5.5
22	Dichlorophenol, 2,4-	162.0 -> 63.0	5.12	0.5-1000	0.5	Avg RF		13.2	13.2
23	1,2,4-Trichlorobenzene	179.9 -> 145.0	5.20	0.5-1000	0.5	Avg RF		6.3	6.3
24	Naphthalene	128.1 -> 102.1	5.27	0.5-1000	0.5	Avg RF		17.5	17.5
25	4-Chloroaniline	127.0 -> 65.0	5.33	0.5-1000	0.5	Avg RF		8.4	8.4
26	Hexachlorobutadiene	224.7 -> 189.9	5.39	0.5-1000	0.5	Avg RF		3.0	3.0
27	2-Methylnaphthalene	142.0 -> 141.0	5.93	0.5-1000	0.5	Avg RF		10.8	10.8
28	1-Methylnaphthalene	142.0 -> 114.9	6.03	0.5-1000	0.5	Avg RF		5.7	5.7
29	Hexachlorocyclopentadiene	236.7 -> 143.0	6.08	0.5-1000	0.5	Avg RF		17.5	17.5
30	2,4,6-Trichlorophenol	195.8 -> 97.0	6.20	0.5-1000	0.5	Avg RF		17.3	17.3
31	2,4,5-Trichlorophenol	195.8 -> 97.0	6.24	1.0-500	0.5	Avg RF		16.8	16.8
32	Chloronaphthalene, 2-	162.0 -> 127.1	6.40	0.5-1000	0.5	Avg RF		3.3	3.3
33	2-Nitroaniline	138.0 -> 92.0	6.50	1.0-500	1.0	Avg RF		16.6	16.6
34	1,4-Dinitrobenzene	168.0 -> 75.0	6.64	2.0-1000	2.0	Quadratic	0.9997	31.8	11.7
35	Dimethyl phthalate	163.0 -> 77.0	6.69	0.5-1000	0.5	Avg RF		7.0	7

Automated Calibration Results for Standards

	Compounds	Transition	Retention Time	Cal range (ug/L)	LOD (ug/L)	Fit Type	R^2	Avg RF RSD	RSE %
36	1,3-Dinitrobenzene	168.0 -> 75.0	6.71	2.0-1000	2.0	Quadratic	0.9998	31.7	5.7
37	2,6-Dinitrotoluene	165.0 -> 90.1	6.74	0.5-1000	0.5	Quadratic	0.9995	30.3	15.5
38	1,2-Dinitrobenzene	168.0 -> 78.0	6.79	2.0-1000	2.0	Quadratic	0.9991	28.5	21.4
39	Acenaphthylene	151.9 -> 102.0	6.80	0.5-1000	0.5	Avg RF		6.0	6.0
40	3-Nitroaniline	138.0 -> 92.0	6.91	2.0-1000	2.0	Quadratic	0.9993	36.4	16.7
41	Acenaphthene	152.9 -> 77.0	6.97	0.5-1000	0.5	Avg RF		8.1	8.1
42	2,4-Dinitrophenol	184.0 -> 107.0	7.01	10-1000	10.0	Quadratic	0.9995	39.6	9.1
43	4-Nitrophenol	138.9 -> 109.0	7.08	10-1000	10.0	Quadratic	0.9995	36.4	10.7
44	2,4-Dinitrotoluene	165.0 -> 119.0	7.13	1.0-1000	1.0	Quadratic	0.9997	34.4	12.8
45	Dibenzofuran	167.9 -> 139.1	7.15	0.5-1000	0.5	Avg RF		3.3	3.3
46	2,3,5,6-Tetrachlorophenol	230.0 -> 165.9	7.22	2.0-1000	1.0	Avg RF		17.2	17.2
47	2,3,4,6-Tetrachlorophenol	230.0 -> 165.9	7.27	1.0-1000	1.0	Avg RF		19.6	19.6
48	Diethyl phthalate	149.0 -> 65.0	7.38	2.0-1000	0.5	Avg RF		11.2	11.2
49	Fluorene	166.0 -> 165.1	7.48	0.5-1000	0.5	Avg RF		3.7	3.7
50	4-Chlorophenyl phenyl ether	141.1 -> 115.1	7.49	0.5-1000	0.5	Avg RF		3.5	3.5
51	4-Nitroaniline	138.0 -> 108.1	7.50	5.0-1000	5.0	Quadratic	0.9995	34.5	12.0
52	2-methyl-4,6-dinitrophenol	198.0 -> 121.0	7.53	5.0-1000	5.0	Quadratic	0.9996	24.9	9.6
53	Diphenylamine	167.0 -> 166.2	7.60	0.5-1000	0.5	Avg RF		12.6	12.6
54	Azobenzene	77.0 -> 51.0	7.64	0.5-1000	0.5	Avg RF		10.1	10.1
55	4-bromophenyl phenyl ether	248.0 -> 141.0	7.97	0.5-1000	0.5	Avg RF		3.7	3.7
56	Hexachlorobenzene	248.7 -> 214.0	8.02	0.5-1000	0.5	Avg RF		4.7	4.7
57	Pentachlorophenol	265.7 -> 167.0	8.22	1.0-1000	1.0	Quadratic	0.9997	29.4	13.4
58	Phenanthrene	177.9 -> 152.0	8.43	0.5-1000	0.5	Avg RF		5.2	5.2
59	Anthracene	177.9 -> 152.0	8.48	0.5-1000	0.5	Avg RF		7.3	7.3
60	Carbazole	167.0 -> 139.0	8.64	0.5-1000	0.5	Avg RF		15.8	15.8
61	Di-n-butyl phthalate	149.0 -> 65.0	9.01	1.0-500	0.5	Avg RF		19.4	19.4
62	Fluoranthene	200.9 -> 199.9	9.62	0.5-1000	0.5	Avg RF		8.9	8.9
63	Pyrene	201.1 -> 200.0	9.86	0.5-1000	0.5	Avg RF		7.6	7.6
64	Butyl benzyl phthalate	149.0 -> 65.0	10.72	1.0-1000	0.5	Avg RF		17.8	17.8
65	Benz[a]anthracene	228.1 -> 226.1	11.55	0.5-1000	0.5	Avg RF		15.5	15.5
66	Chrysene	226.1 -> 224.1	11.61	0.5-1000	0.5	Avg RF		11.9	11.9
67	Bis(2-ethylhexyl) phthalate	149.0 -> 65.0	11.7	2.0-1000	0.5	Avg RF		17.2	17.2
68	Di-n-octyl phthalate	149.0 -> 65.0	13.05	0.5-1000	0.5	Avg RF		9.3	9.3
69	Benzo[b]fluoranthene	252.1 -> 250.1	13.65	1.0-500	0.5	Avg RF		15.7	15.7
70	Benzo[k]fluoranthene	252.1 -> 250.1	13.70	0.5-500	0.5	Avg RF		22.6	22.6
71	Benzo[a]pyrene	252.1 -> 250.1	14.21	0.5-500	0.5	Avg RF		20.5	20.5
72	Indeno[1,2,3-cd]pyrene	137.0 -> 136.0	15.81	2.0-500	1.0	Avg RF		13.1	13.1
73	Dibenz[a,h]anthracene	278.1 -> 276.1	15.86	1.0-1000	0.5	Quadratic	0.9973	33.4	24.3
74	Benzo[g,h,i]perylene	138.0 -> 137.0	16.21	0.5-1000	0.5	Avg RF		12.2	12.2

Low Level Spikes

- Concentration Level : 10ppb
- Matrix type: Tap Water
- # of replicates: 7
- Addition of one “Dirty Water” (synthetic wastewater) spike was done as well

Highlights

Compound	Avg Conc 7 Replicates	Dirty Water Spike	DW % recovery compared to Tap water
bis(2-Chloroethyl)ether	9.93	11.5	115.9%
1,4-Dichlorobenzene	9.13	8.5	92.8%
Naphthalene	8.80	8.5	96.5%

	Name	Avg Conc.	Std. Dev.	Conc. RSD	MDL	LOQ	LOD	Dirty Water 10ppb spike
1	NDMA	1.40	0.18	12.7	0.56	1.78	0.53	ND
2	Pyridine	ND	N/A	N/A	N/A	N/A	N/A	ND
3	Phenol	3.23	0.10	3.1	0.32	1.00	0.30	5.6
4	Aniline	0.34	0.20	59.7	0.63	2.01	0.60	0.5
5	bis(2-Chloroethyl)ether	9.93	0.40	4.0	1.26	4.02	1.21	11.5
6	2-Chlorophenol	8.73	0.49	5.6	1.55	4.92	1.48	11.2
7	1,3-Dichlorobenzene	8.47	0.18	2.1	0.57	1.81	0.54	8.0
8	1,4-Dichlorobenzene	9.13	0.26	2.8	0.81	2.58	0.77	8.5
9	1,2-Dichlorobenzene	9.31	0.26	2.8	0.81	2.58	0.77	8.9
10	2-Methylphenol	8.06	0.86	10.6	2.69	8.57	2.57	9.3
11	3+4-Methylphenol	6.63	0.23	3.4	0.71	2.27	0.68	10.8
12	Benzyl alcohol	7.40	0.52	7.0	1.64	5.21	1.56	11.5
13	4-chloro-3-methylphenol	6.77	0.23	3.4	0.72	2.28	0.68	10.6
14	N-Nitrosodi-n-propylamine	11.70	0.38	3.3	1.20	3.83	1.15	14.4
15	Hexachloroethane	7.52	0.18	2.4	0.57	1.83	0.55	5.3
16	Nitrobenzene	10.37	0.87	8.4	2.74	8.72	2.62	185.0
17	Isophorone	9.31	0.38	4.1	1.21	3.84	1.15	13.2
18	2-Nitrophenol	10.07	0.42	4.1	1.31	4.17	1.25	13.9
19	2,2'-oxybis[1-chloropropane]	11.02	0.34	3.1	1.07	3.42	1.03	18.0
20	Dimethylphenol, 2,4-	11.18	0.59	5.2	1.84	5.85	1.75	17.2
21	bis(2-Chloroethoxy)methane	9.52	0.17	1.8	0.54	1.72	0.52	12.4
22	Dichlorophenol, 2,4-	9.59	0.46	4.8	1.44	4.57	1.37	14.3
23	1,2,4-Trichlorobenzene	8.36	0.21	2.5	0.67	2.12	0.64	6.1
24	Naphthalene	8.80	0.27	3.1	0.85	2.69	0.81	8.5
25	4-Chloroaniline	0.23	0.03	11.8	0.09	0.27	0.08	0.2
26	Hexachlorobutadiene	6.09	0.12	1.9	0.37	1.19	0.36	3.3
27	2-Methylnaphthalene	8.92	0.23	2.6	0.73	2.34	0.70	6.5
28	1-Methylnaphthalene	9.51	0.30	3.2	0.95	3.02	0.91	7.5
29	Hexachlorocyclopentadiene	7.06	0.52	7.3	1.62	5.17	1.55	3.4
30	2,4,6-Trichlorophenol	10.27	0.40	3.9	1.25	3.99	1.20	15.4
31	2,4,5-Trichlorophenol	9.35	0.53	5.7	1.68	5.34	1.60	15.2
32	Chloronaphthalene, 2-	9.38	0.29	3.1	0.91	2.91	0.87	6.6
33	2-Nitroaniline	8.81	0.35	4.0	1.11	3.53	1.06	13.2
34	1,4-Dinitrobenzene	9.71	0.94	9.7	2.96	9.43	2.83	18.7
35	Dimethyl phthalate	9.69	0.31	3.1	0.96	3.05	0.92	19.1

Low Level Spikes

- Concentration Level : 10ppb
- Matrix type: Tap Water
- # of replicates: 7
- Addition of one “Dirty Water” (synthetic wastewater) spike was done as well

Highlights

Compound	Avg Conc 7 Replicates	Dirty Water Spike	DW % recovery compared to Tap water
Acenaphthene	9.20	10.5	114.4%
4-Chlorophenyl phenyl ether	9.44	6.5	68.8%
4-bromophenyl phenyl ether	9.00	8.1	90.2%
Chrysene	9.18	10.0	108.7%

	Name	Avg Conc.	Std. Dev.	Conc. RSD	MDL	LOQ	LOD	Dirty Water 10ppb spike
36	1,2-Dinitrobenzene	9.60	0.68	7.1	2.14	6.82	2.05	18.4
37	2,6-Dinitrotoluene	9.10	0.31	3.4	0.98	3.12	0.94	14.9
38	1,3-Dinitrobenzene	8.61	0.91	10.6	2.86	9.09	2.73	15.4
39	Acenaphthylene	7.78	0.19	2.4	0.60	1.90	0.57	11.2
40	3-Nitroaniline	2.48	0.09	3.8	0.29	0.94	0.28	2.6
41	Acenaphthene	9.20	0.30	3.3	0.95	3.03	0.91	10.5
42	2,4-Dinitrophenol	17.51	1.60	9.1	5.02	15.96	4.79	19.0
43	4-Nitrophenol	9.32	0.56	6	1.75	5.58	1.67	17.3
44	2,4-Dinitrotoluene	9.20	0.37	4	1.16	3.69	1.11	15.8
45	Dibenzofuran	9.52	0.30	3.2	0.95	3.03	0.91	9.1
46	2,3,5,6-Tetrachlorophenol	10.40	0.62	6	1.96	6.23	1.87	20.2
47	2,3,4,6-Tetrachlorophenol	10.43	0.50	4.8	1.58	5.01	1.50	23.0
48	Diethyl phthalate	12.59	0.52	4.1	1.64	5.21	1.56	24.3
49	Fluorene	9.55	0.26	2.8	0.83	2.64	0.79	8.4
50	4-Chlorophenyl phenyl ether	9.44	0.34	3.5	1.05	3.35	1.01	6.5
51	4-Nitroaniline	6.58	0.21	3.2	0.66	2.11	0.63	7.2
52	2-methyl-4,6-dinitrophenol	12.65	1.03	8.1	3.24	10.30	3.09	13.5
53	Diphenylamine	6.94	0.58	8.4	1.83	5.83	1.75	19.5
54	Azobenzene	8.82	0.19	2.1	0.59	1.89	0.57	12.4
55	4-bromophenyl phenyl ether	9.00	0.29	3.3	0.92	2.93	0.88	8.1
56	Hexachlorobenzene	8.38	0.27	3.2	0.85	2.70	0.81	6.6
57	Pentachlorophenol	11.78	0.49	4.2	1.54	4.90	1.47	27.0
58	Phenanthrene	9.15	0.31	3.4	0.97	3.08	0.92	9.9
59	Anthracene	7.95	0.25	3.2	0.79	2.50	0.75	10.1
60	Carbazole	8.55	0.13	1.5	0.41	1.29	0.39	26.0
61	Di-n-butyl phthalate	11.98	0.26	2.1	0.80	2.56	0.77	38.3
62	Fluoranthene	9.66	0.61	6.4	1.93	6.14	1.84	12.5
63	Pyrene	9.70	0.52	5.3	1.63	5.18	1.55	13.4
64	Butyl benzyl phthalate	9.39	0.46	4.9	1.44	4.60	1.38	35.0
65	Benz[a]anthracene	8.00	0.17	2.1	0.53	1.67	0.50	10.8
66	Chrysene	9.18	1.31	14.3	4.12	13.12	3.94	10.0
67	Bis(2-ethylhexyl) phthalate	41.60	2.46	5.9	7.73	24.60	7.38	183.8
68	Di-n-octyl phthalate	6.94	0.51	7.4	1.61	5.13	1.54	11.8
69	Benzo[b]fluoranthene	8.17	0.35	4.3	1.12	3.55	1.06	11.4
70	Benzo[k]fluoranthene	6.92	1.73	25	5.43	17.29	5.19	10.1
71	Benzo[a]pyrene	7.24	0.33	4.5	1.03	3.27	0.98	11.5
72	Indeno[1,2,3-cd]pyrene	7.09	0.26	3.7	0.81	2.59	0.78	9.1
73	Dibenz[a,h]anthracene	6.41	0.31	4.9	0.98	3.11	0.93	10.1
74	Benzo[g,h,i]perylene	7.01	0.32	4.5	0.99	3.15	0.95	7.9

High Level Spikes

- Concentration Level : 500ppb
- Matrix type: Tap Water
- # of replicates: 7
- Addition of one “Dirty Water” (synthetic wastewater) spike was done as well

Highlights

Compound	Avg Conc 7 Replicates	Dirty Water Spike	DW % recovery compared to Tap water
Nitrobenzene	553	550	99.4%
bis(2-Chloroethoxy)methane	476	566	118.9%
1-Methylnaphthalene	414	353	85.2%

	Name	Avg Conc.	Std. Dev.	Avg Conc/Std Dev	Conc. RSD	MDL	LOQ	LOD	Dirty Water High spike 500ppb
1	NDMA	82	4.1	19.8	5.0	12.9	41.2	12.4	ND
2	Pyridine	148	29.4	5.0	19.9	92.5	294.2	88.3	98
3	Phenol	194	6.5	30.0	3.3	20.4	64.8	19.4	266
4	Aniline	7	0.8	8.8	11.4	2.4	7.6	2.3	8.6
5	bis(2-Chloroethyl)ether	541	15.2	35.5	2.8	47.9	152.3	45.7	631
6	2-Chlorophenol	498	11.1	45.0	2.2	34.8	110.7	33.2	652
7	1,3-Dichlorobenzene	452	9.9	45.5	2.2	31.2	99.3	29.8	453
8	1,4-Dichlorobenzene	426	12.3	34.6	2.9	38.7	123.1	36.9	425
9	1,2-Dichlorobenzene	426	11.2	38.0	2.6	35.2	112.0	33.6	423
10	2-Methylphenol	398	12.5	31.8	3.1	39.3	125.1	37.5	532
11	3+4-Methylphenol	374	6.8	55.1	1.8	21.4	68.0	20.4	493
12	Benzyl alcohol	389	22.2	17.5	5.7	69.7	221.7	66.5	517
13	4-chloro-3-methylphenol	370	6.4	57.9	1.7	20.1	63.9	19.2	478
14	N-Nitrosodi-n-propylamine	531	10.8	49.0	2.0	34.0	108.3	32.5	629
15	Hexachloroethane	407	13.0	31.2	3.2	41.0	130.4	39.1	303
16	Nitrobenzene	553	13.1	42.3	2.4	41.1	130.7	39.2	550
17	Isophorone	484	12.3	39.2	2.5	38.7	123.3	37.0	607
18	2-Nitrophenol	573	17.5	32.8	3.0	54.9	174.6	52.4	808
19	2,2'-oxybis[1-chloropropane]	486	6.8	71.4	1.4	21.4	68.1	20.4	673
20	Dimethylphenol, 2,4- (2,4-xylenol)	482	8.6	56.2	1.8	26.9	85.7	25.7	644
21	bis(2-Chloroethoxy)methane	476	11.2	42.7	2.3	35.1	111.6	33.5	566
22	Dichlorophenol, 2,4-	557	15.2	36.7	2.7	47.7	151.8	45.5	798
23	1,2,4-Trichlorobenzene	414	10.5	39.3	2.5	33.1	105.5	31.6	340
24	Naphthalene	399	9.9	40.2	2.5	31.2	99.3	29.8	396
25	4-Chloroaniline	11	0.6	16.6	6.0	2.0	6.4	1.9	10.7
26	Hexachlorobutadiene	359	11.8	30.5	3.3	37.0	117.9	35.4	198
27	2-Methylnaphthalene	406	10.8	37.6	2.7	34.0	108.1	32.4	321
28	1-Methylnaphthalene	414	10.5	39.3	2.5	33.1	105.4	31.6	353
29	Hexachlorocyclopentadiene	354	24.5	14.5	6.9	76.9	244.8	73.5	222
30	2,4,6-Trichlorophenol	652	38.7	16.9	5.9	121.5	386.5	116.0	1022
31	2,4,5-Trichlorophenol	701	36.4	19.3	5.2	114.4	364.0	109.2	1027
32	Chloronaphthalene, 2-	452	11.1	40.6	2.5	35.0	111.2	33.4	336
33	2-Nitroaniline	630	23.0	27.4	3.6	72.3	230.0	69.0	843
34	1,4-Dinitrobenzene	525	16.4	32.0	3.1	51.5	163.8	49.1	776
35	Dimethyl phthalate	482	11.9	40.4	2.5	37.5	119.4	35.8	875

High Level Spikes

- Concentration Level : 500ppb
- Matrix type: Tap Water
- # of replicates: 7
- Addition of one “Dirty Water” (synthetic wastewater) spike was done as well

Highlights

Compound	Avg Conc 7 Replicates	Dirty Water Spike	DW % recovery compared to Tap water
Acenaphthylene	467.6	561	120.0%
Dibenzofuran	454.5	453	99.7%
4-Chlorophenyl phenyl ether	408.2	305	74.7%
Chrysene	440.4	447	101.5%

	Name	Avg Conc.	Std. Dev.	Avg Conc/Std Dev	Conc. RSD	MDL	LOQ	LOD	Dirty Water High spike 500ppb
36	1,2-Dinitrobenzene	531.0	17.0	31.3	3.2	53.4	169.8	50.9	795
37	2,6-Dinitrotoluene	533.7	15.3	34.8	2.9	48.1	153.2	46.0	771
38	1,3-Dinitrobenzene	534.2	16.2	33.0	3.0	50.9	162.0	48.6	774
39	Acenaphthylene	467.6	16.3	28.7	3.5	51.3	163.1	48.9	561
40	3-Nitroaniline	81.3	1.9	42.0	2.4	6.1	19.4	5.8	134
41	Acenaphthene	508.9	19.2	26.6	3.8	60.2	191.6	57.5	564
42	2,4-Dinitrophenol	527.4	16.0	32.9	3.0	50.4	160.4	48.1	647
43	4-Nitrophenol	298.8	10.3	29.0	3.5	32.4	103.1	30.9	649
44	2,4-Dinitrotoluene	532.9	18.6	28.7	3.5	58.4	185.7	55.7	748
45	Dibenzofuran	454.5	11.3	40.2	2.5	35.6	113.2	34.0	453
46	2,3,5,6-Tetrachlorophenol	702.1	40.4	17.4	5.8	127.0	404.0	121.2	1313
47	2,3,4,6-Tetrachlorophenol	767.2	50.7	15.1	6.6	159.2	506.6	152.0	1467
48	Diethyl phthalate	506.4	14.5	35.0	2.9	45.5	144.8	43.4	735
49	Fluorene	453.3	12.8	35.4	2.8	40.2	128.0	38.4	408
50	4-Chlorophenyl phenyl ether	408.2	12.7	32.2	3.1	39.9	127.0	38.1	305
51	4-Nitroaniline	306.8	8.0	38.3	2.6	25.2	80.1	24.0	513
52	2-methyl-4,6-dinitrophenol	500.9	13.1	38.4	2.6	41.0	130.6	39.2	807
53	Diphenylamine	482.1	16.7	28.8	3.5	52.6	167.4	50.2	908
54	Azobenzene	473.0	16.4	28.9	3.5	51.4	163.5	49.1	517
55	4-bromophenyl phenyl ether	426.8	12.2	35.1	2.8	38.2	121.6	36.5	389
56	Hexachlorobenzene	349.7	13.5	26.0	3.9	42.3	134.6	40.4	269
57	Pentachlorophenol	552.1	29.9	18.5	5.4	93.9	298.7	89.6	1005
58	Phenanthrene	423.5	12.2	34.7	2.9	38.3	121.9	36.6	447
59	Anthracene	442.2	19.2	23.0	4.4	60.5	192.5	57.7	474
60	Carbazole	591.1	17.9	33.1	3.0	56.1	178.5	53.6	1276
61	Di-n-butyl phthalate	523.3	36.1	14.5	6.9	113.4	360.7	108.2	692
62	Fluoranthene	423.1	40.9	10.4	9.7	128.5	409.0	122.7	503
63	Pyrene	429.2	40.3	10.6	9.4	126.8	403.4	121.0	520
64	Butyl benzyl phthalate	475.9	30.0	15.9	6.3	94.2	299.8	89.9	1051
65	Benz[a]anthracene	504.6	14.9	34.0	2.9	46.7	148.6	44.6	572
66	Chrysene	440.4	9.8	45.0	2.2	30.8	97.9	29.4	447
67	Bis(2-ethylhexyl) phthalate	485.2	65.4	7.4	13.5	205.4	653.6	196.1	802
68	Di-n-octyl phthalate	401.2	41.3	9.7	10.3	129.8	412.9	123.9	796
69	Benzo[b]fluoranthene	586.8	18.2	32.2	3.1	57.3	182.2	54.7	539
70	Benzo[k]fluoranthene	538.8	30.9	17.5	5.7	97.0	308.8	92.6	460
71	Benzo[a]pyrene	643.2	19.3	33.3	3.0	60.7	193.0	57.9	584
72	Indeno[1,2,3-cd]pyrene	581.7	22.1	26.4	3.8	69.4	220.8	66.2	475
73	Dibenz[a,h]anthracene	468.5	14.8	31.7	3.2	46.5	148.0	44.4	416
74	Benzo[g,h,i]perylene	456.3	21.6	21.1	4.7	67.9	215.9	64.8	337

Phenol spike recoveries

Low Spikes: Conc 10ppb N=7 for spike replicates

	1,4 DCB-d4 used as ISTD				Phenol-d6 used as ISTD			
	Avg Conc.	% Recovery	Dirty Water spike	% Recovery	Avg Conc	% Recovery	Dirty Water Spike	% Recovery
Phenol	3.3ppb	33%	5.6ppb	56%	10.3ppb	103%	11.5ppb	115%

High Spikes: Conc 500ppb N=7 for spike replicates

	1,4 DCB-d4 used as ISTD				Phenol-d6 used as ISTD			
	Avg Conc.	% Recovery	Dirty Water spike	% Recovery	Avg Conc	% Recovery	Dirty Water Spike	% Recovery
Phenol	194ppb	39%	266ppb	53%	410ppb	82%	364ppb	73%

Conclusion

- Automated calibration preparation was very accurate, 80% using RSD % and 20% using quadratic fits
- Total time for automated preparation of 18 water samples was between 4.5-5hrs, with only short lead time to set instrument up. Capacity for 70 samples.
- Running prepared samples on 7000E GCMSMS leads to lower background, better detection limits, allowing for micro extraction prep
- Phenol Recovery typically around 40% (external std quantitation) and 80-100% (surrogate quantitation)
- Blank Tap water sample and blank dirty water sample prepared with spike samples; no carryover observed
- LOD instrument calibration observed at 0.5ppb or 1.0ppb for most compounds (88% of targets)

Questions?

Thank you!

Agilent

Trusted Answers

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