SPE in US EPA Method 625, the Performance of Smaller Samples

Zoe Grosser, Michael Ebitson, Alicia Cannon,
Horizon Technology, Salem NH USA
Brahm Prakash, William Lipps, and Tairo Ogura,
Shimadzu Scientific Instruments, Columbia, MD USA

Introduction

- Smaller samples provide many advantages for laboratories, including:
  - Less shipping costs
  - Easier to handle and store than large bottles
- The use of solid phase extraction (SPE), rather than liquid-liquid extraction uses:
  - Less solvent and
  - Creates less waste
- Although concerns about homogeneity of smaller samples (100 mL vs 1L) have been raised, there has been no evidence of problems related to homogeneity
- This work examines the use of small samples for reagent water and two challenging matrices using SPE with method 625 for a full suite of analytes

Introduction

- Solid-phase extraction has been developing for more than three decades and is well characterized and used in both disk and cartridge formats
- Used extensively in environmental applications to capture analytes
- Used in food sample preparation to capture analytes or for cleanup, capturing unwanted materials

Regulatory Methods

- Many drinking water methods include SPE as an alternative or the only extraction method
- Included in US EPA SW-846 sample prep method 3535A
- Can be coupled with methods 8270, 8081, 8082, 8061, 8141, 8330, 8095 and 8321 for the determinative step
- US EPA method 608, a wastewater method incorporating solid phase extraction (ATP for disk technology), included in MUR
- Method 1664 is a popular method incorporating SPE for Oil & Grease extraction
- Method 625 in the MUR will include SPE as an alternative with certain requirements

Surrogates

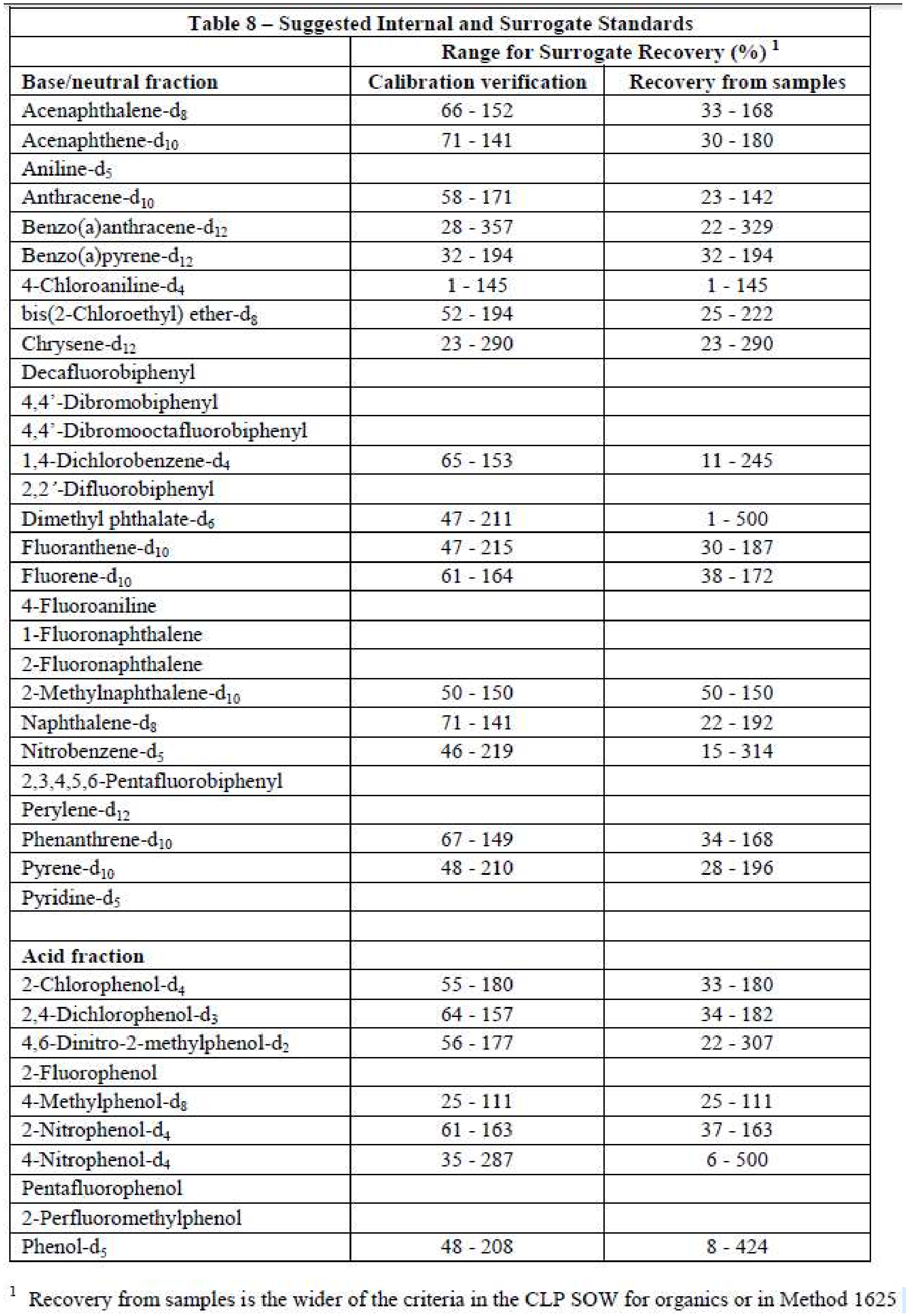


Table 8 – Suggested Internal and Surrogate Standards

	Range for Surrogate Recovery (%)[1]	
Base/neutral fraction	**Calibration verification**	**Recovery from samples**
Acenaphthalene-d$_8$	66 - 152	33 - 168
Acenaphthene-d$_{10}$	71 - 141	30 - 180
Aniline-d$_5$		
Anthracene-d$_{10}$	58 - 171	23 - 142
Benzo(a)anthracene-d$_{12}$	28 - 357	22 - 329
Benzo(a)pyrene-d$_{12}$	32 - 194	32 - 194
4-Chloroaniline-d$_4$	1 - 145	1 - 145
bis(2-Chloroethyl) ether-d$_8$	52 - 194	25 - 222
Chrysene-d$_{12}$	23 - 290	23 - 290
Decafluorobiphenyl		
4,4'-Dibromobiphenyl		
4,4'-Dibromooctafluorobiphenyl		
1,4-Dichlorobenzene-d$_4$	65 - 153	11 - 245
2,2'-Difluorobiphenyl		
Dimethyl phthalate-d$_6$	47 - 211	1 - 500
Fluoranthene-d$_{10}$	47 - 215	30 - 187
Fluorene-d$_{10}$	61 - 164	38 - 172
4-Fluoroaniline		
1-Fluoronaphthalene		
2-Fluoronaphthalene		
2-Methylnaphthalene-d$_{10}$	50 - 150	50 - 150
Naphthalene-d$_8$	71 - 141	22 - 192
Nitrobenzene-d$_5$	46 - 219	15 - 314
2,3,4,5,6-Pentafluorobiphenyl		
Perylene-d$_{12}$		
Phenanthrene-d$_{10}$	67 - 149	34 - 168
Pyrene-d$_{10}$	48 - 210	28 - 196
Pyridine-d$_5$		
Acid fraction		
2-Chlorophenol-d$_4$	55 - 180	33 - 180
2,4-Dichlorophenol-d$_3$	64 - 157	34 - 182
4,6-Dinitro-2-methylphenol-d$_2$	56 - 177	22 - 307
2-Fluorophenol		
4-Methylphenol-d$_8$	25 - 111	25 - 111
2-Nitrophenol-d$_4$	61 - 163	37 - 163
4-Nitrophenol-d$_4$	35 - 287	6 - 500
Pentafluorophenol		
2-Perfluoromethylphenol		
Phenol-d$_5$	48 - 208	8 - 424

[1] Recovery from samples is the wider of the criteria in the CLP SOW for organics or in Method 1625

Older 625 Versions

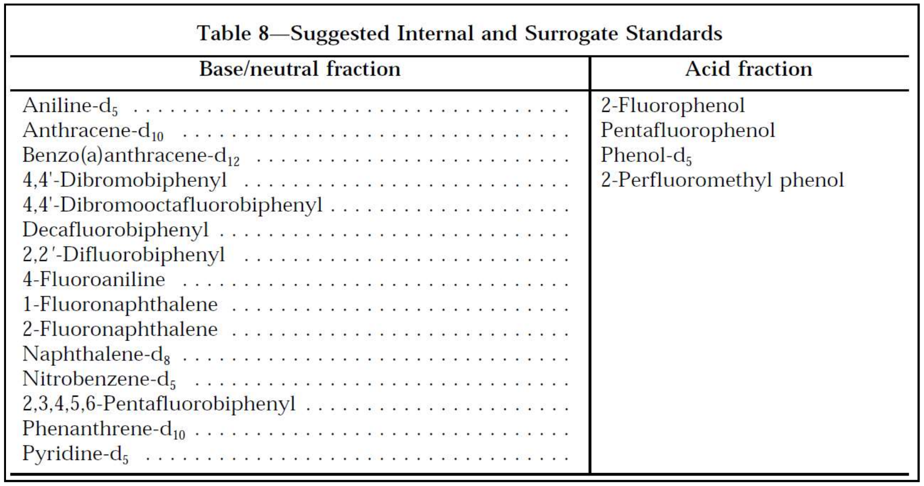


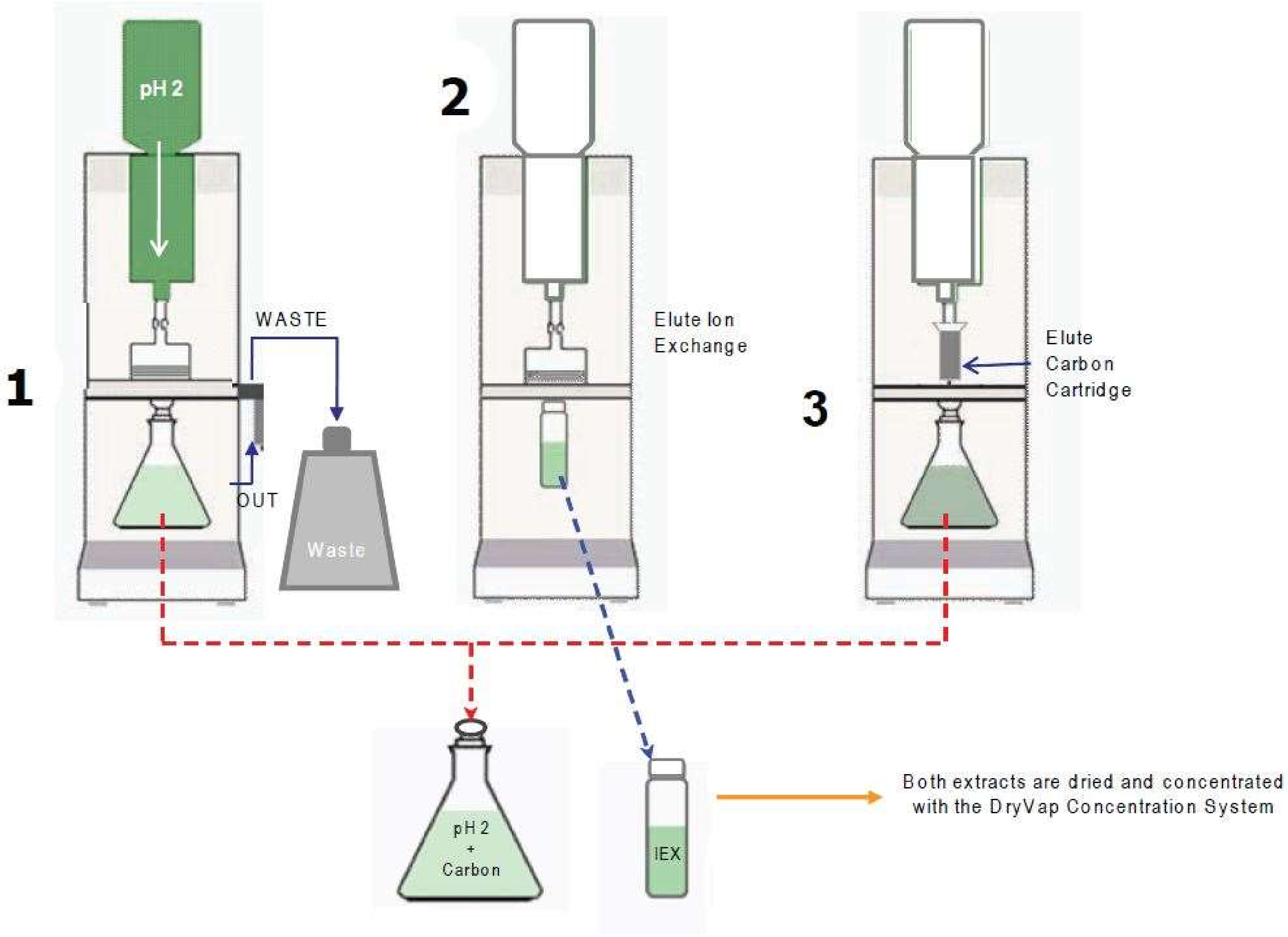
Table 8—Suggested Internal and Surrogate Standards

Base/neutral fraction	Acid fraction
Aniline-d$_5$	2-Fluorophenol
Anthracene-d$_{10}$	Pentafluorophenol
Benzo(a)anthracene-d$_{12}$	Phenol-d$_5$
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthalene	
2-Fluoronaphthalene	
Naphthalene-d$_8$	
Nitrobenzene-d$_5$	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene-d$_{10}$	
Pyridine-d$_5$	

Spiking Material

- Spiking with a full suite of analytes was done for wastewater samples
- Single blind mix with a variety of compounds (Phenova Reference Materials) was used for spiking water, wastewater and TCLP matrix

One-Pass process



Both extracts are dried and concentrated with the DryVap Concentration System

Hardware for Automated SPE, Drying, and Concentration

SPE-DEX® 4790
Extractor

DryVap®
Drying and Concentrator System

Solid Phase Extraction and Drying Consumables

Atlantic® 8270 One Pass Disk (47 mm)

- Multi-modal media disk.
- Extracts BNA (bases, neutrals and acids) at pH 2.
- Eliminates sample basification step and extraction.
  - Saves time
  - Avoids metal hydroxide precipitation.

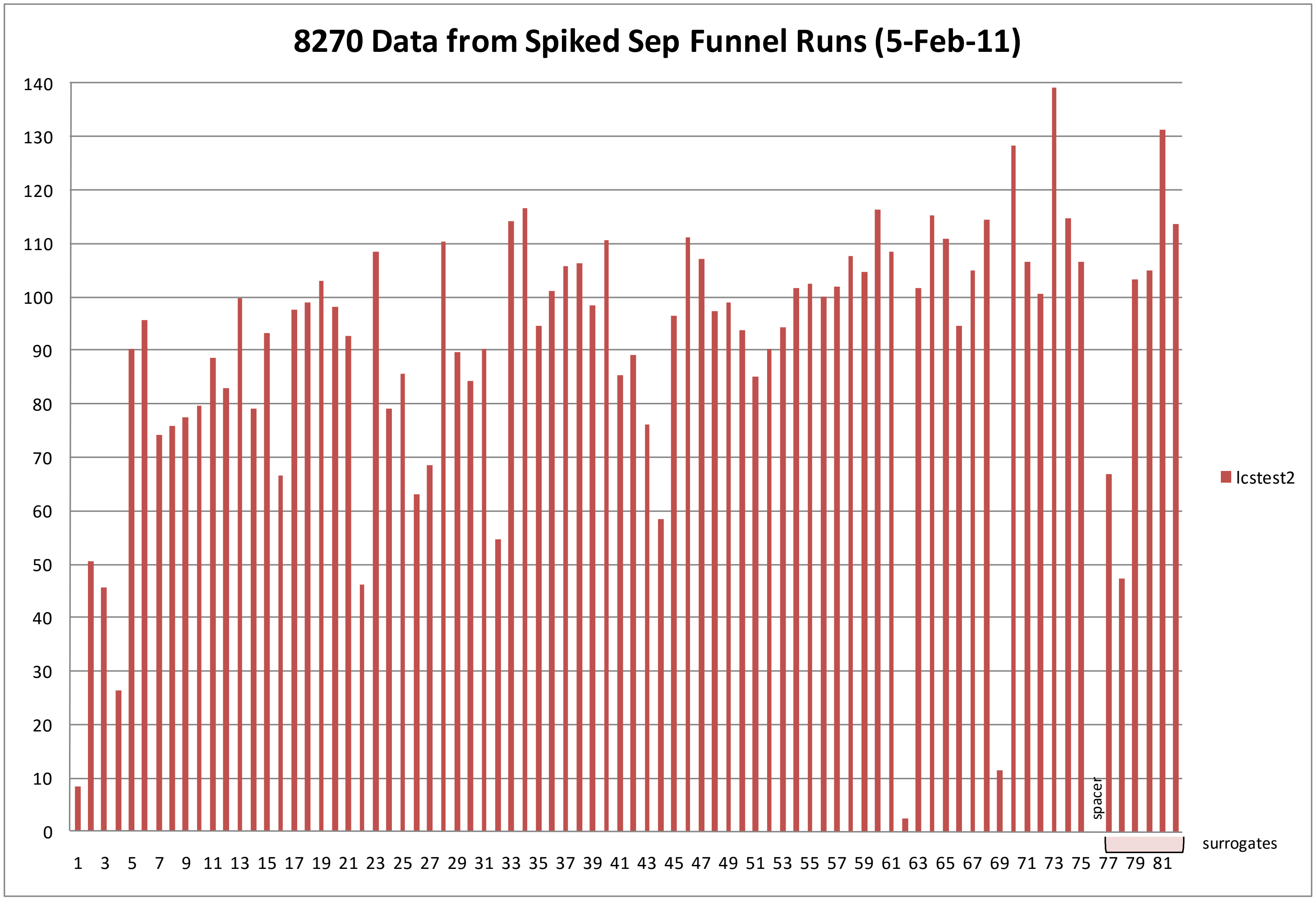
Max Detect Carbon Cartridge

- Recovers light-end organics from post-disk sample effluent.
- e.g., NDMA, benzyl alcohol, & methyl methanesulfonate.

DryDisk® Separation Membrane

- Efficiently removes water from extract.
- Unlimited capacity for water.
- Eliminates sodium sulfate.

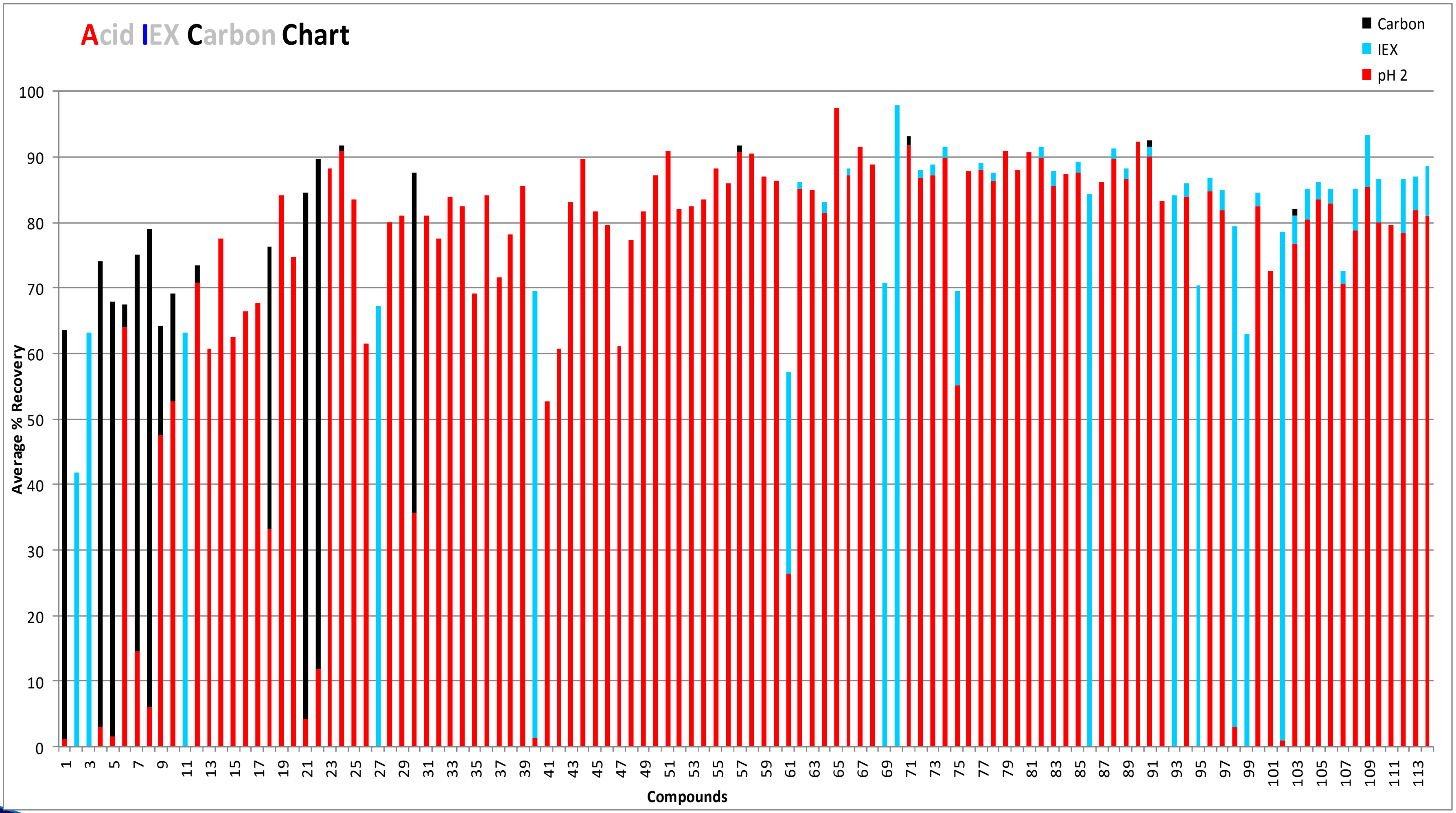
8270 – LLE, Na_2SO_4, KD/N-Evap



Problem compounds

Pyridine	8%	Di-n-octyl phthalate	12%
Aniline	26%	Indeno (1,2,3,-cd)pyrene	140%
Benzidine	3%	2,4,6,Tribromophenol (surr)	135%

Recoveries on One Pass SPE Disk



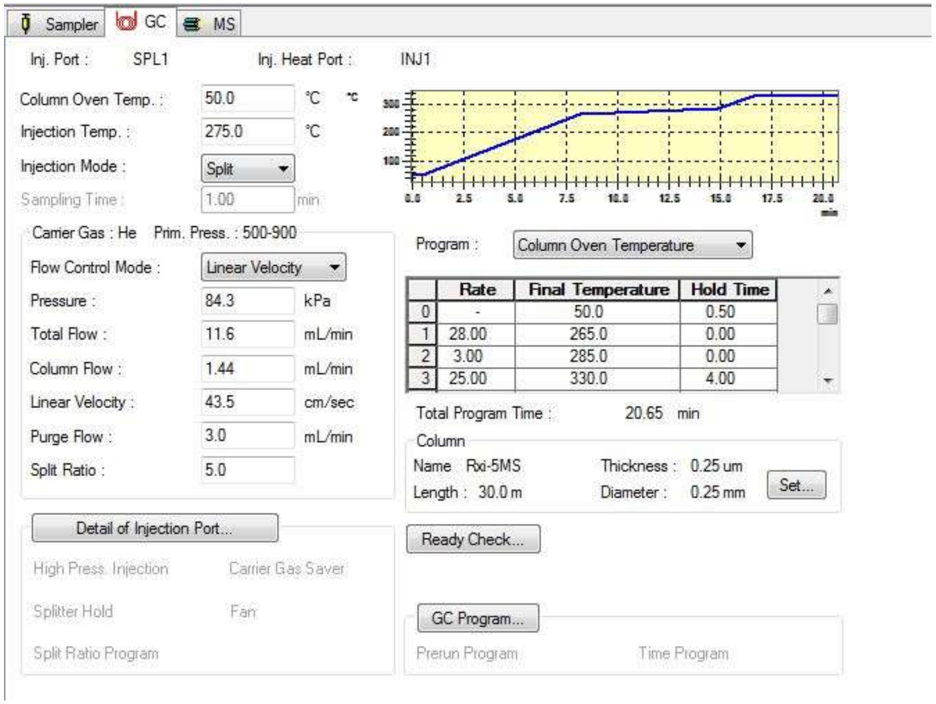
Method for 100 mL Sample Volume

100 mL
Sample

47 mm
Disk Holder

- 80 mL extract volume
- **1 hr 30 min to extract, dry and concentrate.**

GC/MS Conditions



Inj. Port : SPL1 Inj. Heat Port : INJ1

Column Oven Temp. : 50.0 °C

Injection Temp. : 275.0 °C

Injection Mode : Split

Sampling Time : 1.00 min

Carrier Gas : He Prim. Press. : 500-900

Flow Control Mode : Linear Velocity

Pressure : 84.3 kPa

Total Flow : 11.6 mL/min

Column Flow : 1.44 mL/min

Linear Velocity : 43.5 cm/sec

Purge Flow : 3.0 mL/min

Split Ratio : 5.0

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	50.0	0.50
1	28.00	265.0	0.00
2	3.00	285.0	0.00
3	25.00	330.0	4.00

Total Program Time : 20.65 min

Column

Name Rxi-5MS Thickness : 0.25 um

Length : 30.0 m Diameter : 0.25 mm

MS Conditions	
Ion Source Temp.	230°C
Interface Temperature	290°C
Cut Time	1.75 min

Shimadzu QP-2020

Results and Discussion

- Approximately 55 compounds were in the analyte list representing
- Acids
- Base/neutrals
- Plus deuterated surrogates

- Reagent water plus spikes
- Synthetic wastewater plus spikes, full list and Phenova Reference Material
- TCLP extract matrix plus spikes, Phenova reference material

Results–Full Spike Recoveries (%) for Selected Bases

Synthetic Wastewater

	Spike 1	Spike 2	Spike 3	Spike 4	Avg	SD	RSD (%)
Acenaphthene	94.5	86.3	88.1	86.3	88.8	5.1	5.8
Acenaphthylene	75.7	75.2	74.2	74.4	74.9	4.6	6.2
Anthracene	88.4	83.5	84.3	82.3	84.6	6.9	8.2
Azobenzene (1,2 Diphenylhydrazine)	73.9	71.7	72.8	67.9	71.5	2.3	3.2
Benzo(a)anthracene	92.1	96.4	87.8	87.2	90.9	3.7	4.1
Benzo[b]fluoranthene	94.5	95.5	93.4	93.5	94.2	0.9	0.9
Benzo(k)fluoranthene	87.4	91.4	91.5	91.6	90.5	2.3	2.6
Benzo(g,h,i)perylene	91.4	92.2	91.8	90.7	91.5	0.6	0.6
Benzo(a)pyrene	85.9	85.5	85.4	87.5	86.1	2.8	3.2
4-Bromophenyl-phenylether	93.4	88.7	88.6	87.8	89.6	2.4	2.7
Butyl benzyl phthalate	131.7	124.8	126.6	116.5	124.9	10.9	8.8
bis(2-Chloroethyl)ether	74.6	74.1	76.1	75.0	74.9	0.7	1.0
bis(2-Chloroisopropyl) ether	75.2	76.1	75.5	73.9	75.2	0.8	1.1
2-Chloronaphthalene	73.3	72.2	67.9	69.7	70.8	4.1	5.8
Dibenzo(a,h)anthracene	88.6	89.7	91.2	89.2	89.7	1.9	2.1
Di-n-butylphthalate	119.2	115.8	110.4	109.6	113.7	12.4	10.9
1,2-Dichlorobenzene	64.3	62.3	67.2	63.1	64.2	5.0	7.8
1,3-Dichlorobenzene	62.8	58.2	59.1	58.8	59.7	1.8	3.0
1,4-Dichlorobenzene	62.7	57.9	63.2	60.7	61.1	4.6	7.5
Diethyl phthalate	83.4	80.2	79.5	77.3	80.1	4.4	5.5

Results–Full Spike Recoveries (%) for Acids

Synthetic Wastewater

	Spike 1	Spike 2	Spike 3	Spike 4	Avg	SD	RSD (%)
4-Chloro-3-methylphenol	96.6	100.7	95.1	87.4	95.0	8.9	9.4
2-Chlorophenol	75.8	77.3	78.2	76.5	77.0	4.7	6.1
2,4-Dichlorophenol	82.7	84.9	77.6	75.9	80.2	4.4	5.4
2,4-Dimethylphenol	80.5	80.4	79.1	78.5	79.6	3.0	3.8
2-Methyl-4,6-Dinitrophenol	170.1	151.1	145.6	143.6	152.6	11.3	7.4
2-Nitrophenol	86.5	91.6	93.7	90.0	90.5	4.9	5.4
4-Nitrophenol	113.5	109.9	119.6	105.7	112.2	12.1	10.8
Phenol	80.7	80.6	80.5	80.8	80.6	3.7	4.6
Pentachlorophenol	117.4	113.1	112.9	104.4	112.0	4.2	3.7

Results – Phenova Spike Recoveries (%) for Selected Bases

Horizon technology

Synthetic Wastewater

	Spike 1	Spike 2	Spike 3	Avg.	SD	RSD (%)
Acenaphthene	101.7	97.8	97.4	99.0	2.4	2.4
Acenaphthylene	65.5	65.0	65.9	65.5	0.4	0.7
Anthracene	72.7	71.5	70.4	71.5	1.2	1.6
Benzo(k)fluoranthene	96.0	95.2	90.2	93.8	3.1	3.3
Benzo(a)pyrene	93.1	92.1	90.8	92.0	1.2	1.3
4-Bromophenyl-phenylether	87.5	85.4	88.4	87.1	1.5	1.8
Butyl benzyl phthalate	109.6	104.0	104.9	106.2	3.0	2.8
4-Chlorophenyl-phenylether	81.4	79.9	82.5	81.3	1.3	1.6
Dibenzo(a,h)anthracene	90.0	93.4	87.5	90.3	2.9	3.2
Di-n-butylphthalate	91.1	88.5	89.9	89.9	1.3	1.4
1,4-Dichlorobenzene	54.6	50.4	63.4	56.1	6.6	11.8
1,2 Dichlorobenzene	54.9	51.8	65.2	57.3	7.0	12.2
Diethyl phthalate	71.5	72.4	71.4	71.8	0.6	0.8

Results–Phenova Spike Recoveries (%) for Acids

Synthetic Wastewater

	Spike 1	Spike 2	Spike 3	Avg.	SD	RSD (%)
4-Chloro-3-methylphenol	78.2	80.1	77.0	78.4	1.6	2.0
2-Chlorophenol	64.8	65.2	70.7	66.9	3.3	5.0
2,4-Dichlorophenol	71.5	74.4	73.2	73.1	1.4	2.0
2,4-Dimethylphenol	69.1	73.0	74.3	72.1	2.7	3.7
2-Methyl-4,6-Dinitrophenol	156.3	157.6	134.5	149.5	13.0	8.7
2-Nitrophenol	78.5	78.8	87.7	81.7	5.2	6.4
4-Nitrophenol	91.0	91.7	86.6	89.8	2.8	3.1
Phenol	69.9	72.0	74.4	72.1	2.3	3.2
Pentachlorophenol	112.7	114.4	108.8	112.0	2.8	2.5
2,4,6-Trichlorophenol	77.6	74.6	75.2	75.8	1.6	2.1

Results–Phenova Spike Recoveries (%) for Selected Bases

Horizon technology

TCLP Solution Matrix

	Spike 1	Spike 2	Spike 3	Spike 4	Avg.	SD	RSD (%)
Acenaphthene	87.7	84.6	87.4	83.3	85.8	2.17	2.53
Acenaphthylene	68.4	70.2	67.3	64.5	67.6	2.37	3.50
Anthracene	75.3	76.4	73.7	71.8	74.3	1.96	2.64
Benzo(k)fluoranthene	90.7	89.8	93.9	91.1	91.4	1.79	1.96
Benzo(a)pyrene	90.3	89.2	90.4	85.0	88.7	2.53	2.85
4–Bromophenyl–phenylether	89.2	88.2	90.5	81.3	87.3	4.13	4.74
Butyl benzyl phthalate	114.3	110.7	111.1	105.5	110.4	3.65	3.31
4–Chlorophenoxyether	88.0	84.4	86.7	79.8	84.7	3.62	4.28
Dibenzo(a,h)anthracene	90.6	93.4	100.5	93.4	94.5	4.19	4.44
Di–n–butylphthalate	96.2	96.6	97.6	88.3	94.7	4.27	4.51
1,4–Dichlorobenzene	54.7	39.1	53.4	50.5	49.4	7.08	14.33
1,2 Dichlorobenzene	55.5	40.4	53.8	52.5	50.6	6.90	13.64
Diethyl phthalate	80.5	79.6	77.7	71.3	77.3	4.18	5.40

Results–Phenova Spike Recoveries (%) for Acids

TCLP Solution Matrix

	Spike 1	Spike 2	Spike 3	Spike 4	Avg.	SD	RSD (%)
4-Chloro-3-methylphenol	80.3	83.2	80.9	77.0	80.4	2.58	3.21
2-Chlorophenol	73.3	67.2	70.0	68.1	69.7	2.71	3.89
2,4-Dichlorophenol	76.7	74.0	75.3	72.0	74.5	1.99	2.66
2,4-Dimethylphenol	73.3	72.9	71.2	68.3	71.4	2.27	3.18
2-Methyl-4,6-Dinitrophenol	118.1	105.9	129.4	109.3	115.7	10.5	9.08
2-Nitrophenol	81.3	77.9	81.6	78.4	79.8	1.95	2.44
4-Nitrophenol	90.9	89.7	94.2	83.4	89.6	4.50	5.02
Phenol	96.6	92.7	94.7	91.9	94.0	2.14	2.28
Pentachlorophenol	90.6	90.8	95.1	103.1	94.9	5.85	6.17
2,4,6-Trichlorophenol	73.7	78.1	73.7	74.0	74.9	2.14	2.85

Sensitivity Concerns with Smaller Samples

- Modern GC/MS are more sensitive than previous systems
- Lower split ratio
- Large volume injection

Conclusions

- Horizon Technology one-pass disk and automation system worked well for both matrices (wastewater and TCLP)
- Horizon Technology one-pass disk and automation system worked well for small volumes (100 mL)
- Recoveries for both acids and bases were very good
- The time for the sample to drain through the disk is fast and even when particulates are present , prefilters can help the system maintain a reasonable flow, even for 1L or more
- Modern GC/MS has improved sensitivity and flexibility to adjust the sensitivity required for the situation
- Solid phase extraction is clearly a good performance option for method 625