ILI Study for SPE and Method 625
Horizon Technology Perspective

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Introduction

- Horizon Technology participated in both rounds of the Mini-round Robin
- Because of trends toward smaller sample sizes we demonstrated the method with
  - Traditional 1000 mL sample size
  - Smaller 100 mL sample size
- To minimize efforts of participating labs we asked each lab only to measure one sample size 1 L or 100 mL


Cardiovascular Research Ltd
EPA-625
DHA-245
High Potency Omega-3
90 Softgels

Laboratories

- Worked with eight different laboratories for the two studies
- 1 Government
- 2 Municipal
- 5 Commercial testing

- To cover all perspectives and needs

- Horizon Technology also provided data from its own laboratory

EPA 625 Mini Round Robin I Study Overview

- Materials provided by Phenova
  - Substitute wastewater mix
  - Spiking mix with containing a subset of Tables 1 and 2 compounds from revised US EPA 625
  - Only concentration ranges were given, not exact amounts
- Each vendor worked with three labs, including their own if desired, for each SPE material
- Although Horizon Technology worked with one SPE material and set-up, two different volumes of sample were used, 1000 mL and 100 mL
- Therefore, additional labs were recruited
- More replicates possible with material when 100-mL samples used

Process

- Shipped equipment to the lab or checked if any accessories needed for labs with already-installed equipment
- Provided One-pass SPE Disks, carbon cartridges and DryDisk® drying membranes
- Laboratories used their own evaporation equipment
- When the Round Robin materials had arrived from Phenova, an application chemist from Horizon would visit the laboratory
  - Install the 4790 equipment
  - Train the laboratory personnel
  - Be available for questions during the sample prep part of the study
- The laboratory would generate the GC/MS data and deliver the results to Phenova

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.

8270 Carbon Cartridge

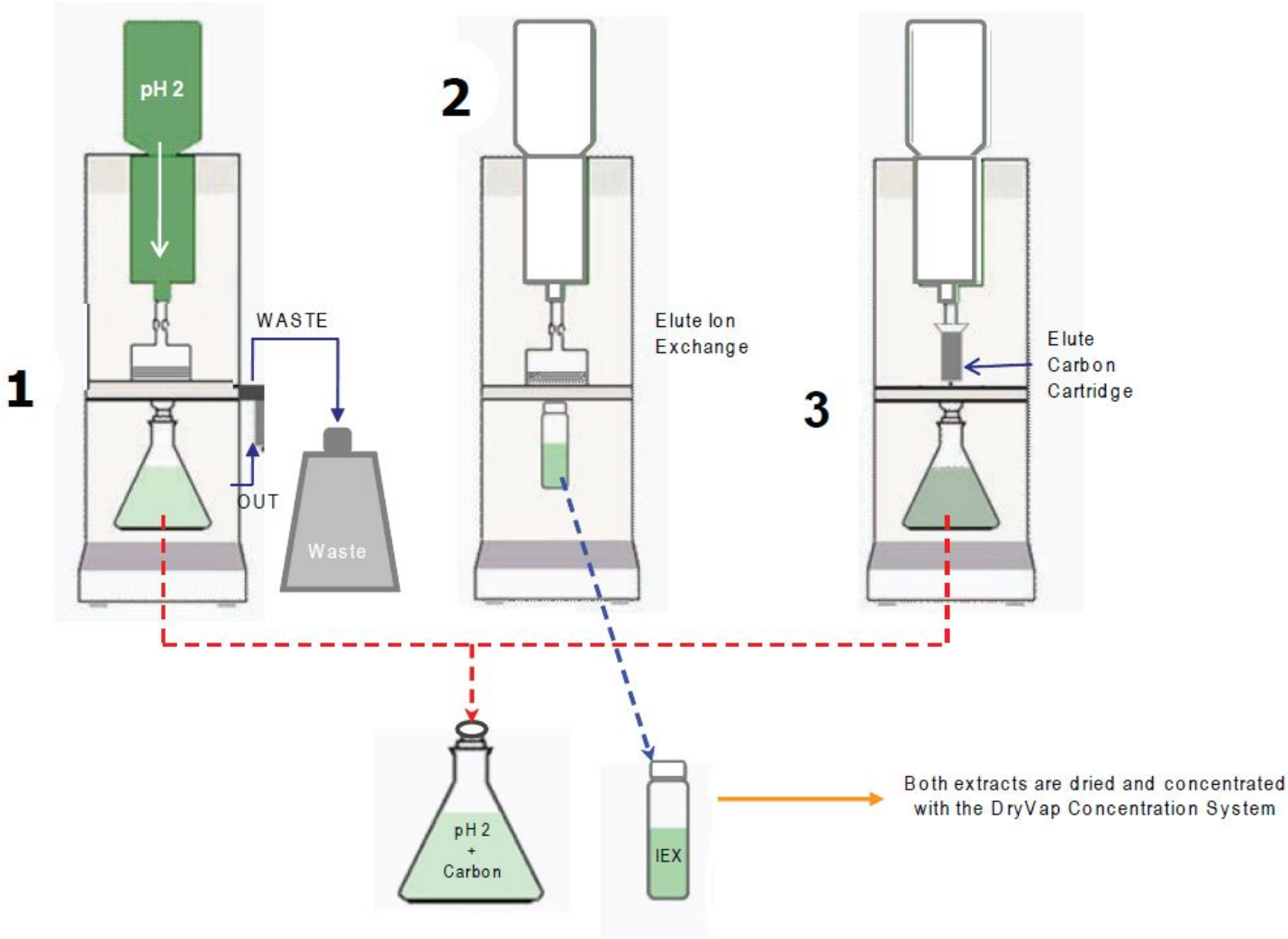
- Recovers light-end organics from post-disk sample effluent.
- e.g., NDMA, benzyl alcohol, & methyl methanesulfonate.

DryDisk® Separation Membrane

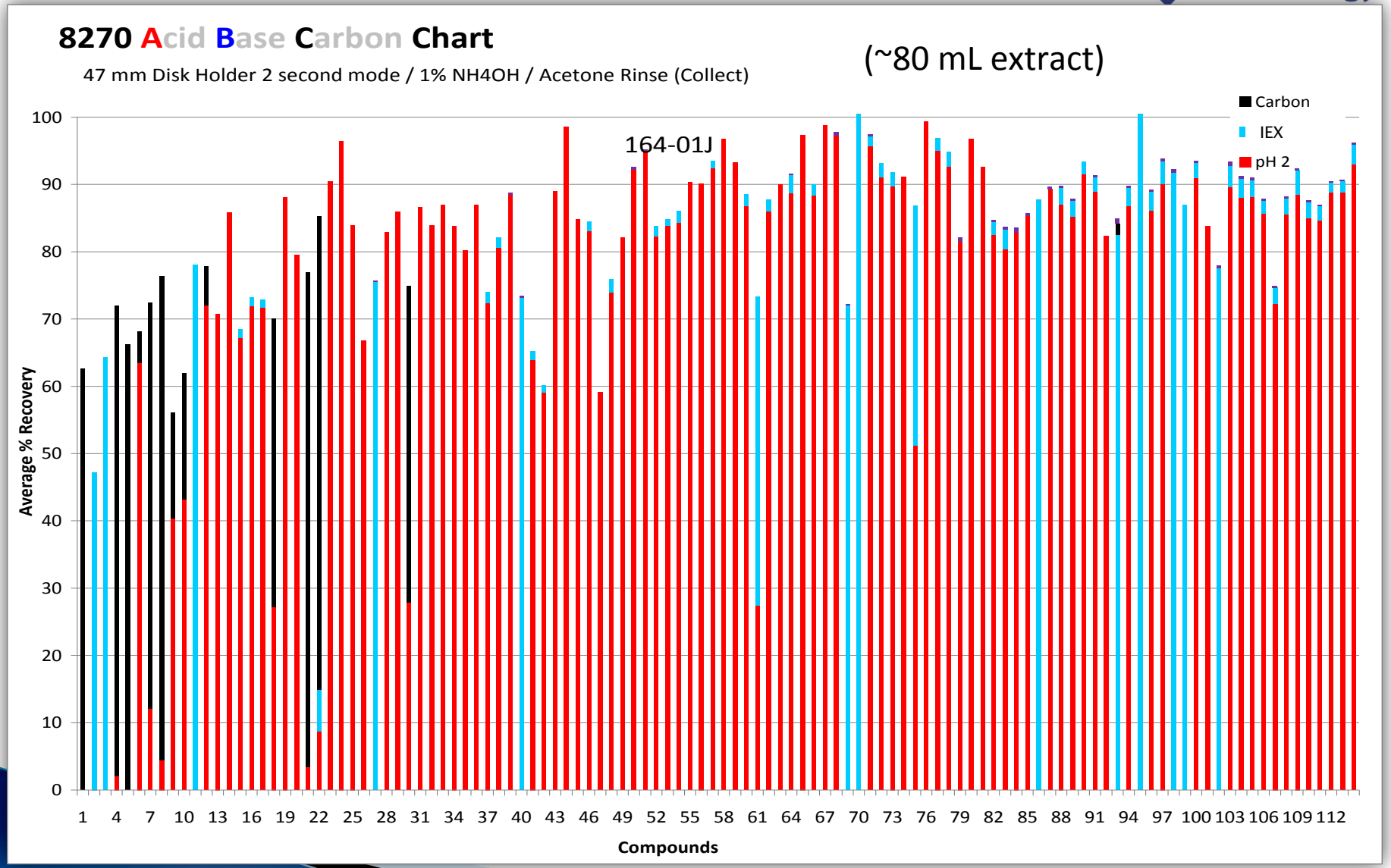
- Efficiently removes water from extract.
- Unlimited capacity for water.
- Eliminates sodium sulfate.

Horizon technology

One-Pass process



50 µg Spike into 1L DI Water, conc. to 1 mL
Standard 47 mm Disk Holder



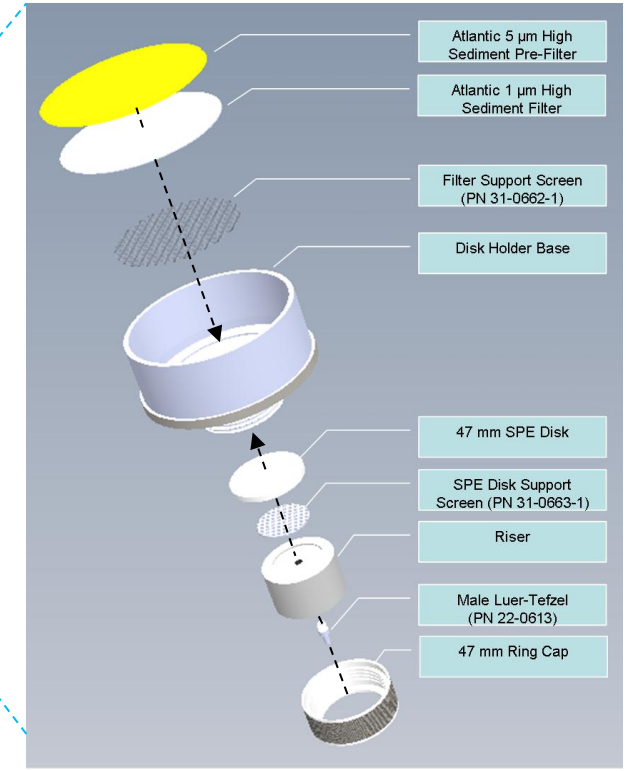
Method 1 for Mini-Round Robin Study
1 Liter Sample Volume

1L Sample

1 µL is injected (10/90 split mode) into the GC-MS.

EZ Flow Disk Holder

- 6x more filtering surface area for 47 mm disk
- Uses 100 mm pre-filters (1 and 5 µm)



- 200 mL extract volume
- **3 hr to extract, dry and concentrate.**

Method 2 for Mini-Round Robin Study
100 mL Sample Volume

100 mL Sample

47 mm Disk Holder

1 µL is injected into the GC-MS.
No split
This maintains the same mass loading as the 1 Liter Sample Method.

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

Results- Round 1
Selected Compounds

- Approximately 65 compounds were in the analyte list representing
- Acids
- Base/neutrals
- Pesticides

- Synthetic Wastewater
- 12 sets of data representing four laboratories

Results–Selected Bases

Base
Acid
OC pest

Analytes	EPA Table 6 RANGE P%	Ps%	LLE ILI study %recv	HTI 625 12 pt Low	HTI625 12pt High	HTI 625 Avg -2 sdev	Avg	625HTI 625 Avg +2 sdev
Acenaphthene	47	145	78.8	59.9	93.6	52.8	76.9	100.9
Anthracene	27	133	70.8	58.9	111.0	51.0	81.8	112.5
Benzo(a)anthracene	33	143	63.1	55.3	96.3	52.8	78.1	103.3
Benzo(k)fluoranthene	11	162	67.3	57.9	127.5	44.9	84.7	124.6
Benzo(g,h,i)perylene	d	219	67.5	66.7	137.3	48.2	90.4	132.7
Benzo(a)pyrene	17	163	58.0	62.1	123.6	52.5	90.1	127.6
4-Bromophenyl-phenylether	53	127	68.7	60.2	103.3	57.4	82.9	108.4
Butyl benzyl phthalate	d	152	66.1	61.1	105.8	58.9	84.9	110.8
bis(2-Chloroethyl)ether	12	158	64.3	52.5	97.5	47.9	70.6	93.3
bis(2-Chloroisopropyl) ether	36	166	83.0	72.7	108.2	63.6	85.8	108.0
4-Chlorophenyl-phenylether	25	158	69.0	57.0	94.3	55.4	77.7	100.0
Dibenzo(a,h)anthracene	d	227	61.1	61.8	94.4	60.0	80.8	101.6
Dibenzofuran			77.4	56.5	98.6	52.9	77.0	101.1
Di-n-butylphthalate	1	120	61.9	62.3	106.9	53.1	84.2	115.4

Results–Selected Acids

Base
Acid
OC pest

Analytes	EPA Table 6 RANGE P%	Ps%	LLE ILI study %recv	HTI 625 12 pt Low	HTI625 12pt High	HTI 625 Avg -2 sdev	625 Avg	HTI 625 Avg +2 sdev
4-Chloro-3-methylphenol	22	147	78.0	67.8	102.7	65.7	86.6	107.6
2-Chlorophenol	23	134	70.1	66.2	95.3	59.5	77.2	94.8
2,4-Dichlorophenol	39	135	74.5	75.7	102.0	67.6	85.6	103.5
2,6-Dichlorophenol			75.9	82.1	91.2	78.2	86.2	94.2
2,4-Dimethylphenol	32	120	78.9	70.8	106.3	67.2	89.9	112.6
2-Methyl-4,6-Dinitrophenol	d	181	46.6	43.1	103.2	31.4	80.5	129.6
2-Methylphenol			68.1	70.0	93.6	66.7	83.4	100.0
4-Methylphenol (and/or 3-Methylphenol)			65.4	75.0	106.9	67.5	87.3	107.1
2-Nitrophenol	29	182	72.1	57.2	92.6	52.2	74.3	96.4
4-Nitrophenol	d	132	29.5	59.2	90.9	60.1	77.6	95.1
Phenol	5	120	41.3	46.2	96.6	43.5	73.8	104.2
Pentachlorophenol	5	120	85.2	66.0	202.3	4.3	119.3	234.3
2,4,5-Trichlorophenol			74.7	70.1	109.0	64.3	88.4	112.5
2,4,6-Trichlorophenol	37	144	71.7	70.6	96.7	64.3	82.5	100.8

Results–Selected Pesticides

Base
Acid
OC pest

Analytes	EPA Table 6 RANGE P%	Ps%	LLE ILI study %recv	HTI 625 12 pt Low	HTI625 12pt High	HTI 625 Avg -2 sdev	625 Avg	HTI 625 Avg +2 sdev
Aldrin	d	166	81.4	70.2	107.9	54.8	86.2	117.5
alpha-BHC			69.0	67.5	120.7	39.4	86.4	133.4
beta-BHC	24	149	76.1	61.5	105.6	56.5	88.0	119.5
delta-BHC				76.7	98.9	65.8	85.4	105.0
gamma-BHC (Lindane)	d	120		68.4	101.0	54.4	83.2	112.1
alpha-Chlordane				54.7	80.2	45.6	66.6	87.7
gamma-Chlordane				55.3	123.9	30.3	86.2	142.1
4,4'-DDD	d	145	72.3	44.7	118.2	18.0	72.6	127.1
4,4'-DDE	4	136		62.5	98.5	54.2	82.2	110.3
4,4'-DDT	d	203	68.5	66.7	111.1	56.5	90.4	124.4
Dieldrin	29	136	74.6	56.4	111.0	41.5	82.1	122.6
Endosulfan I			39.7	37.1	48.1	32.4	41.0	49.6

Results- Round 2
Selected Compounds

- Approximately 65 compounds were in the analyte list representing
- Acids
- Base/neutrals
- Pesticides

- TCLP Matrix:
- Treated as a wastewater matrix and both 1 L samples and 100 mL samples extracted
- However, when TCLP performed, rare to use 1L of leaching medium, therefore more severe test for SW-846 and WW

- Four sets of data representing four laboratories

Results – Selected Bases

Surrogate Name	AnalyteName	Avg %
Acenaphthylene-d8	2-Chloronaphthalene	67.9
	2-Methylnaphthalene	63.8
	Acenaphthene	79.8
	Acenaphthylene	81.6
	Acenaphthylene-d8	77.7
Anthracene-d10	Anthracene	74.8
	Anthracene-d10	69.4
	Hexachlorobenzene	77.3
	Phenanthrene	88.1
Benzo(a)pyrene-d12	Benzo(a)pyrene	89.0
	Benzo(k)fluoranthene	92.0
	Chrysene	87.4
	Dibenzo(a,h)anthracene	86.8
	Indeno(1,2,3-cd)pyrene	81.9
Bis(2-chloroethyl)ether-d8	1,2-Dichlorobenzene	49.8
	1,4-Dichlorobenzene	47.5
Dimethylphthalate-d6	bis(2-ethylhexyl) phthalate	97.9
	Butyl benzyl phthalate	96.0
	Diethyl phthalate	86.2
	Di-n-butylphthalate	83.3
	Di-n-octylphthalate	100.5

n=4 Labs,
TCLP and LCS samples at both volumes included

Results – Selected Acids

	2,4-Dichlorophenol-d3	2,4,5-Trichlorophenol	73.2
		2,4,6-Trichlorophenol	107.3
		2,4-Dichlorophenol	87.7
		2,6-Dichlorophenol	
		4-Chloro-3-methylphenol	90.5
	2-Chlorophenol-d4	2-Chlorophenol	80.0
	2-Nitrophenol-d4	2,4-Dimethylphenol	90.2
		2-Nitrophenol	91.0
	4,6-Dinitro-2-methylphenol-d2	2-Methyl-4,6-Dinitrophenol	92.2
		4,6-Dinitro-2-methylphenol-d2	80.7
		Pentachlorophenol	87.8
	4-Methylphenol-d8	2-Methylphenol	85.5
		4-Methylphenol (and/or 3-Methylphenol)	74.7
	4-Nitrophenol-d4	2,4-Dinitrophenol	78.3
		4-Nitrophenol	71.8
		4-Nitrophenol-d4	75.7
	Phenol-d5	Phenol	64.3

Results Summary

- 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 both sample volumes (100 mL and 1 L)
- 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

Comments–Vendor

- This process was less expensive than for an individual ATP
  - Some organizational efforts handled by ILI
- Perhaps there is less barrier to entry for other vendors with this approach
- Might be quicker than an ATP if only one mini-robin round is required

Questions for Collaborative Labs

1. Is this multivendor process with volunteer labs a good process for developing methodology with new technology? Why?
2. What would you do differently, now that you have participated in this process once?
3. Any other comments welcome

Laboratory Comments

- In response to your questions, we think this multi-lab approach was very beneficial. Having the coordinating organization not a specific vendor allowed us (a government agency) to participate without showing favoritism to a particular vendor. This approach allowed us to fully validate a generic method (SPE) for multiple vendors and products.
- Personally, our laboratory was able to start up a method in an expedited manner with assistance from your company. We both benefited from this partnership-we can now reduce our solvent usage, and you will have another customer of the SPE products.

Laboratory Comments

- For a first project like this it went fairly well, and we would like to see more of this type of collaboration for future developments.
- The project could have had even better planning related to the details. We received corrected surrogate spiking directions after we had performed our extractions, for example.
- Another consideration would be to send the matrix ahead to all labs so they can verify the proper instrument operation. For example, we had peak splitting with the second matrix, and if resolved may have had better results.
- I personally appreciated being a part of the general planning discussions for the project, and I hope I provided some good information and ideas to the team. In the future, I would recommend that ILI and the vendors have one or two chemists from a working laboratory on the planning team to ensure reasonableness of the approach.

Laboratory Comments

- I feel it was good to use multiple vendors. This way you get to try out different types of SPE systems and can make a decision on which system works best for you laboratory.

- I don't feel there's anything that can be done differently. I would try to come up with a better way to keep some the SPE systems more stable. I forget which vendor(s), but I know we had to stack tubes on top of each other that made it seem that it could fall over at any time during the extraction.

Laboratory Comments

- I thought the process was very good because it connected vendors with the laboratory in a very technical fashion. Laboratories want to help make processes better and what better way than to work with the resources that are available with vendors. Many times vendors allow demo units to be placed in labs but this had a much bigger purpose.
- I thought the interactions I had were very positive. Ideas from the laboratory and from the vendors were equally weighted and equally important.
- I am very happy with how this process was conducted and very excited with how the data turned out. I would certainly like to participate in other studies where me or my team could be helpful.

Laboratory Comments

- I strongly believe that using volunteer labs and multi vendors is not only a good process but critical for the resulting validation and acceptance of the data. With only a single vendor and lab, any variability that will be apparent when labs nationwide are preforming this method may not be evident.
- I felt very comfortable with the instrumentation and procedure. Procedurally and analytically, I would have done nothing different. The instructions were very clear and so I didn't have any issues with the preparation of standards or the SPE extraction procedure. …I let the management here know about this study and they allowed it but I don't feel I had a full "buy in" from them. The next time, I would lay out exactly the amount of time that needed to be cleared for me the complete the project in the time frame needed by the data users. In my case, I had time to work on the extraction while David was here but once he left, I was pulled to do other tasks and it took a while before I could get to the actually analysis of the samples.

Laboratory Comments

- I think was a wonderful process for our lab and myself as a chemist. It is rare to get this opportunity so I am thankful. I am curious about how our lab results compared to study results as a whole to the other labs involved. I did see some of the data that was released but it was in recovery format and so I didn't know which results were ours. Just curious how we did especially on those new surrogates that were added.

Conclusions

- SPE Results were comparable to LLE methods.
- Good recoveries within method guidelines obtained.
- Excellent mass sensitivity for both 1000 mL and 100 mL sample methods.
- 100-mL SPE Sample Method
  - Slightly better recoveries obtained over 1000 mL SPE method.
  - Low extract volume of 80 mL as compared to LLE and CLLE.
  - Faster processing time, as low as 1hr 30 minutes from extraction, drying and concentration to 1- mL volume endpoint
- These same test methods were distributed and performed by four independent labs
- The results from these labs show excellent agreement
- There are benefits for the vendor-cost, perhaps time to approval
- There are benefits for the laboratory-experience, chance to compare technologies, etc…