Automated GPC With Inline SPE to Improve Sample Cleanup for PAH Analysis

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PAHs

- Many PAHs have been identified as mutagens and carcinogens
- PAHs are lipophilic and frequently found in challenging matrices like soil and seafood
- The EPA has identified 16 PAHs as Priority Pollutants:

naphthalene	**phenanthrene**	**benzo(a)anthracene**	**benzo(a)pyrene**
acenaphthylene	**anthracene**	**chrysene**	**indeno(1,2,3-cd)pyrene**
acenaphthene	**fluoranthene**	**benzo(b)fluoranthene**	**dibenzo(a,h)anthracene**
fluorene	**pyrene**	**benzo(k)fluoranthene**	**benzo(ghi)perylene**

Sample Cleanup for PAH Analysis

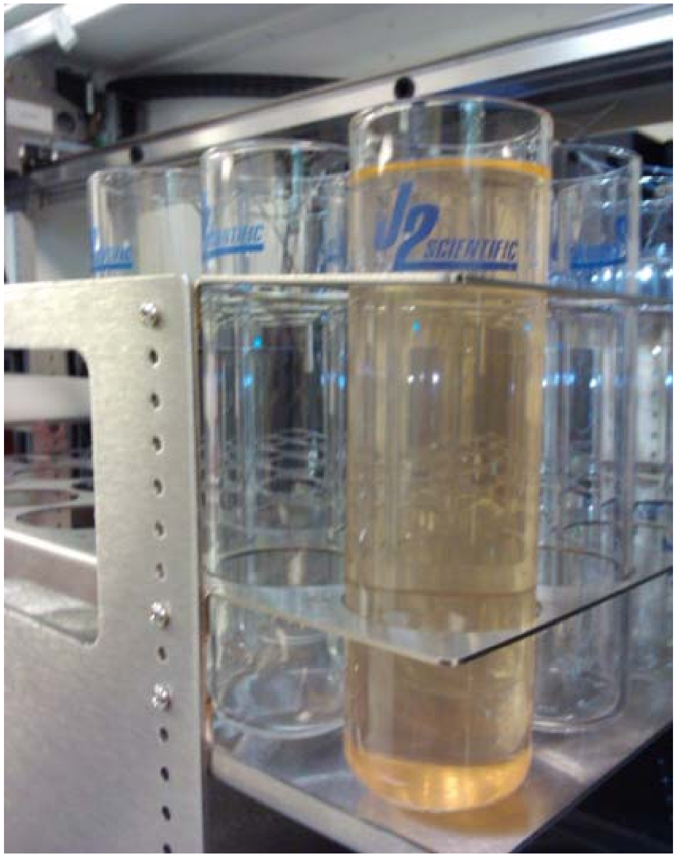
- Sample cleanup is critical prior to analysis for most matrices to minimize interfering peaks and extend the lifetime of the analytical equipment
- SPE requires multiple manual steps and sometimes cannot handle high-lipid samples
- GPC removes lipids, but cleanup may be incomplete
- For problematic matrices, GPC can be combined with traditional SPE methods, but these methods require additional steps that increase the time and solvent required to process each sample

GPC with inline SPE

- Non-retentive SPE for the analytes of interest can remove many matrix interferences
- Adding inline SPE to a GPC method on the PrepLinc™ system takes no additional time or solvent per sample
- Common SPE Cartridge Types:
  - Silica
  - Florisil™
  - Alumina

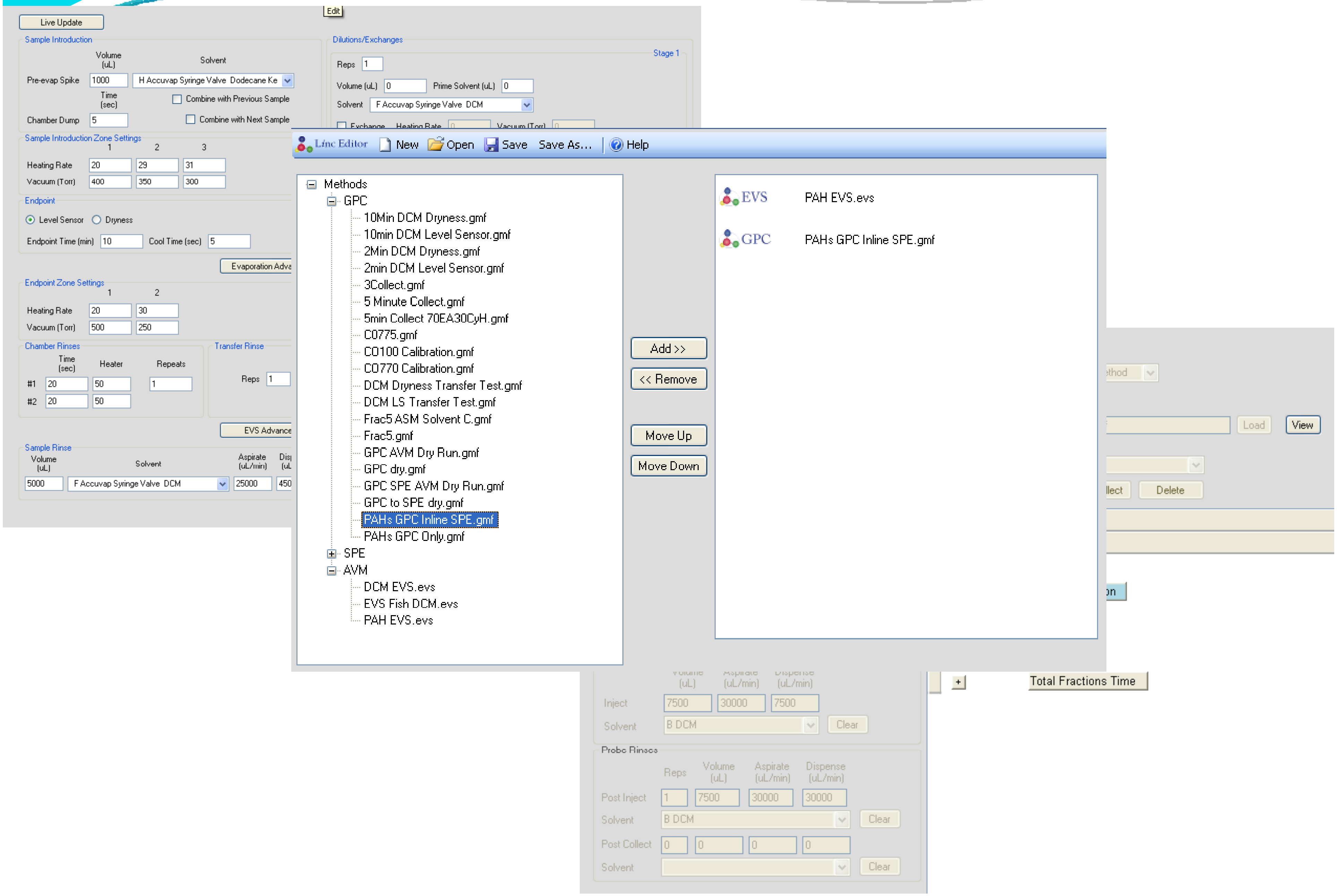
Extract Preparation

Matrices Tested:
- Topsoil
- Red Snapper filet (skin on)
- Shucked oysters



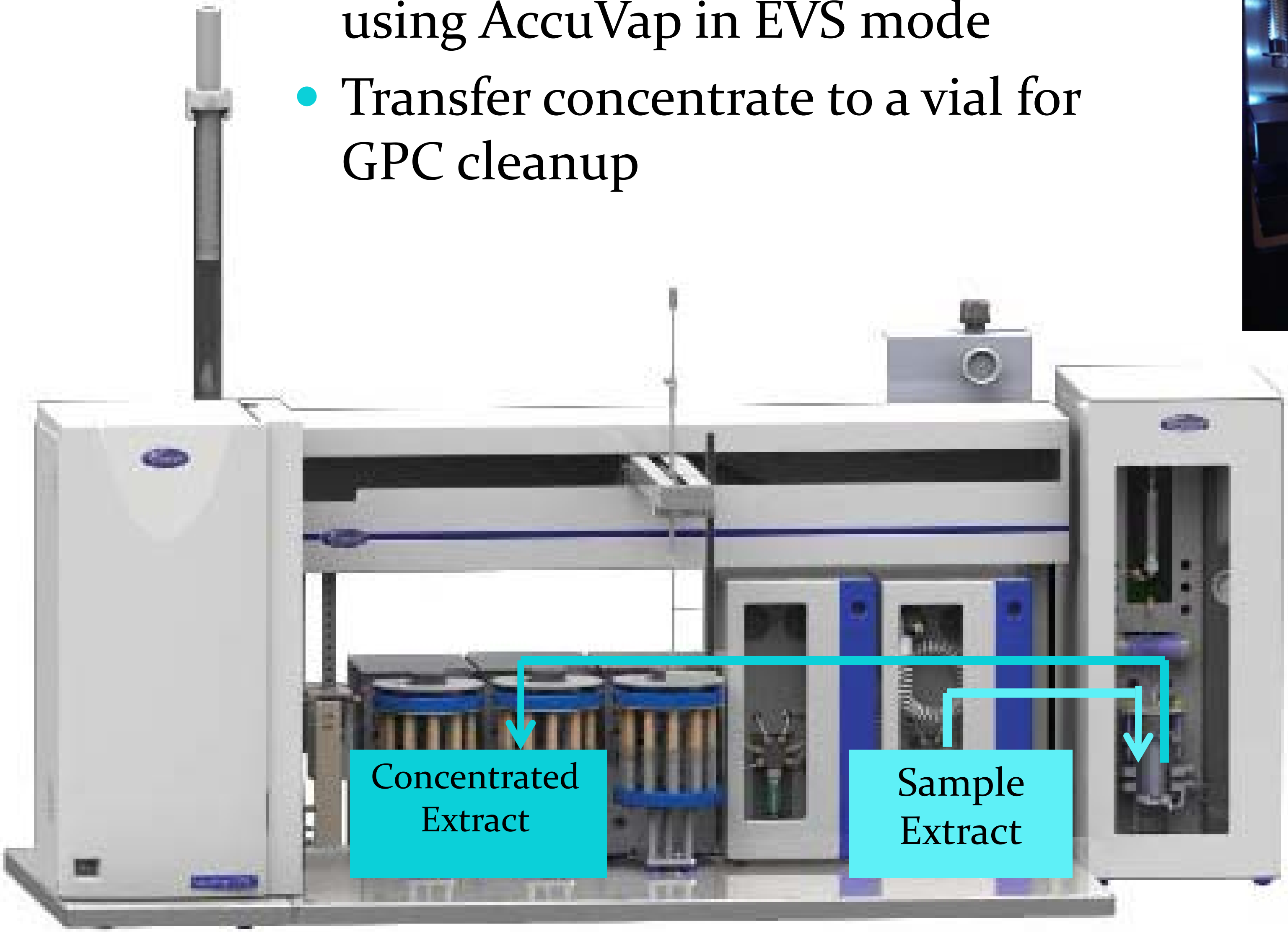
- Add methylene chloride (50mL per 10g sample) and blend until homogenous
- Remove suspended solids and water from extract
- Spike extract with PAH Standard prior to loading onto PrepLinc System

Automated Concentration and Cleanup



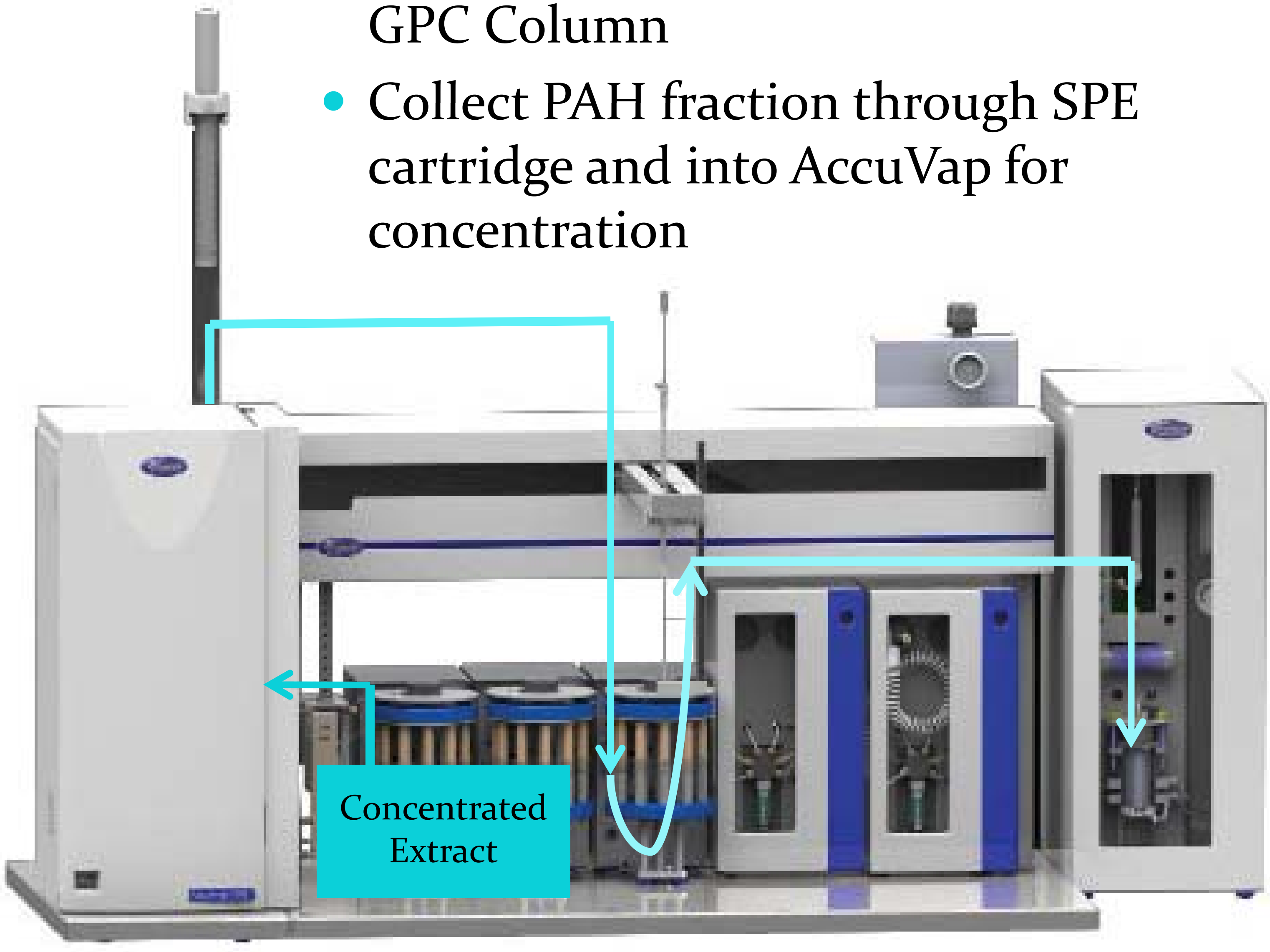
Cleanup – Extract Concentration

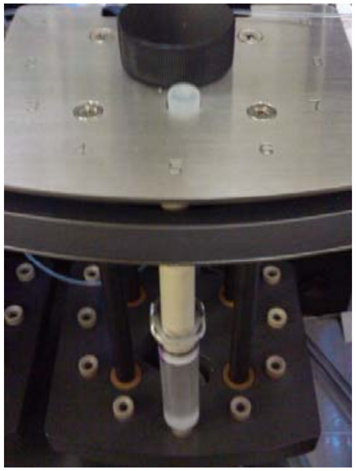
- Concentrate 50mL extract to 2mL using AccuVap in EVS mode
- Transfer concentrate to a vial for GPC cleanup



Cleanup – GPC-SPE

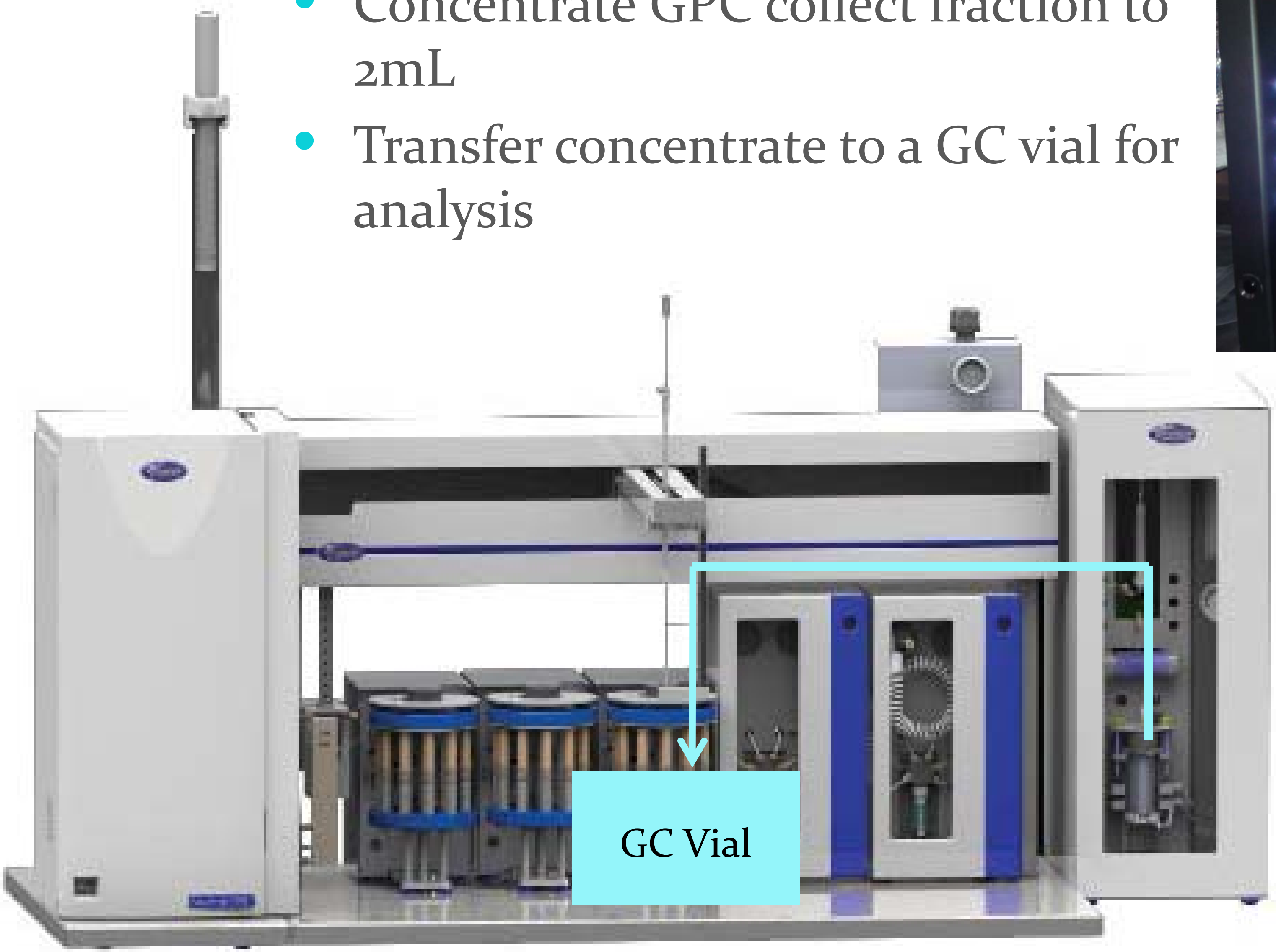
- Load concentrated sample onto Express GPC Column
- Collect PAH fraction through SPE cartridge and into AccuVap for concentration



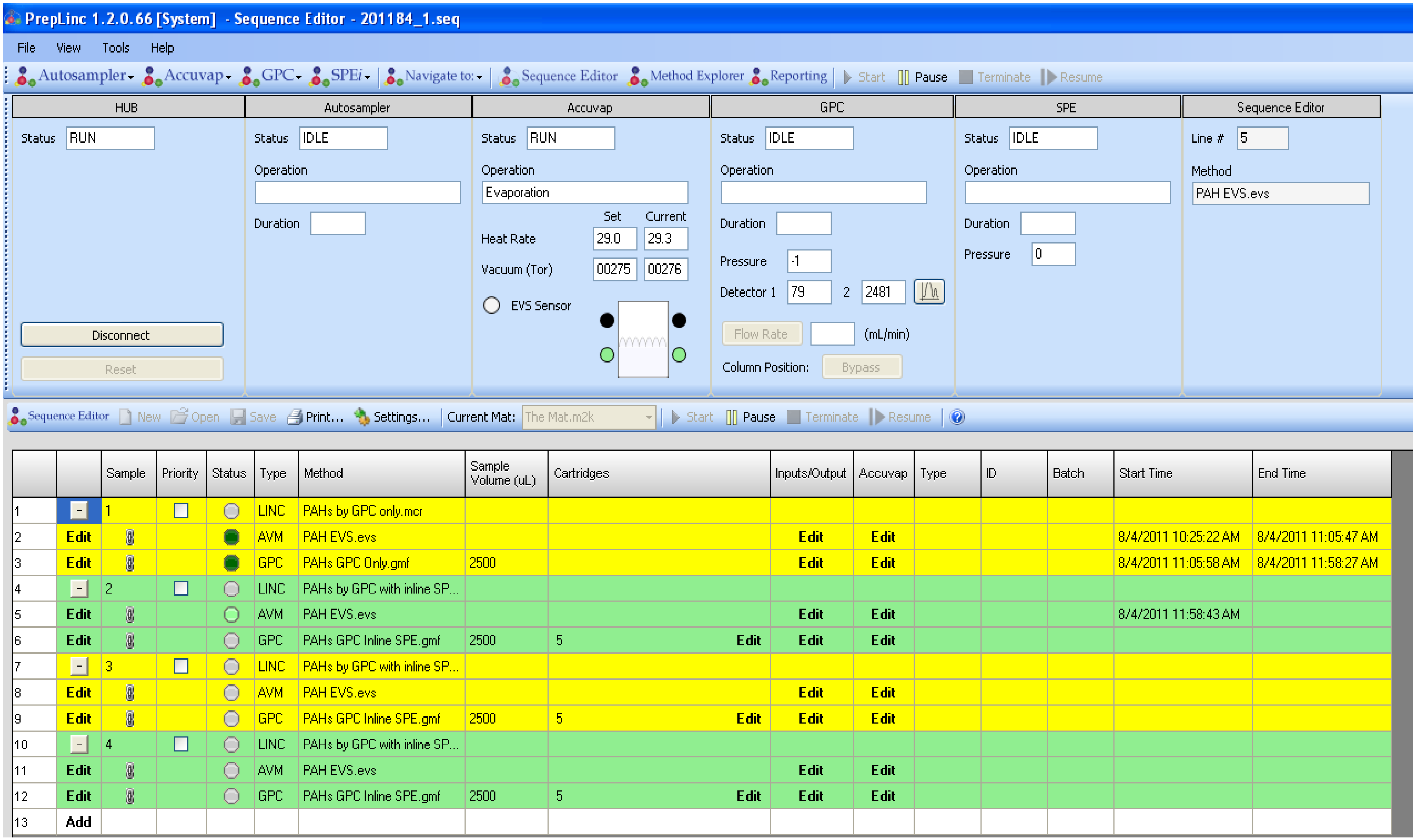


Cleanup – Final Concentration

- Concentrate GPC collect fraction to 2mL
- Transfer concentrate to a GC vial for analysis



Automated Concentration and Cleanup

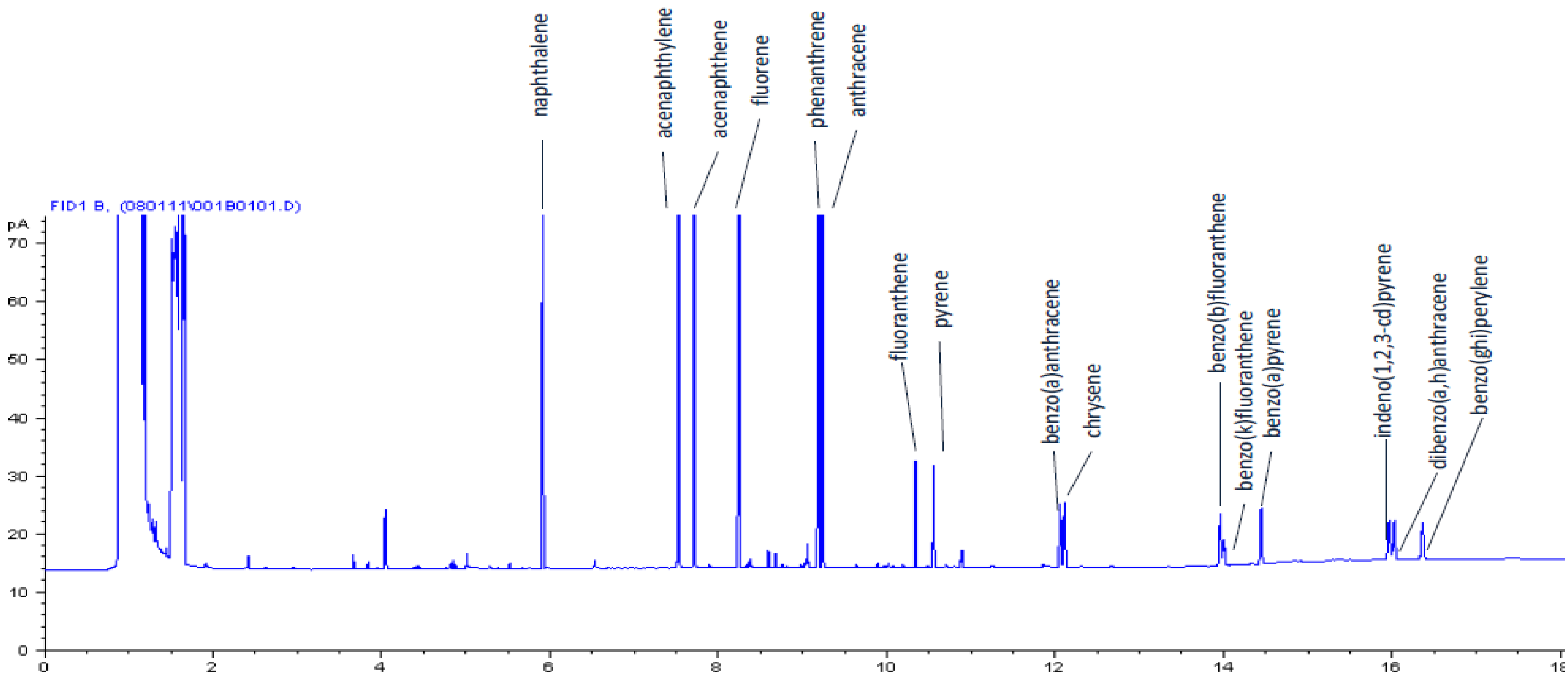


		Sample	Priority	Status	Type	Method	Sample Volume (uL)	Cartridges	Inputs/Output	Accuvap	Type	ID	Batch	Start Time	End Time
1	-	1			LINC	PAHs by GPC only.mcr									
2	Edit				AVM	PAH EVS.evs			Edit	Edit				8/4/2011 10:25:22 AM	8/4/2011 11:05:47 AM
3	Edit				GPC	PAHs GPC Only.gmf	2500		Edit	Edit				8/4/2011 11:05:58 AM	8/4/2011 11:58:27 AM
4	-	2			LINC	PAHs by GPC with inline SP...									
5	Edit				AVM	PAH EVS.evs			Edit	Edit				8/4/2011 11:58:43 AM	
6	Edit				GPC	PAHs GPC Inline SPE.gmf	2500	5 Edit	Edit	Edit					
7	-	3			LINC	PAHs by GPC with inline SP...									
8	Edit				AVM	PAH EVS.evs			Edit	Edit					
9	Edit				GPC	PAHs GPC Inline SPE.gmf	2500	5 Edit	Edit	Edit					
10	-	4			LINC	PAHs by GPC with inline SP...									
11	Edit				AVM	PAH EVS.evs			Edit	Edit					
12	Edit				GPC	PAHs GPC Inline SPE.gmf	2500	5 Edit	Edit	Edit					
13	Add														

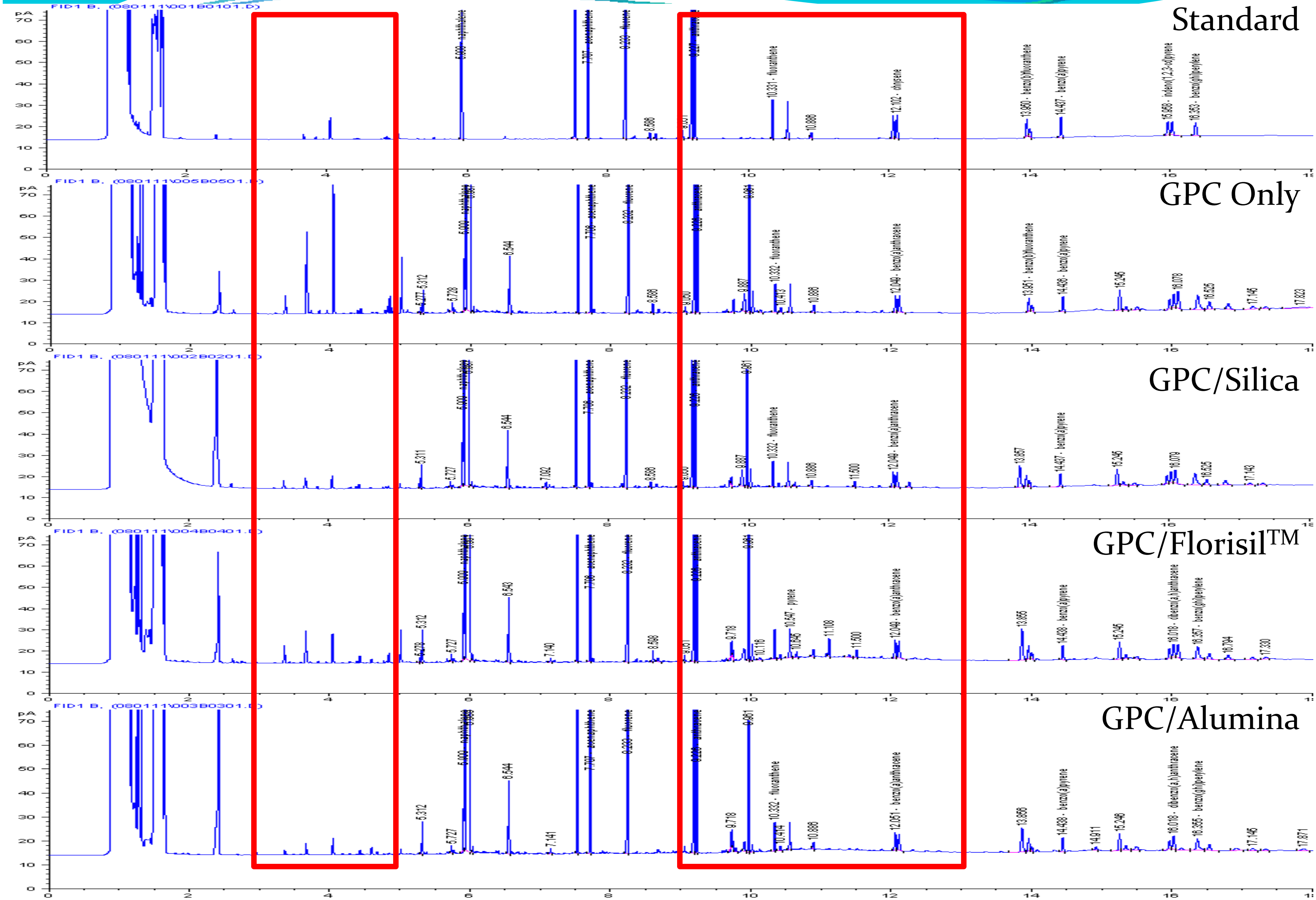
GC Analysis

Detector	FID, 350°C
Injection	1μl, splitless, 330°C
Column	Restek 12723: RTX®-5Sil MS 30m x 0.25mm x 0.25μm
Flow	He, 4 mL/min

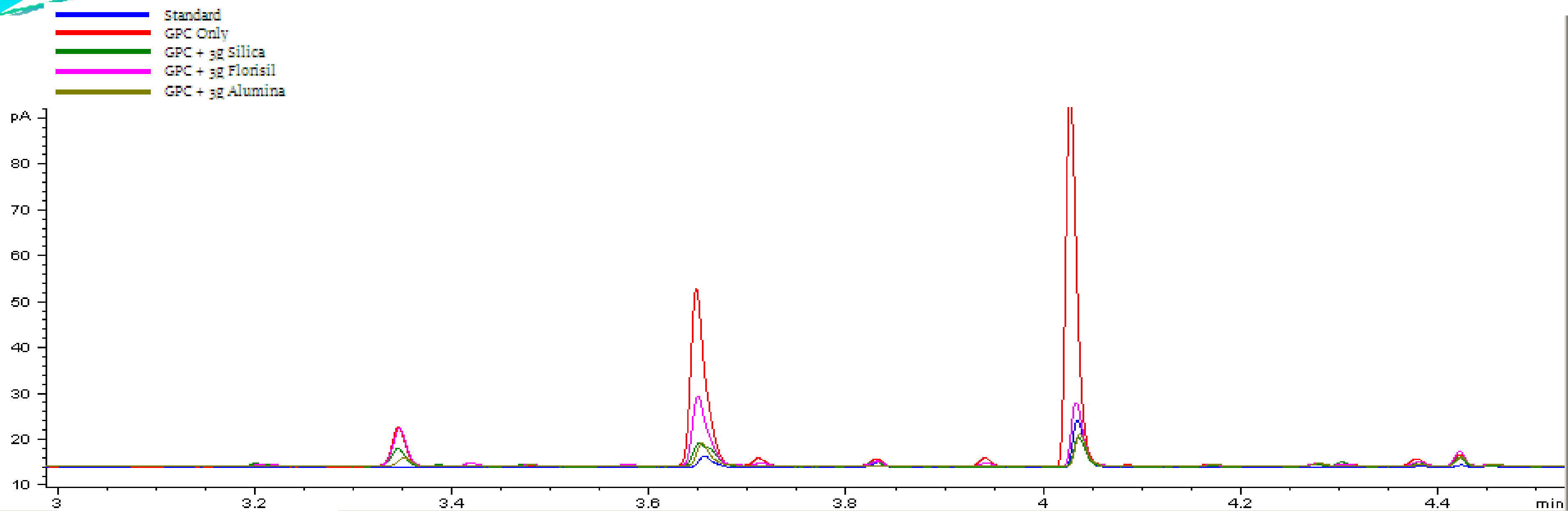
Oven Temperature	Ramp Rate (°C/min)	Temperature (°C)	Hold Time (minutes)
		40	2
	25	250	0
	5	265	0
	25	300	4

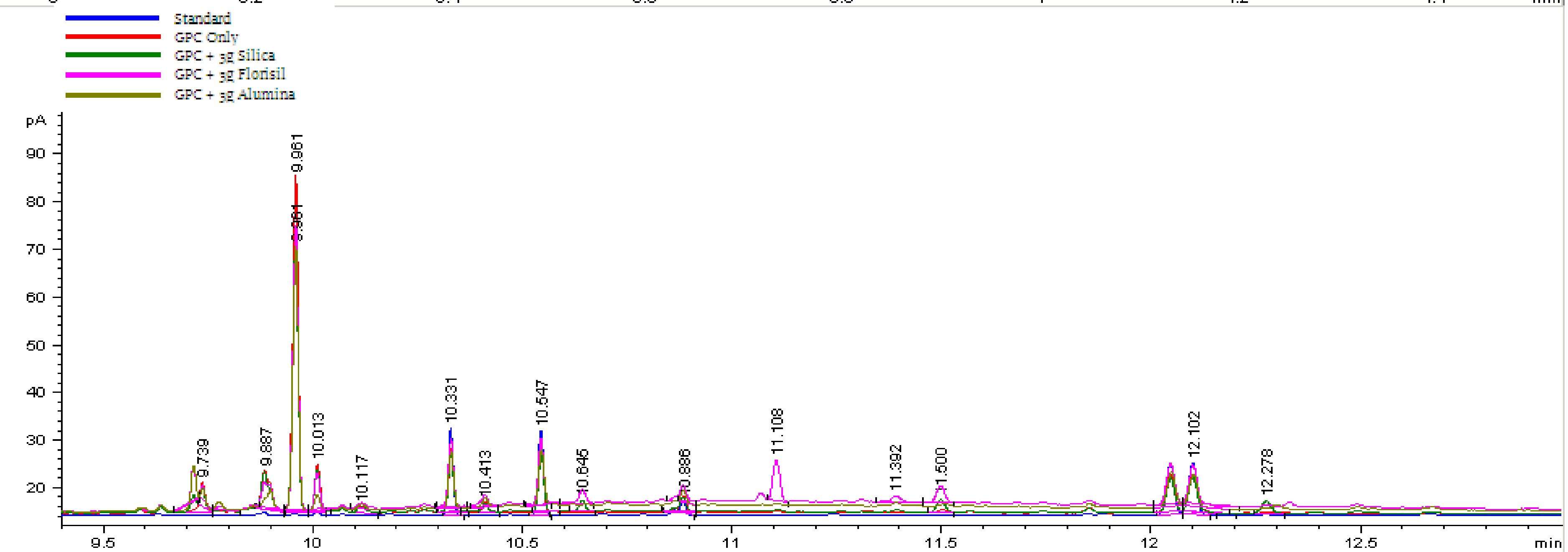


Soil Extract

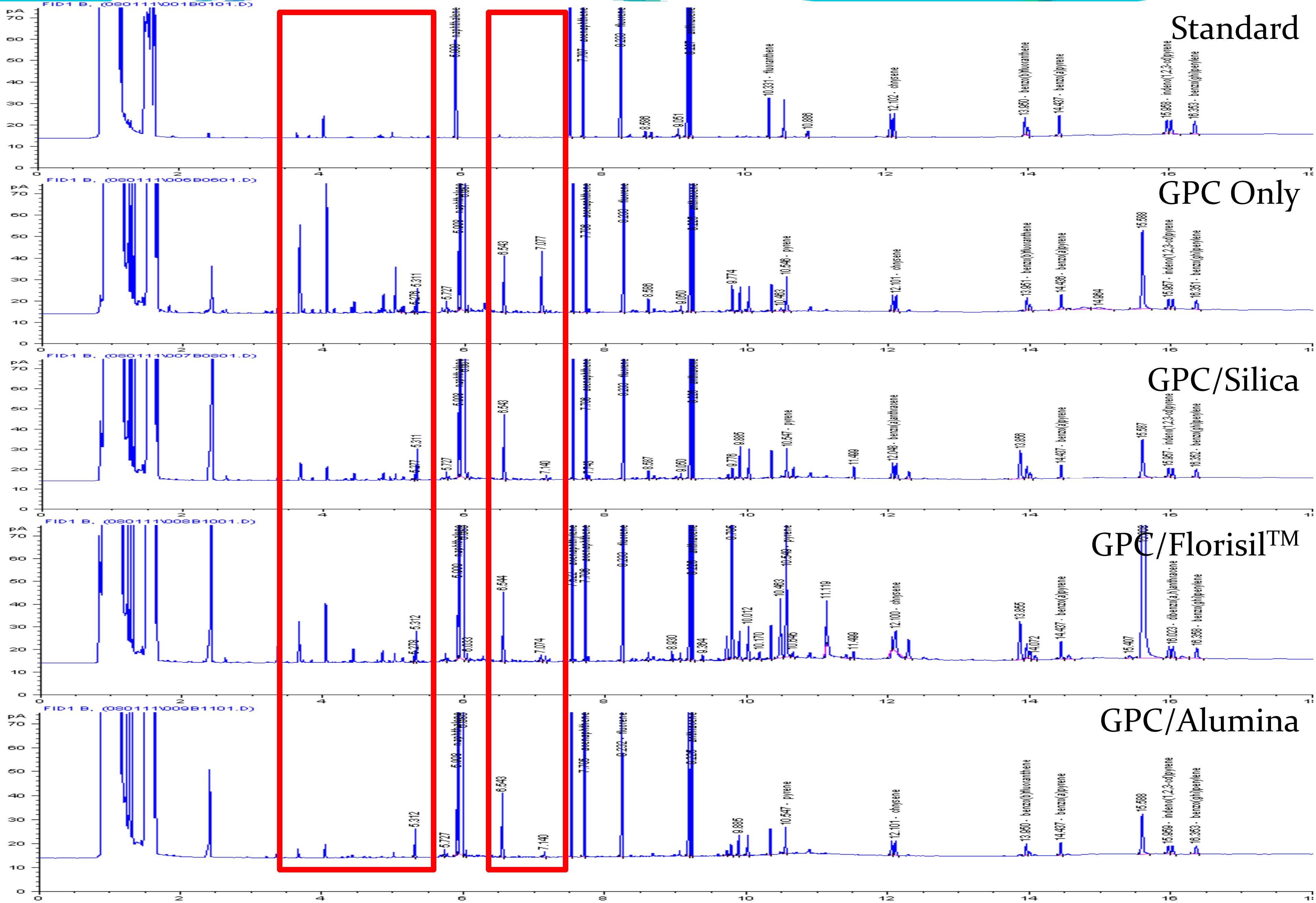


Soil Extract

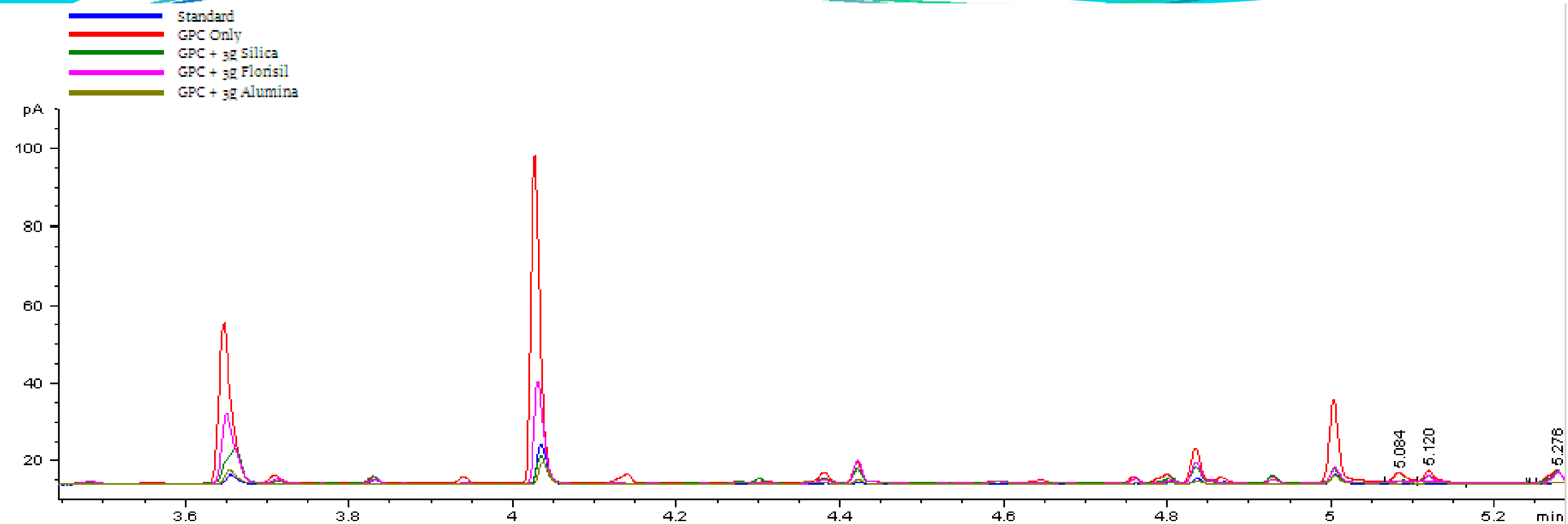


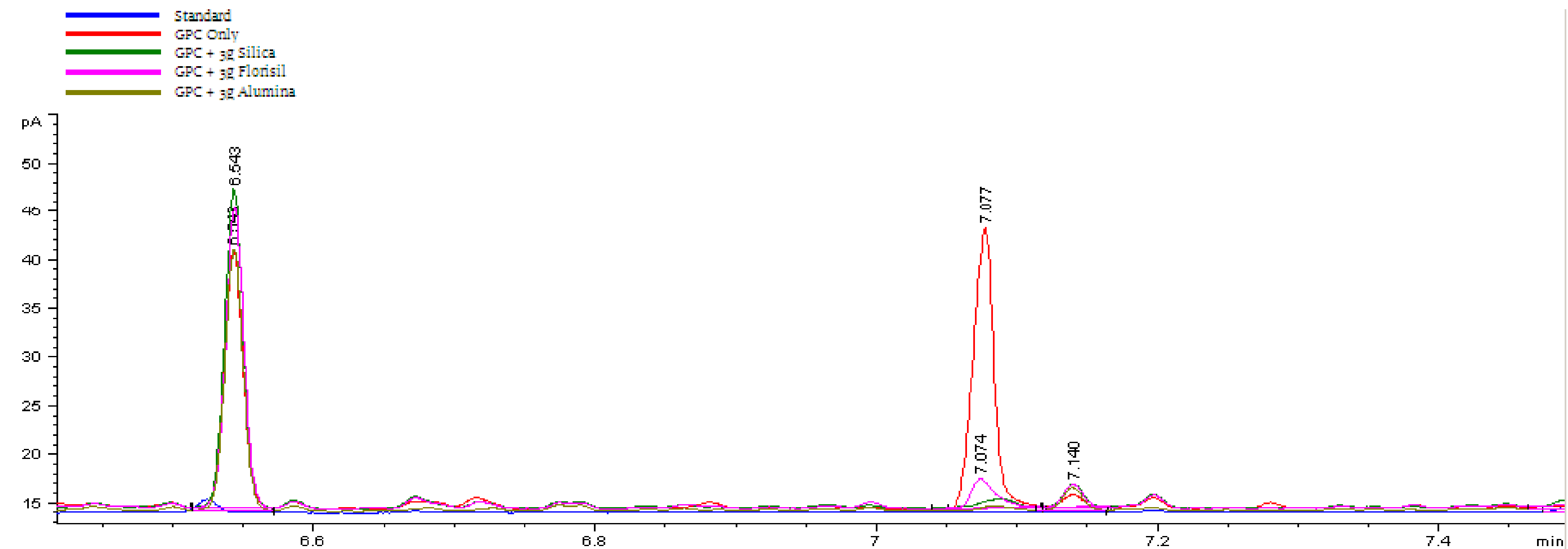


Fish Extract

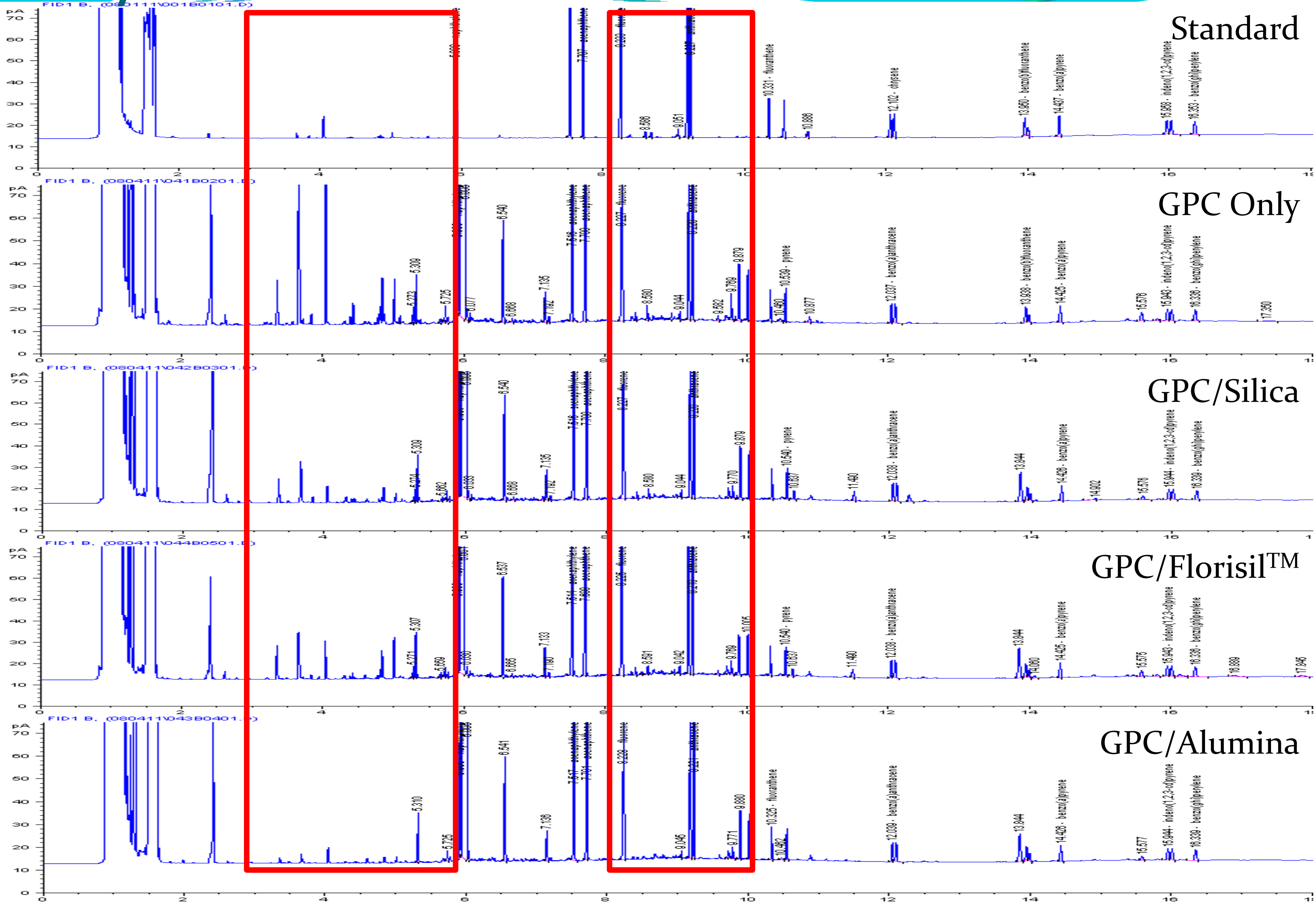


Fish Extract





Oyster Extract



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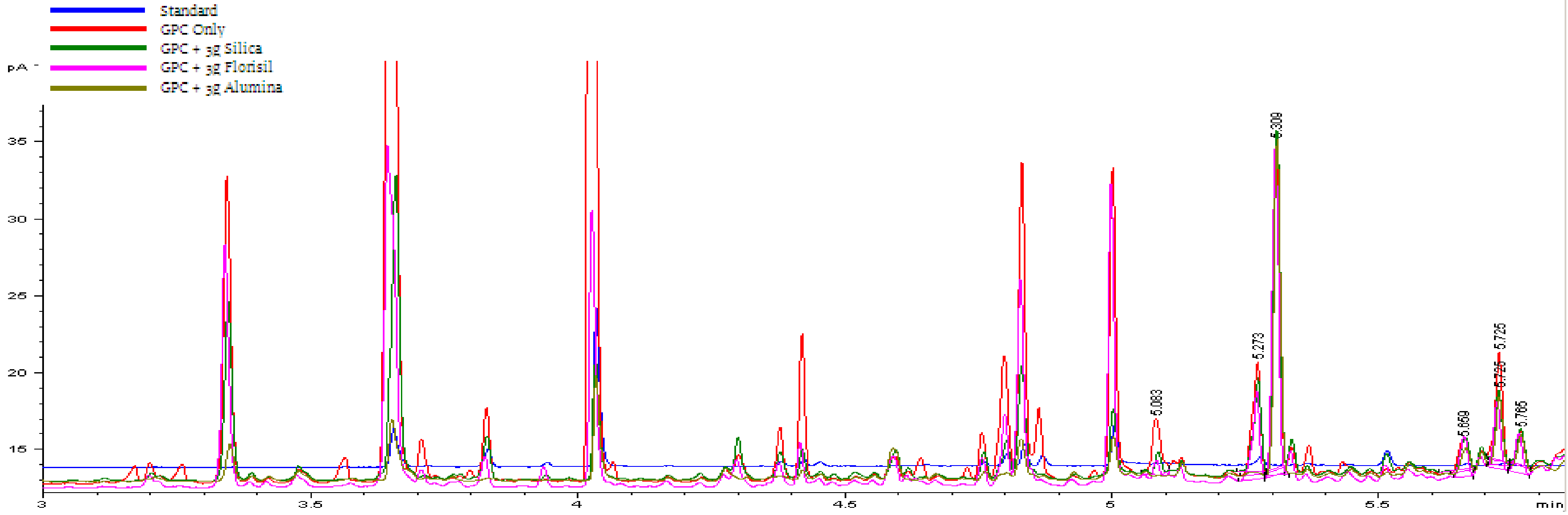
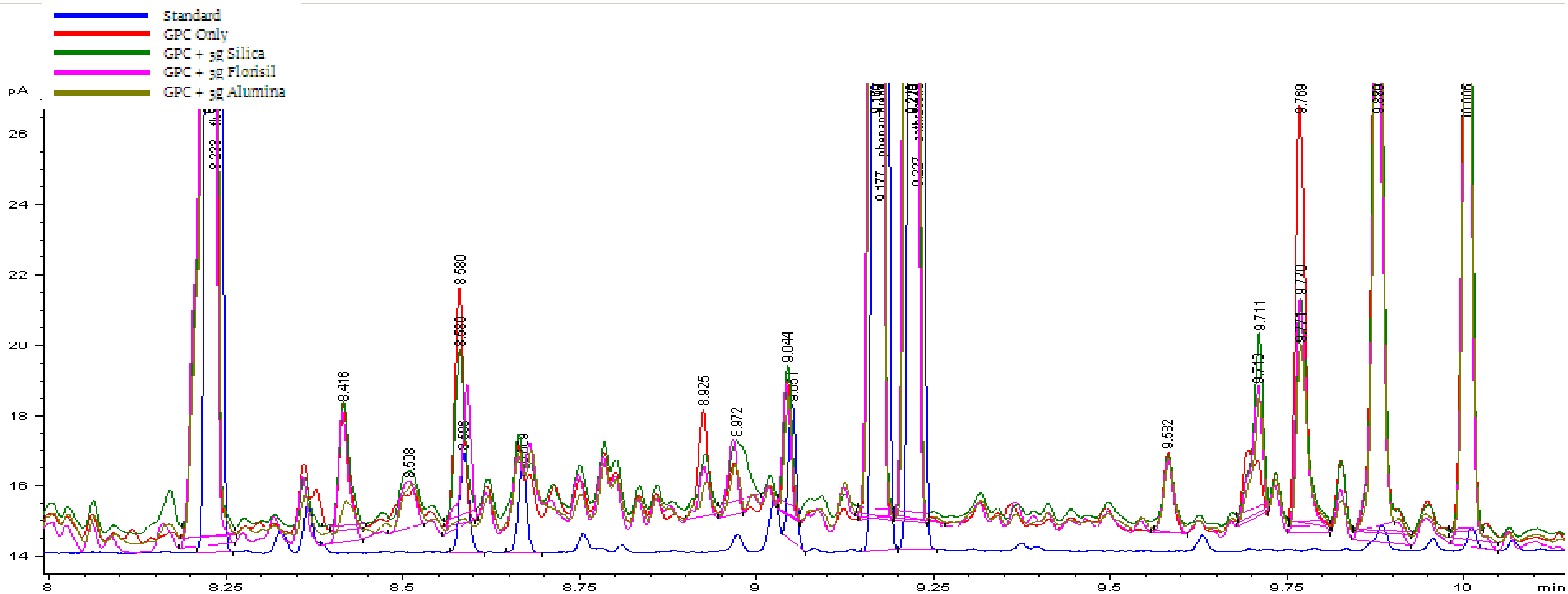
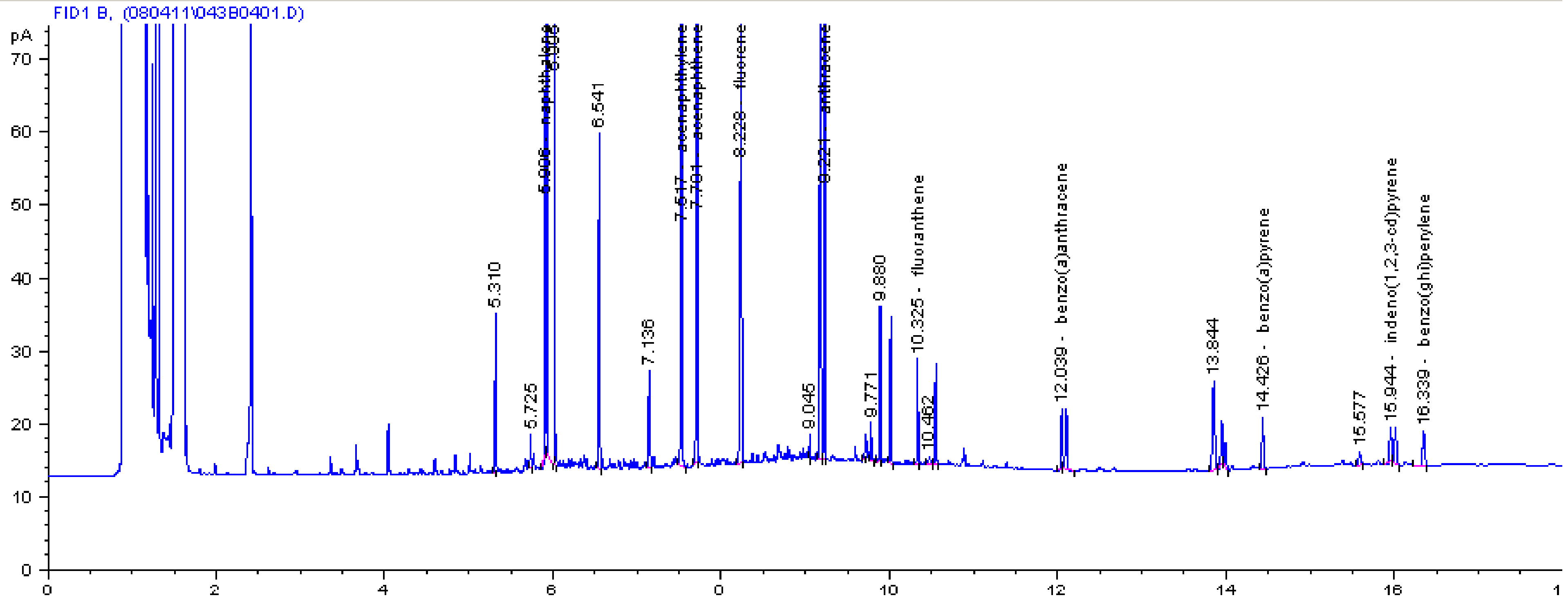




Oyster Extract Cleanup



GPC with Inline Alumina

Recovery

Analyte	50mL Extract (ppb)	GC Analysis (ppm)	Soil Average (n=3)	Soil RSD	Fish Average (n=3)	Fish RSD	Oyster Average (n=3)	Oyster RSD
naphthalene	401.6	10.04	80.5	3.0	82.7	2.6	79.8	2.6
acenaphthylene	401.6	10.04	85.6	2.6	87.9	3.9	79.9	5.5
acenaphthene	401.6	10.04	87.9	2.8	91.6	3.4	91.2	4.3
fluorene	401.6	10.04	90.6	3.1	92.8	5.8	91.0	4.1
phenanthrene	401.6	10.04	91.0	2.9	94.5	3.9	87.2	3.6
anthracene	401.6	10.04	90.1	2.9	93.7	3.4	85.9	3.6
fluoranthene	40.16	1.004	94.5	6.4	95.2	3.8	88.5	4.0
pyrene	40.16	1.004	93.0	3.1	103.8	3.4	91.4	5.1
benzo(a)anthracene	40.16	1.004	93.4	2.5	94.9	4.4	88.4	4.0
chrysene	40.16	1.004	93.4	1.9	90.9	5.1	84.0	2.7
benzo(b)fluoranthene	40.16	1.004	89.7	1.3	93.6	3.5	84.4	1.8
benzo(k)fluoranthene	20.00	0.500	96.5	1.5	102.6	4.7	86.5	7.4
benzo(a)pyrene	40.16	1.004	90.5	2.0	96.3	2.0	84.1	3.9
indeno(1,2,3-cd)pyrene	40.16	1.004	105.0	1.6	96.0	1.1	77.6	5.6
dibenzo(a,h)anthracene	40.16	1.004	115.1	1.6	96.9	3.9	78.9	7.5
benzo(ghi)perylene	40.16	1.004	133.1	2.7	94.4	3.6	84.8	5.0

Conclusions

- Inline SPE can provide additional cleanup at a low cost, with no additional time or solvent requirements
- Additional cleanup can improve accuracy and precision and extend the life of the analytical instrument
- Future Studies:
  - GPC with multiple columns inline (silica then alumina, for example) to remove additional interferences
  - SPE to separate two groups of compounds (GPC with inline carbon column to separate PCBs from dioxins)

Thank You

- Thank you co-authors Tom Dobbs, Jeff Wiseman and Jennifer Salmons
- Thank you everyone else at J2 Scientific
- Thank you Restek for supplying the GC Column used in this study

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