A New SPE Sorbent for Improved EPH Fractionation

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UCT

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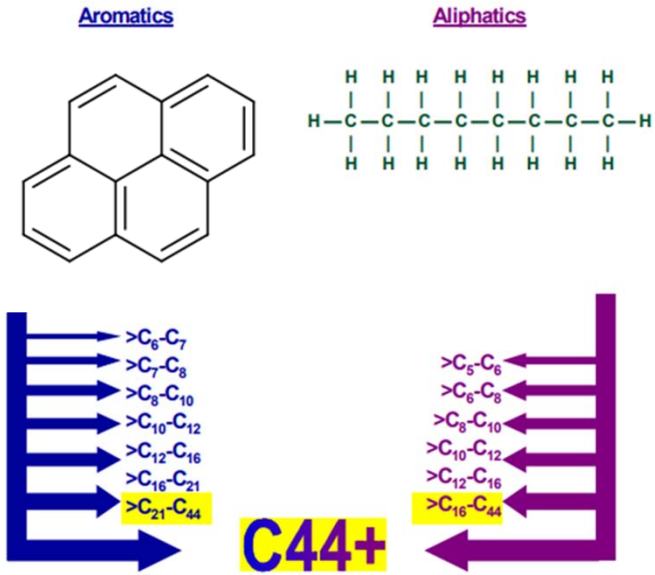
EPH Fractionation

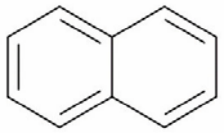
- Extractable Petroleum Hydrocarbons (EPHs)
- Assess risk of petroleum products in environment
  - Water, Sediment, Soil
- Separate aliphatic & aromatic hydrocarbons using SPE
  - Quantify separately
  - Improved toxicological profile / risk assessment



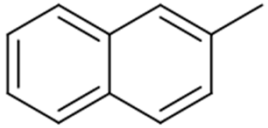
EPH Fractionation

Approved Methods:

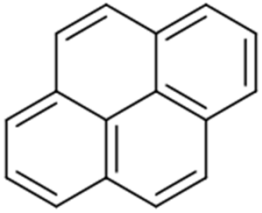
- No fixed Federal / EPA method
- Most labs follow MA DEP method
- States can have different requirements
  - MA DEP Method:
    - 40–140% Recovery for Analytes and Surrogates
    - <5% Breakthrough for Naphthalene and 2-Methylnaphthalene
  - NJ DEP Method:
    - Based off MADEP EPH Method
    - Requires monitoring of additional analytes
  - TCEQ Method:
    - Uses Pentane instead of Hexane
    - 60–140% Recovery for Analytes
    - 70–130% Recovery for Surrogates
    - <10–20% Crossover



Naphthalene



2-Methylnaphthalene



Pyrene

EPH Fractionation

Sample Extraction:

- Soil/Sediment/Solids – prepared according to EPA Method 3540 (Soxhlet extraction) or EPA Method 3546 (microwave extraction)
- Water samples – prepared according to EPA Method 8015D (SPE) or EPA Method 3510 (LLE)
- Sample extract should be in *n*-Hexane for EPH fractionation
  - May necessitate solvent exchange

Analysis:

- Typically GC-FID
  - Non-selective
  - Extraction cartridges should be very clean (no significant background)

Current EPH Methods

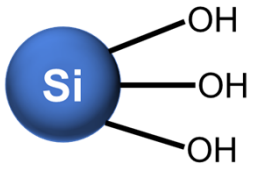
- Solid-Phase Extraction with silica gel
  - Weak electrostatic interaction of aromatic ring and -OH group

SPE Cartridge:

- Special heat-treated silica
- UCT cartridges are capped at both ends to ensure silica integrity
- No moisture - deactivates sorbent!

UCT Products:

- XRSIHT15M25 (5g/25mL)
- XRSIHT13M15 (3g/15mL)

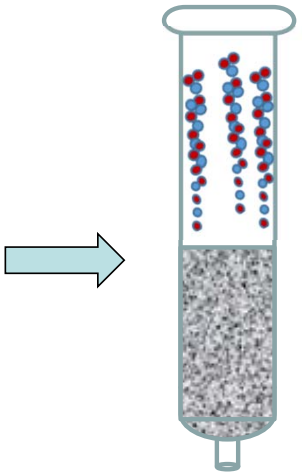


SPE Procedure
(5g/25mL Cartridge)

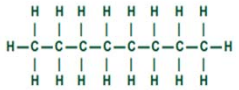
1. Condition

- 30 mL Hexane:

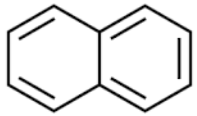
2. Load Sample (1 mL Hexane)



● **Aliphatic**



● **Aromatic**

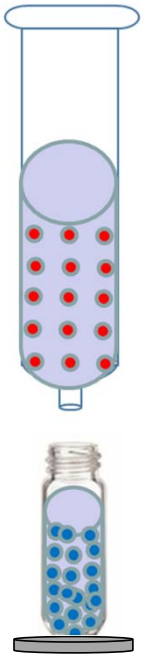


Note: Some procedures use DCM & Hexane

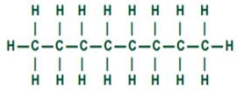
SPE Procedure
(5g / 25mL Cartridge)

3. Elute Aliphatic Fraction

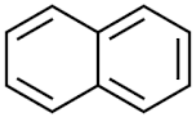
≈20 mL
Hexane



Aliphatic

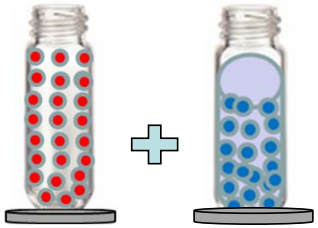


Aromatic



4. Elute Aromatic Fraction

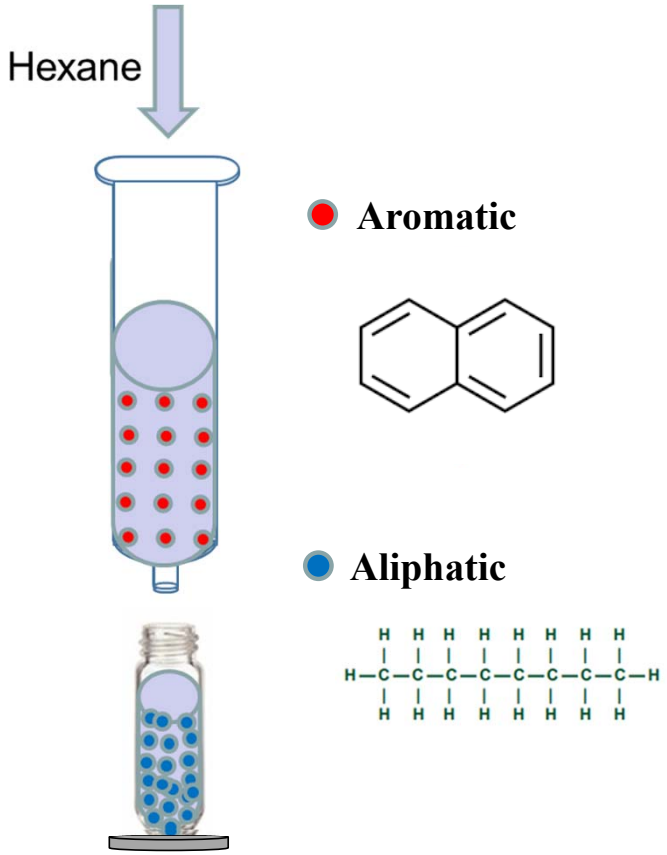
20 mL
DCM



5. Concentrate

Critical Step!

- Hexane elution volume
- The amount of hexane required needs to be optimized for each batch of cartridges
  - Too little = incomplete elution of aliphatic fraction
  - Too much = breakthrough of aromatic fraction (naphthalene & 2-methylnaphthalene)

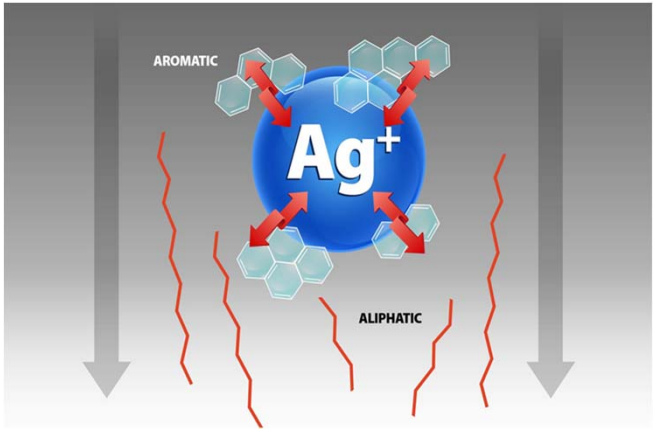


Problems Encountered

- Deactivation of silica gel (hygroscopic!)
  - Inconsistent results
  - Low recoveries
  - Breakthrough of aromatic fraction into aliphatic fraction
    - Naphthalene and 2-Methylnaphthalene (most polar)
- Tedious
  - Do not let sorbent go dry!
  - Use stopcocks to control solvent level in SPE cartridge
- Capacity (polar aromatics)
- Optimization of Hexane volume for each batch of Si-OH
- Storage - unused cartridges must be stored in desiccator

New Sorbent

- Silver ions functionalized onto a solid support
  - Improved stability
  - Excellent reproducibility



- High Selectivity
  - Strong retention of aromatic & unsaturated compounds
  - Forms a charge-transfer complex with silver ions
  - No breakthrough of aromatic fraction into the aliphatic fraction
    - Naphthalene and 2-Methylnaphthalene

UCT

- **High Capacity** – of aromatic hydrocarbons (25 mg/g)
- **Simplified Procedure** – simple, fast protocol
  - No optimization of solvent volume for each batch of cartridges
- **More Environmentally Friendly** – less solvent, no DCM
- **Moisture Stability** – no deactivation of sorbent
- **Lot-To-Lot Reproducibility**
- **Three Formats Available** – 0.5g, 1g, 2g (6mL cartridge)
- **Amenable to Automation** – improved reproducibility & increased sample throughput

Compounds Evaluated

	Aliphatics	Aromatics
1	1-Chlorooctadecane (surrogate)	o-Terphenyl (surrogate)
2	(C9) n-Nonane	2-Bromonaphthalene (fractionation surrogate)
3	(C10) n-Decane	2-Fluorobiphenyl (fractionation surrogate)
4	(C12) n-Dodecane	1,2,3-Trimethylbenzene
5	(C14) n-Tetradecane	2-Methylnaphthalene
6	(C16) n-Hexadecane	Acenaphthene
7	(C18) n-Octadecane	Acenaphthylene
8	(C19) n-Nonadecane	Anthracene
9	(C20) n-Eicosan	Benzo[a]anthracene
10	(C21) n-Heneicosane	Benzo[a]pyrene
11	(C22) n-Docosane	Benzo[b]fluoranthene
12	(C24) n-Tetracosane	Benzo[ghi]perylene
13	(C26) n-Hexacosane	Benzo[k]fluoranthene
14	(C28) n-Octacosane	Chrysene
15	(C30) n-Triacontane	Dibenz[a,h]anthracene
16	(C32) n-Dotriacontane	Fluoranthene
17	(C34) n-Tetratriacontane	Fluorene
18	(C36) n-Hexatriacontane	Indeno[1,2,3-cd]pyrene
19	(C38) n-Octatriacontane	Naphthalene
20		Phenanthrene
21		Pyrene

GC Conditions Used

GC-MS Conditions:

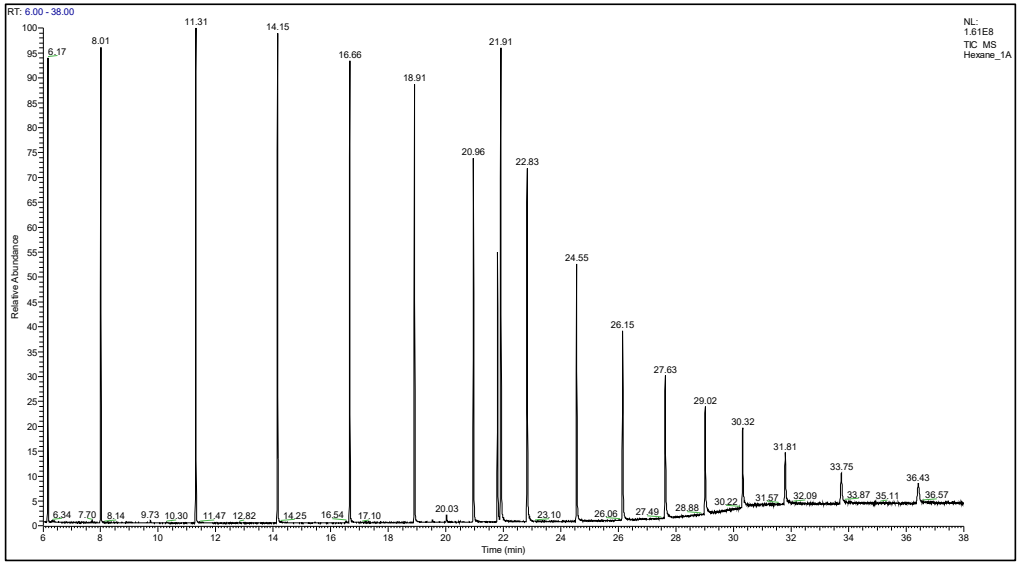
Parameter	Conditions
GC-MS system	Thermo Trace 1300 GC & ISQ MS
GC column	Restek Rxi®-5sil MS, 30m x 0.25mm, 0.25µm with Integra-Guard
GC liner	4 mm split liner with deactivated glass wool
Injection	1 µL split (1:100) at 300°C
Carrier gas	Ultra-high purity Helium at a constant flow of 1.2 mL/min
Oven temp. program	Initial temperature at 50°C, hold for 3 min; ramp at 10°C/min to 320°C, hold for 10 min
Temperatures	Transfer line = 275°C; Ion source = 275°C
Full scan range	35 - 600 amu

GC-FID Conditions:

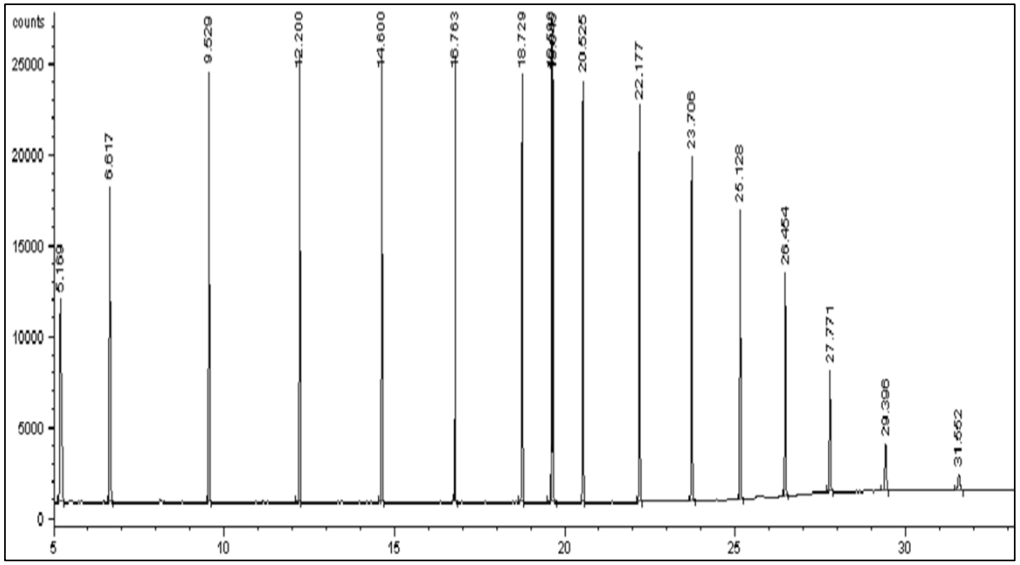
Parameter	Conditions
GC-FID system	HP5890 Series II
GC column	Restek Rrx®-5 MS, 30m x 0.32mm, 0.5µm
GC liner	4 mm split/splitless liner with deactivated glass wool
Injection	1 µL splitless at 280°C
Carrier gas	Ultra-high purity Helium at a constant flow of 1.3 mL/min
Oven temp. program	Initial temperature at 55°C, hold for 0.3 min; ramp at 10°C/min to 320°C, hold for 10 min
FID temp.	320°C
Make-up gas	Ultra-high purity Hydrogen at a constant flow of 30 mL/min
Air flow	350 mL/min

Chromatogram - Aliphatic Fraction (Hexane)

GC-MS:

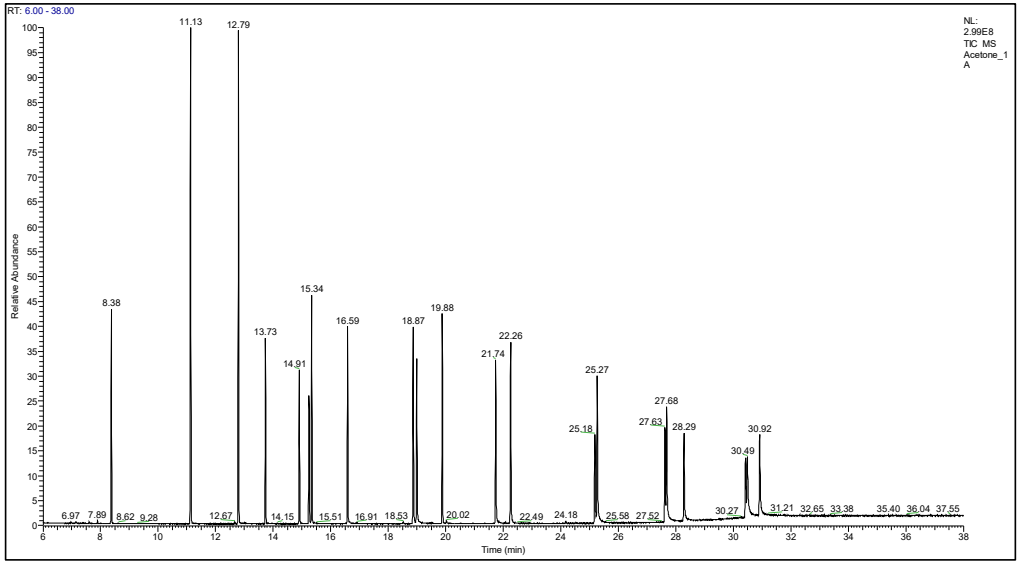


GC-FID:

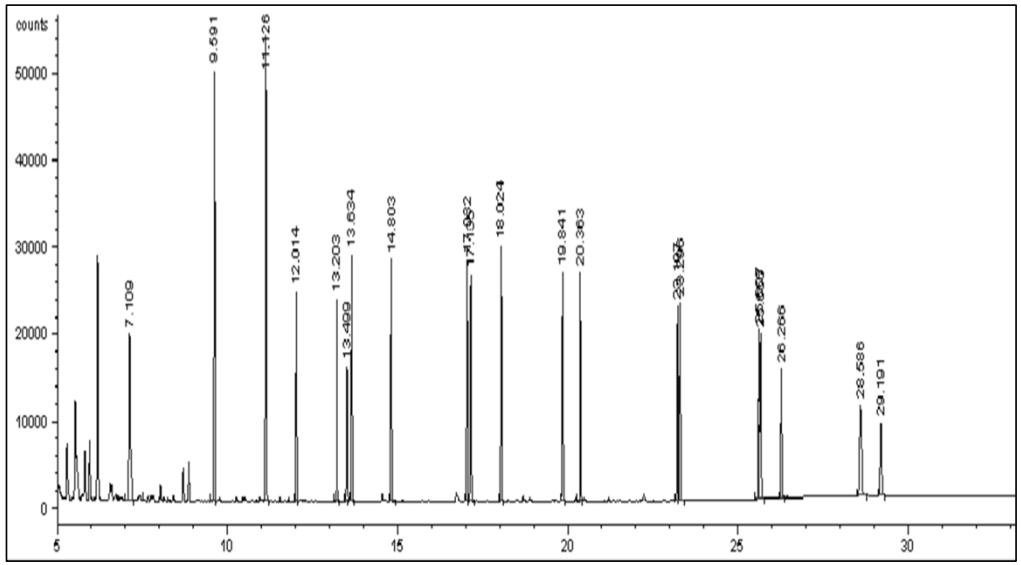


Chromatogram - Aromatic Fraction (Acetone)

GC-MS:



GC-FID:

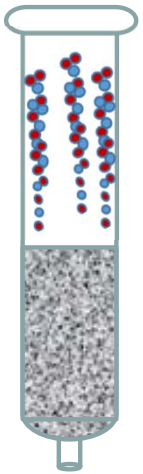


Fusion Ag⁺ Procedure
(1g/6mL Cartridge)

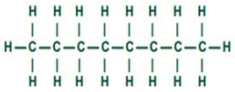
1. Condition

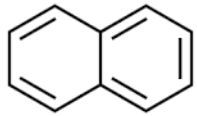
- 4 mL Acetone
- 4 mL Hexane

2. Load Sample (1 mL Hexane)



Aliphatic **Aromatic**



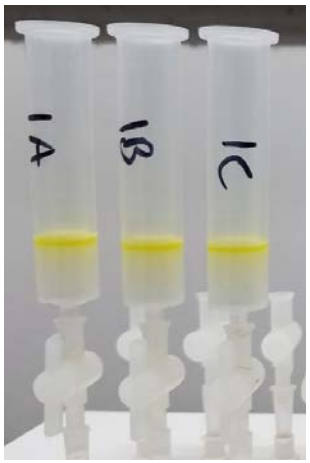


- No need to close stopcock in between steps
- Simply perform each step until dripping stops

Fusion Ag^+ Procedure

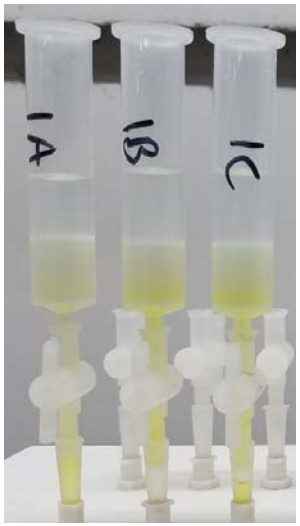
3. Elute Aliphatic Fraction

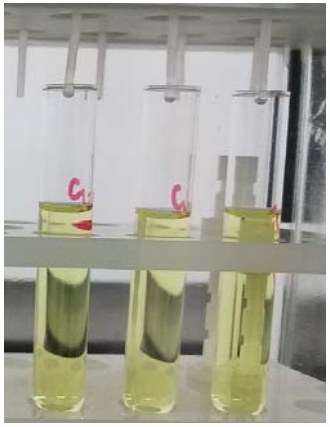
4 mL
Hexane



4. Elute Aromatic Fraction

4 mL
Acetone





5. Concentrate or Direct Analysis

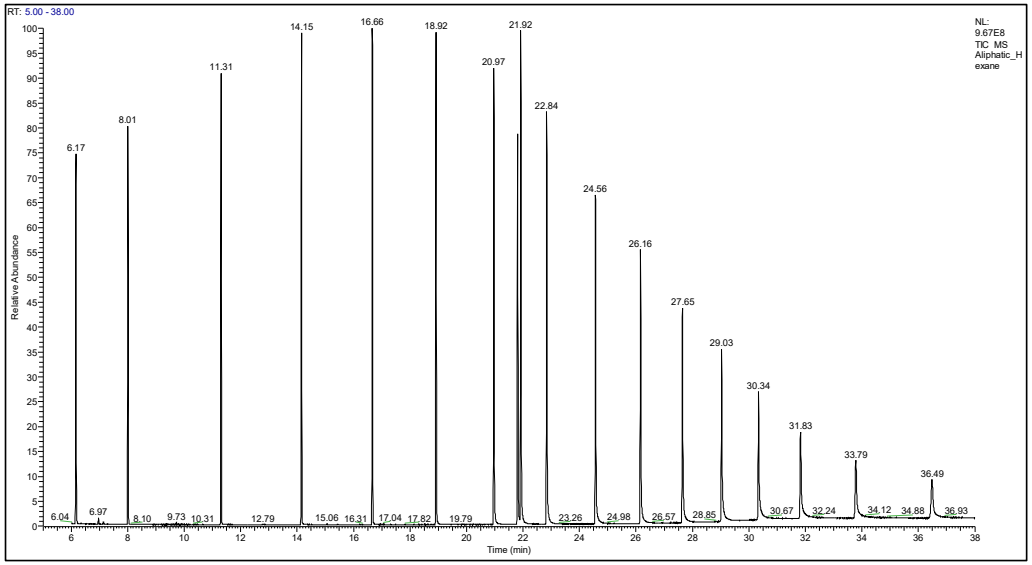
Fusion Ag^+ Procedure

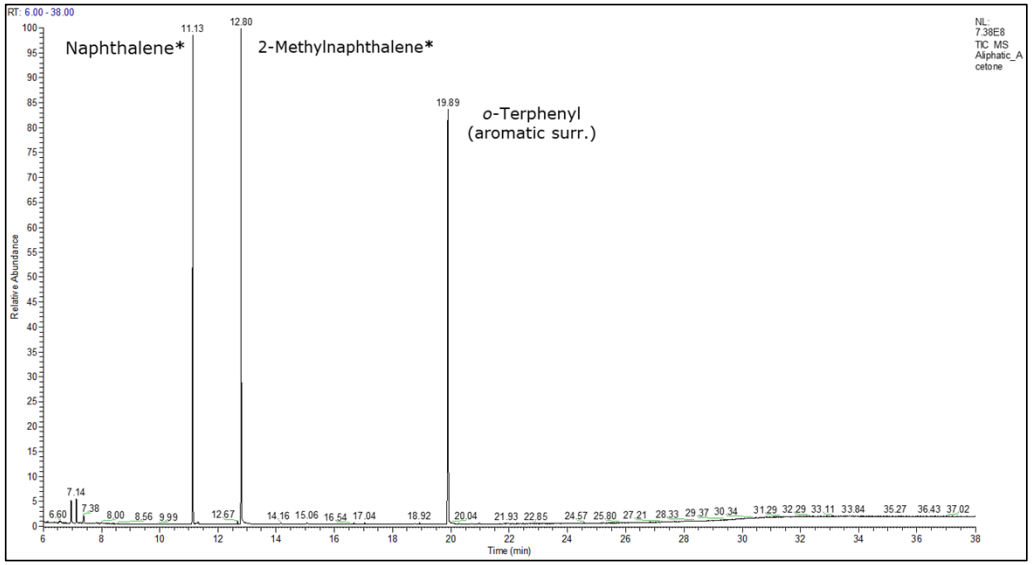
		0.5g, 6mL	1g, 6mL	2g, 6mL
Condition	1. Acetone	2 mL	4 mL	6 mL
	2. Hexane	2 mL	4 mL	6 mL
Elute	1. Hexane	2 mL	4 mL	6 mL
	2. Acetone	2 mL	4 mL	6 mL

Complete Separation - Aliphatics

- 200 µg/mL Aliphatics Standard + Surrogates

Hexane (Aliphatic) Fraction





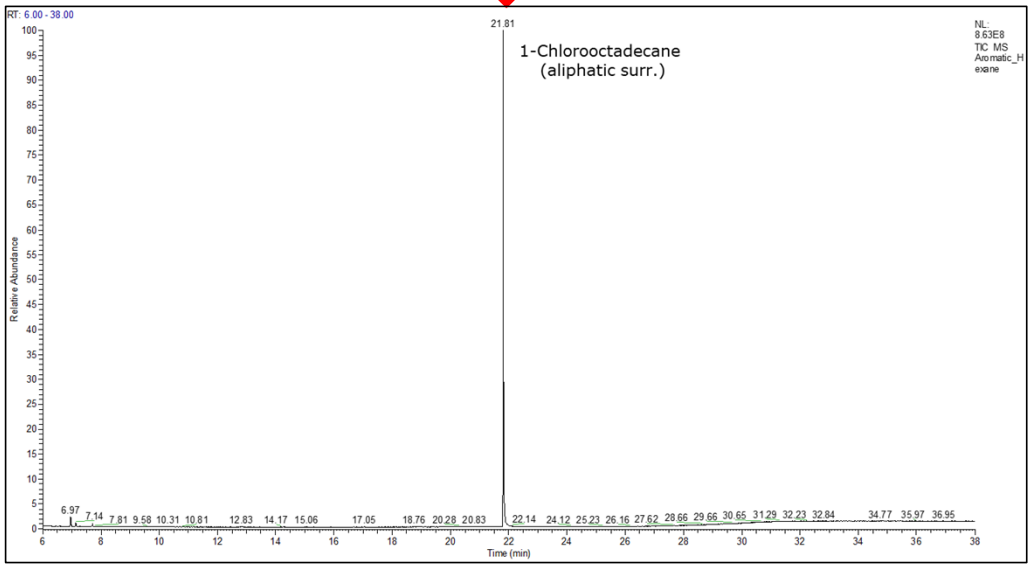
Acetone (Aromatic) Fraction

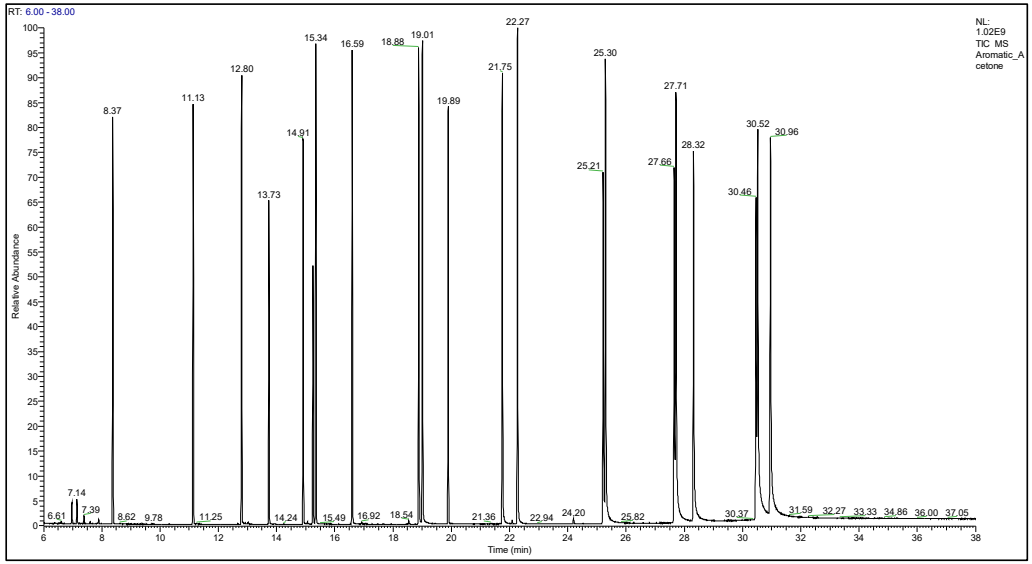
*Included in aliphatic standard

Complete Separation - Aromatics

- 200 µg/mL Aromatics Standard + Surrogates

Hexane (Aliphatic) Fraction





Acetone (Aromatic) Fraction

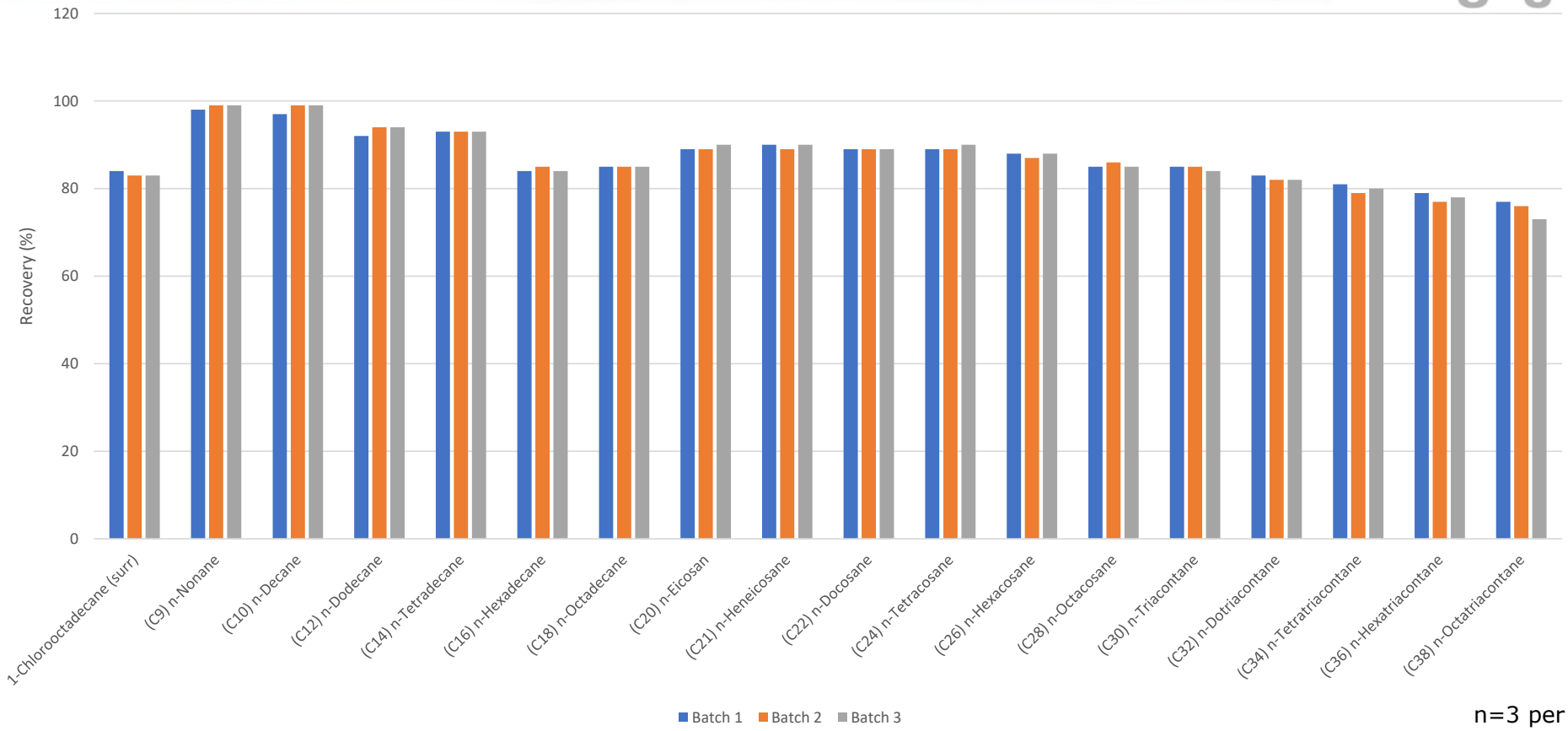
Recovery - Aliphatics

	Sample 1	Sample 2	Sample 3	Sample 4	Mean Rec (%)	RSD (%)
1-Chlorooctadecane (surr.)	92	92	95	95	**93**	**1.69**
(C9) n-Nonane	96	97	99	98	**98**	**1.37**
(C10) n-Decane	96	97	99	98	**98**	**1.31**
(C12) n-Dodecane	98	98	100	100	**99**	**1.21**
(C14) n-Tetradecane	96	97	99	98	**98**	**1.27**
(C16) n-Hexadecane	95	96	98	98	**97**	**1.56**
(C18) n-Octadecane	91	92	94	94	**93**	**1.67**
(C19) n-Nonadecane	93	93	96	96	**94**	**1.64**
(C20) n-Eicosan	111	112	119	119	**115**	**3.71**
(C22) n-Docosane	91	92	94	94	**93**	**1.74**
(C24) n-Tetracosane	87	88	90	90	**89**	**1.76**
(C26) n-Hexacosane	89	89	92	92	**90**	**1.80**
(C28) n-Octacosane	87	88	90	90	**89**	**1.84**
(C30) n-Triacontane	82	83	85	85	**84**	**1.92**
(C36) n-Hexatriacontane	80	80	83	84	**82**	**2.53**

Recovery - Aromatics

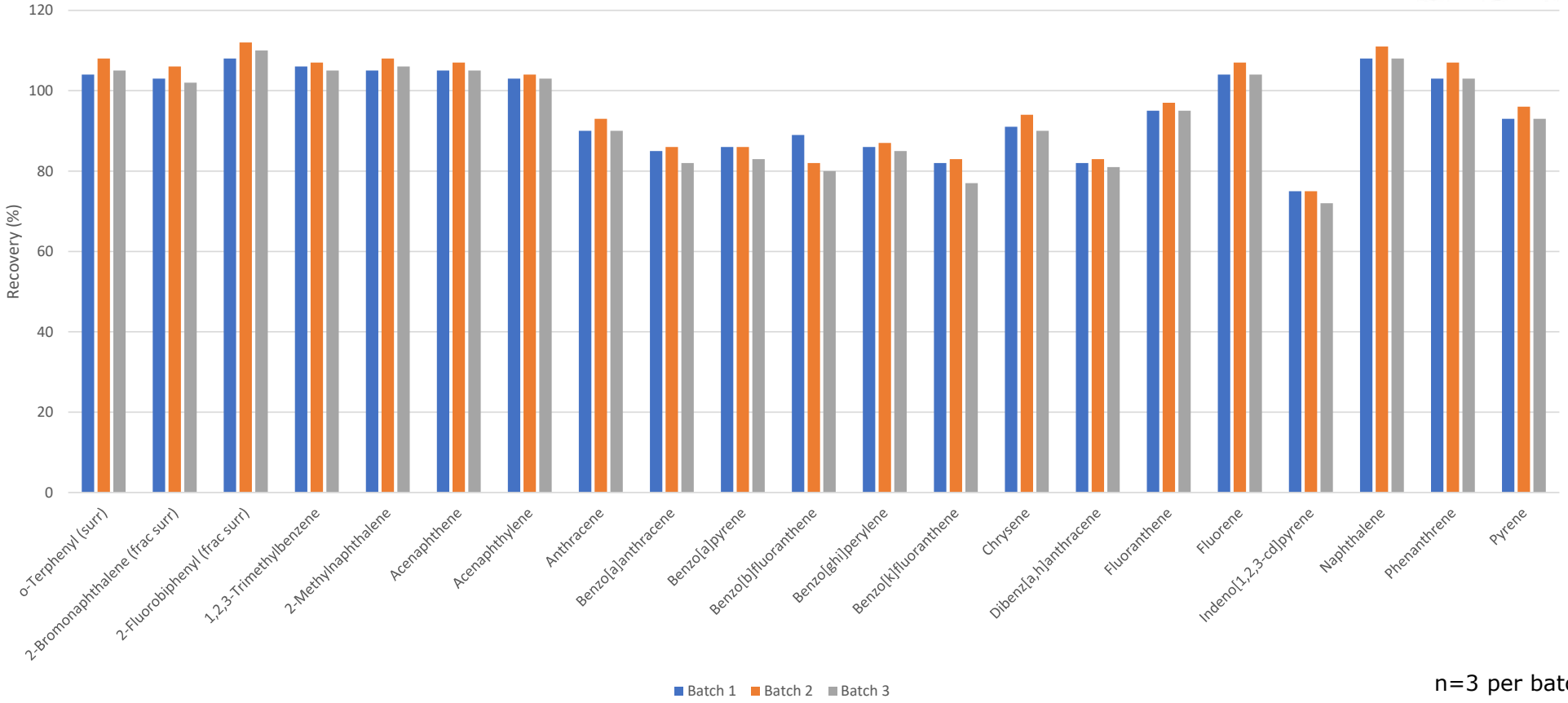
	Sample 1	Sample 2	Sample 3	Sample 4	Mean Rec (%)	RSD (%)
o-Terphenyl (surr.)	92	98	111	102	**101**	**8.05**
2-Bromonaphthalene (frac. surr.)	92	98	112	102	**101**	**8.27**
2-Fluorobiphenyl (frac. surr.)	93	98	112	103	**101**	**8.07**
2-Methylnaphthalene	92	97	111	101	**100**	**8.15**
Acenaphthene	83	87	98	91	**90**	**7.24**
Acenaphthylene	92	98	112	103	**101**	**8.21**
Anthracene	93	99	113	103	**102**	**8.32**
Benz[a]anthracene	91	97	111	102	**100**	**8.34**
Benzo[a]pyrene	91	94	106	99	**97**	**6.98**
Benzo[b]fluoranthene	91	97	112	103	**101**	**8.74**
Benzo[k]fluoranthene	90	96	110	100	**99**	**8.48**
Chrysene	91	97	111	102	**100**	**8.57**
Dibenz [a,h] anthracene	85	93	108	99	**96**	**10.07**
Dibenzo[ghi]perylene	86	94	108	99	**97**	**9.83**
Fluoranthene	90	96	109	100	**99**	**8.13**
Fluorene	92	97	111	102	**100**	**8.22**
Indeno[1,2,3-cd]pyrene	84	90	103	95	**93**	**8.56**
Naphthalene	108	115	136	124	**121**	**9.89**
Phenanthrene	91	97	111	101	**100**	**8.20**
Pyrene	91	97	112	102	**101**	**8.52**

Batch-to-Batch Consistency - Aliphatics



n=3 per batch

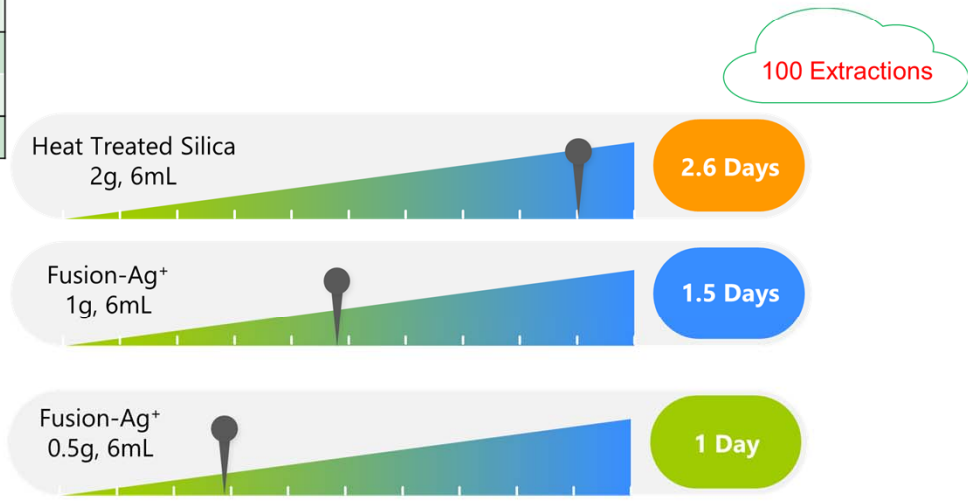
Batch-to-Batch Consistency - Aromatics



n=3 per batch

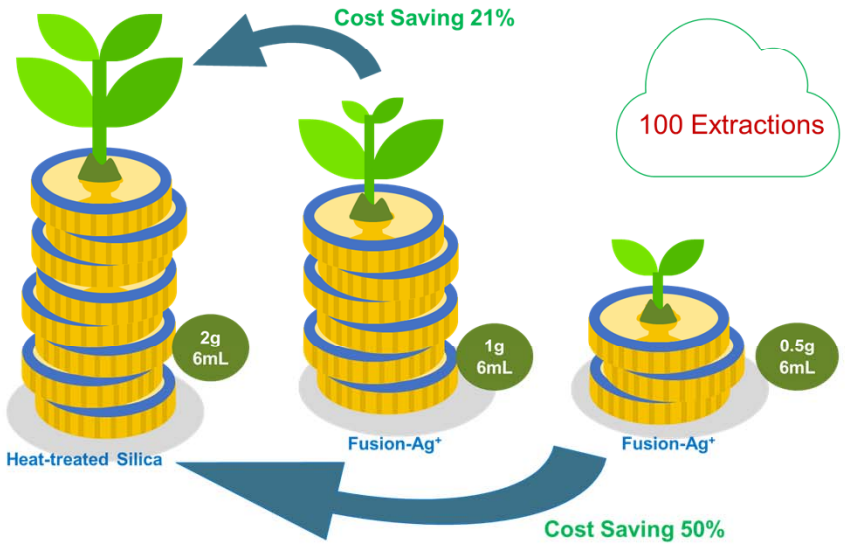
Time Savings vs. HT Silica

Fractionation Step		Extraction Time (min)		
		Fusion-Ag+ 0.5g, 6mL	Fusion-Ag+ 1g, 6mL	Heat Treated Silica 2g, 6mL
Conditioning	Acetone	0.8	1.8	
	DCM (+5 min hold)			5.8
	Hexane	0.8	1.7	1.9
Sample Loading	Hexane	0.3	0.5	0.5
Elute Aliphatics	Hexane	0.75	1.7	1.4
Elute Aromatics	Acetone	0.8	1.5	
	DCM			2.8
Total extraction time		**3.5**	**7.2**	**12.4**

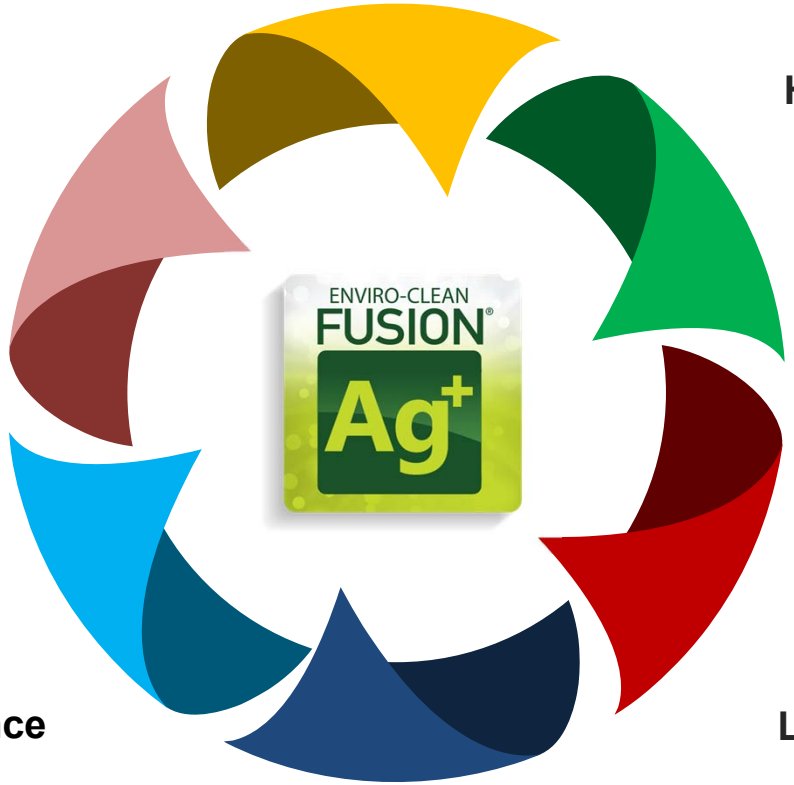


Solvent Savings vs. HT Silica

Fractionation Step		Solvent Consumption (mL)		
		Fusion-Ag$^+$ 0.5g, 6mL	Fusion-Ag$^+$ 1g, 6mL	Heat Treated Silica 2g, 6mL
Conditioning	Acetone	2	4	
	DCM			3
	Hexane	2	4	6
Sample Loading	Hexane	1	1	1
Elute Aliphatics	Hexane	2	4	4
Elute Aromatics	Acetone	2	4	
	DCM			6
Total solvent consumption		**9**	**17**	**20**
Total chlorinated solvent used		**0**	**0**	**9**



Summary



Simplified Procedure

High Selectivity

Less Solvent (no DCM)

High Capacity

Improved Productivity

Complete Fractionation

Excellent Analytical Performance

Lot-to-Lot Consistency

Questions?