

Extractable Petroleum Hydrocarbons Fractionation and Cleanup with the Massachusetts and Washington State Methods

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- Soil contamination from diesel fuel, gasoline, heating oil, jet fuel leaks, kerosene or spills is a common occurrence and a global environmental concern.
- EPA 8015B: Total Petroleum Hydrocarbon (TPH) with GC/FID (semi-volatiles)
- Petroleum has > 250 compounds, complex matrix



- Extractable Petroleum Hydrocarbons (EPH): Massachusetts and Washington State methods
- Toxicological approach: evaluate aliphatic and aromatic compounds in extracts
- Semi volatiles evaluated: C₉-C₃₆ aliphatics
- Also range of seventeen aromatics (PAHs)



- **Method quantitates aliphatics within two ranges, $C_9 - C_{18}$ and $C_{19} - C_{36}$**
- **PAHs are quantitated within $C_{11} - C_{22}$ range**
- **Collective data reporting**
- **Method can determine health hazards**
- **Also used by other states and some Canadian provinces**

- **Uses neutral silica cartridges or columns to separate aliphatics from aromatics in extract**
- **Aliphatics eluted with hexane, aromatics with dichloromethane**
- **Surrogates used to determine quality of separation between aliphatics and aromatics**
- **Breakthrough of naphthalene and 2-methyl naphthalene into aliphatic fraction is regulated**
- **Samples analyzed with GC/FID**

- Manual method is labor intensive, prone to error
- Certified 6 g neutral silica columns can be used with very low native background
- Less interferences in analysis
- Less glassware and solvent use



Specification:

- Simple to run, no computerized instrumentation
- Fast: 20 min
- Closed loop system to give a clean background, low level detection
- Use certified columns
- One column per sample
- No capital equipment cost
- No electronics or mechanical equipment to fail
- No downtime

Small Solvent
Reservoir
Rack

Small Solvent
Reservoir 40 mL

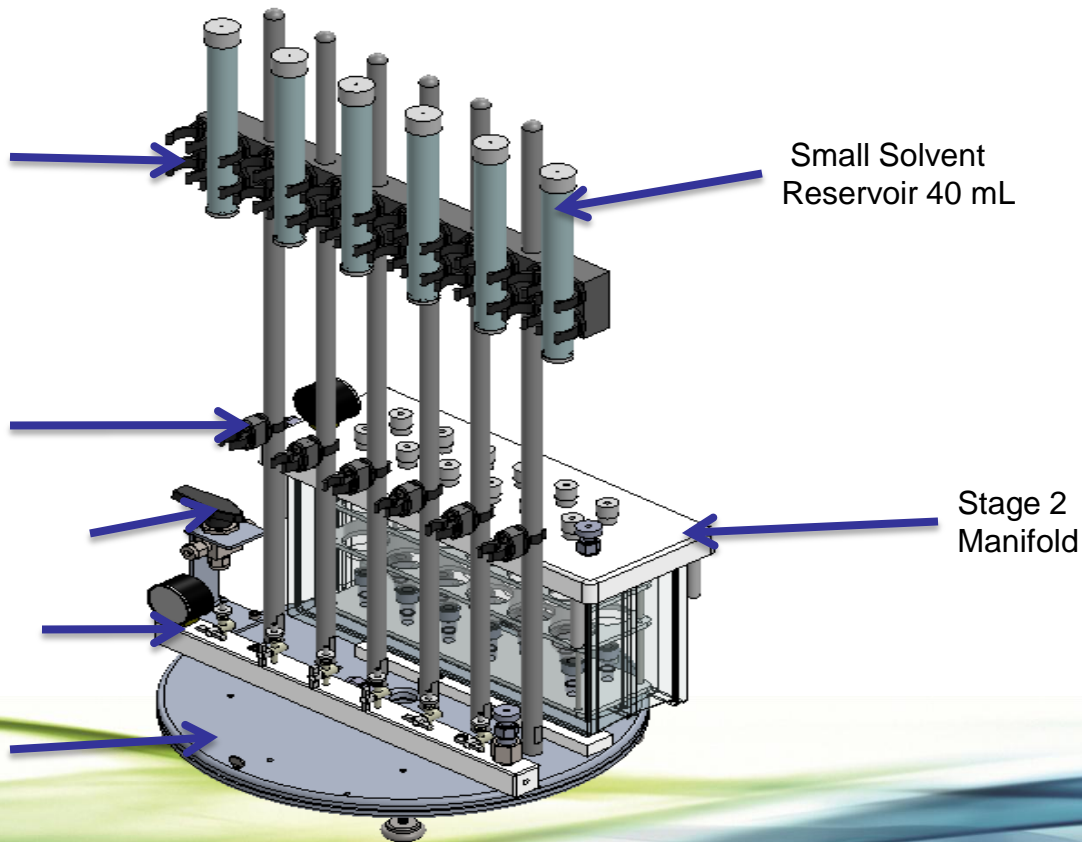
Regular
Column Holder

3 Way
Valve

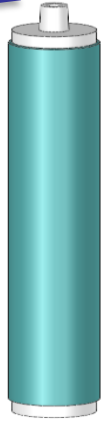
Stage 1
Manifold

Stage 2
Manifold

Turn
Table

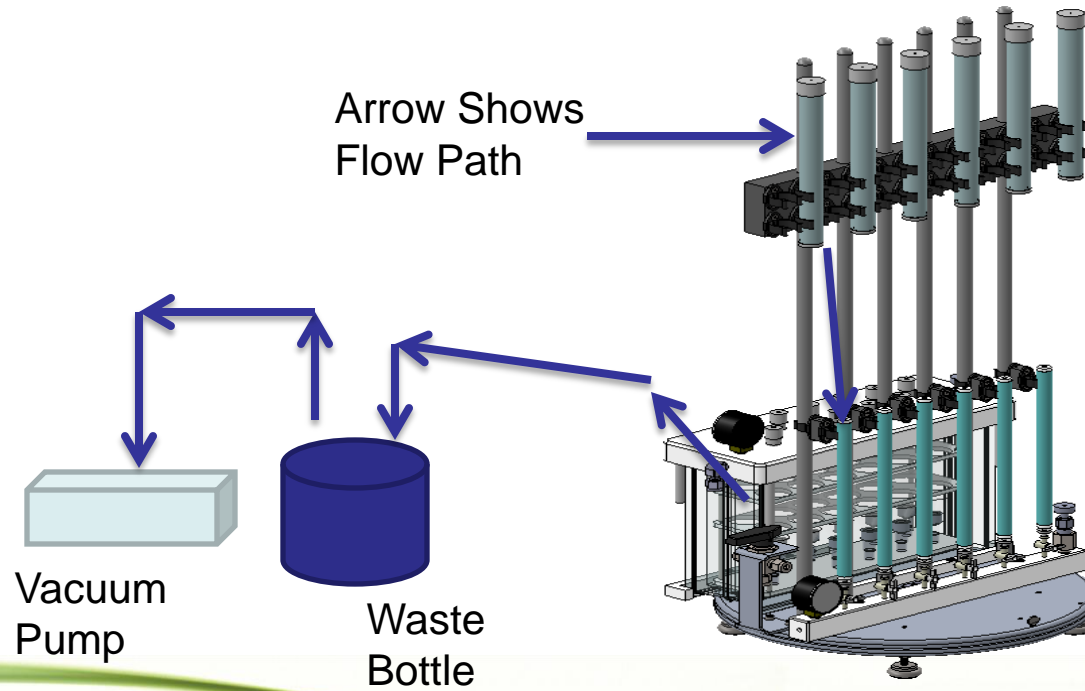


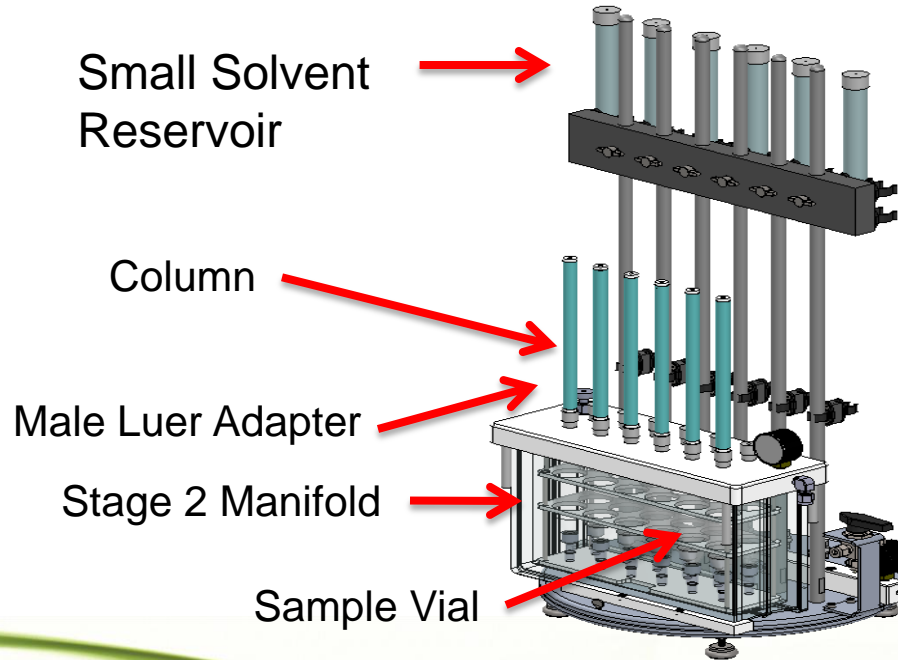
Male Luer



Female Luer







- **Stage 1:**
- **Assemble silica column with EZPrep set-up**
- **Syringe vial at top is used for conditioning and sample loading**
- **Condition silica column with 30 mL hexane (vacuum, waste)**



- **Stage 2:**
- **Dilute sample extract to 9 mL hexane and spike surrogate compounds (dissolved in 1 mL hexane) into sample extract**
- **Load sample extract onto silica column**
- **Elute column with 10 mL hexane, collecting aliphatic fraction**
- **Elute column with 35 mL dichloromethane, collecting aromatic fraction**



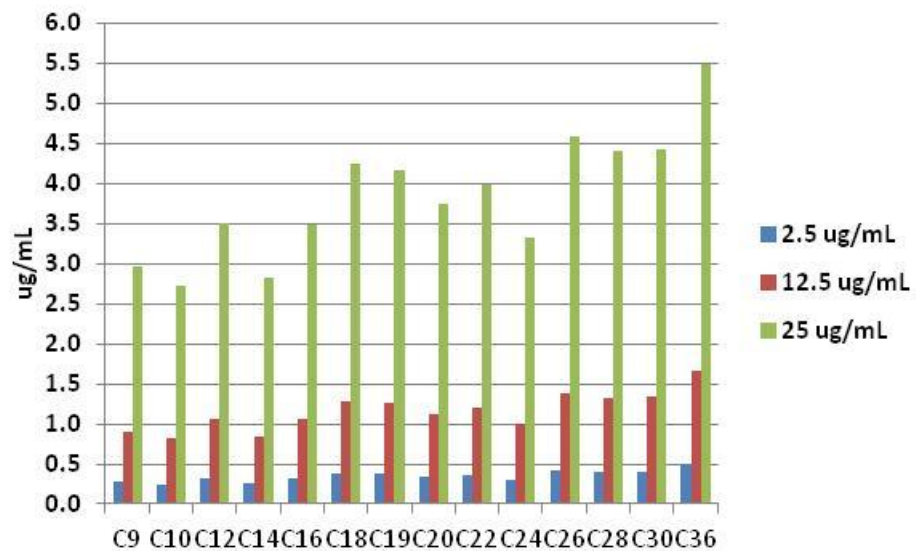


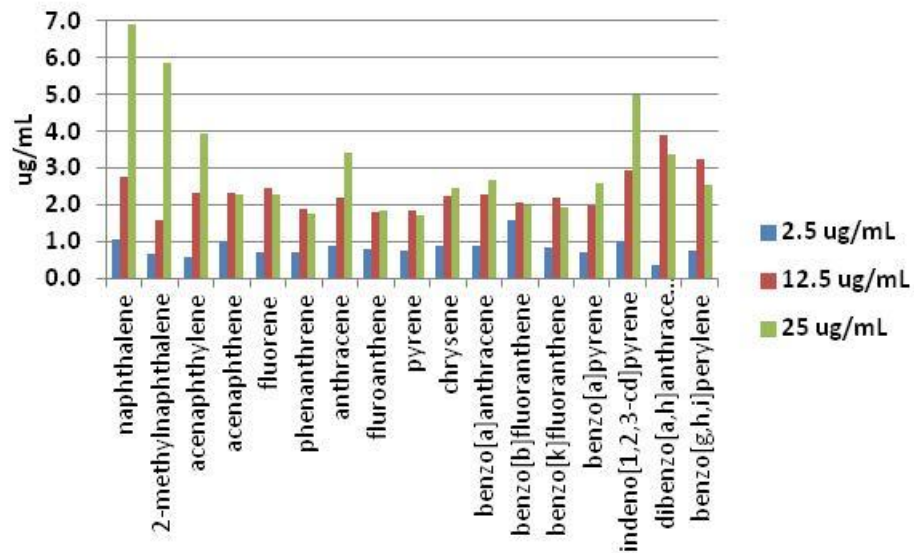
- **System pre-heated to 30 °C.**
- **Samples evaporated at stable T under 5-6 psi nitrogen.**
- **1 mL extract vial transferred to GC vial (can have direct-to-vial feature)**
- **Analyze on Agilent GC/FID**
- **Samples (hexane) were spiked with 2.5, 12.5 or 25 ug/mL aliphatic and aromatic standards and surrogates before cleanup**



	Average Recoveries (%)	RSD (%)	EPA Limit (%)
Nonane (C9)	74.7	7.3	30-130
Decane (C10)	78.6	8.4	40-140
Dodecane (C12)	80.9	4.5	40-140
Tetradecane (C14)	87.0	5.0	40-140
Hexadecane (C16)	81.4	3.9	40-140
Octadecane (C18)	85.6	3.3	40-140
Nonadecane (C19)	88.6	3.5	40-140
Eicosane (C20)	91.5	4.1	40-140
Docosane (C22)	92.6	4.9	40-140
Tetracosane (C24)	93.2	4.9	40-140
Hexacosane (C26)	93.2	4.8	40-140
Octacosane (C28)	92.4	4.7	40-140
Triacontane (C30)	92.9	4.5	40-140
Hexatriacontane (C36)	98.0	3.9	40-140

benzo[g,h,i]perylene	103.7	3.5	40-140
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- Average naphthalene breakthrough in aliphatic fraction < 0.02 (limit is < 0.05)
- Average 2-methyl naphthalene breakthrough in aliphatic fraction < 0.01 (limit is < 0.05)

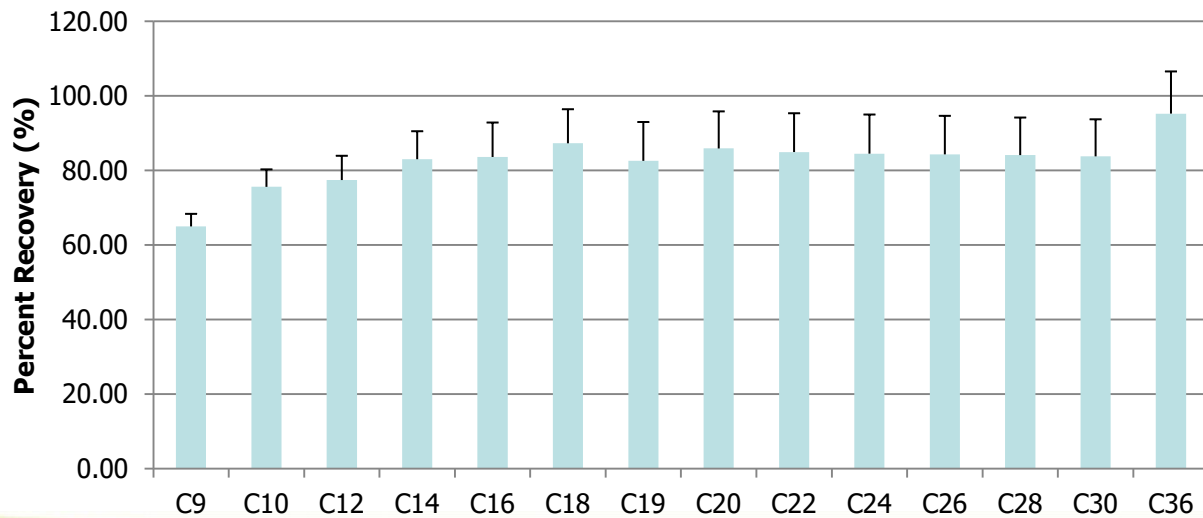
- 1-chloro-octadecane: $83\% \pm 12\%$
- O-terphenyl: $89\% \pm 14\%$
- 2-bromonaphthalene: $70\% \pm 13\%$
- 2-fluorobiphenyl: $104\% \pm 8\%$

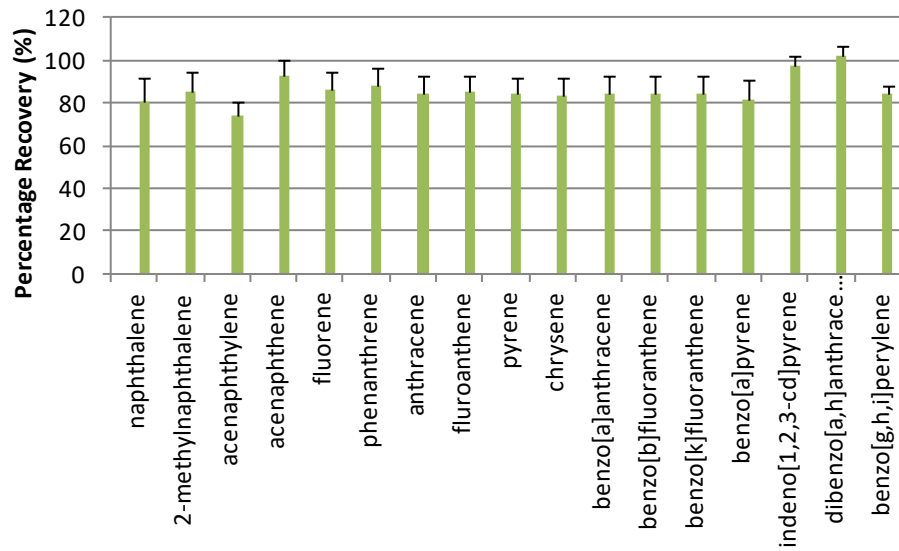


	C9-C18 Aliphatic			C19-C36 Aliphatic			C11-C22 Aromatic	
	Other Lab	Toxic Report		Other Lab	Toxic Report		Other Lab	Toxic Report
Sample 1	17	16		144	115		191	176
Sample 2	410	292		4314	3925		1313	1019
Sample 3	185	136		2335	2222		797	412
Sample 4	33	58		57	41		88	85
Sample 5	28	46		50	68		171	163
Sample 6	82	58		188	89		140	178
Sample 7	16	30		183	171		241	226
Sample 8	22	22		152	138		181	204
Sample 9	27	44		119	93		213	215
Sample 10	2931	2167		1232	1574		a	a
Sample 11	171	128		89	64		113	110
Sample 12	19	20		38	40		33	73
Sample 13	245	135		198	100		682	340
Sample 14	61	69		364	240		334	252
Sample 15	113	91		447	200		860	740
Sample 16	39	51		17	28		23	25

**Extracts
from
commercial
lab vs Toxic
Reports lab
Data in
ug/mL**

- **Stage 1: As before but condition 6 g neutral silica column with 10 mL pentane**
- **Stage 2: Spike surrogate compounds in 1 mL pentane or sample extract**
- **Load sample extract onto silica column**
- **Elute column with 15 mL pentane, collecting aliphatic fraction**
- **Elute column with 40 mL dichloromethane, collecting aromatic fraction**





- Excellent recoveries for aliphatics and aromatics with low RSDs
- All well within MA and WA method windows
- Very good MDL data
- Breakthrough of naphthalene's well within limits



- All surrogates give very good recoveries
- Comparison semi-automated method with manual method for commercial lab samples shows very good agreement
- Can process 6 samples in parallel in 20 min





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