



Fast Semi-Automated Extractable Petroleum Hydrocarbons Fractionation and Cleanup

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Introduction (1)

- 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



Introduction (2)

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



Features of MA method (1)

- 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

Features of MA method (2)

- 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

Semi-automated approach

- Manual method is labor intensive, prone to error
- Certified 6 g neutral silica columns can be used with very low native background. Consistent packing assures similar density between columns and reproducibility of clean up. Teflon chips are added upstream of column material for processing tough samples.
- Less interferences in analysis
- Less glass ware and solvent use

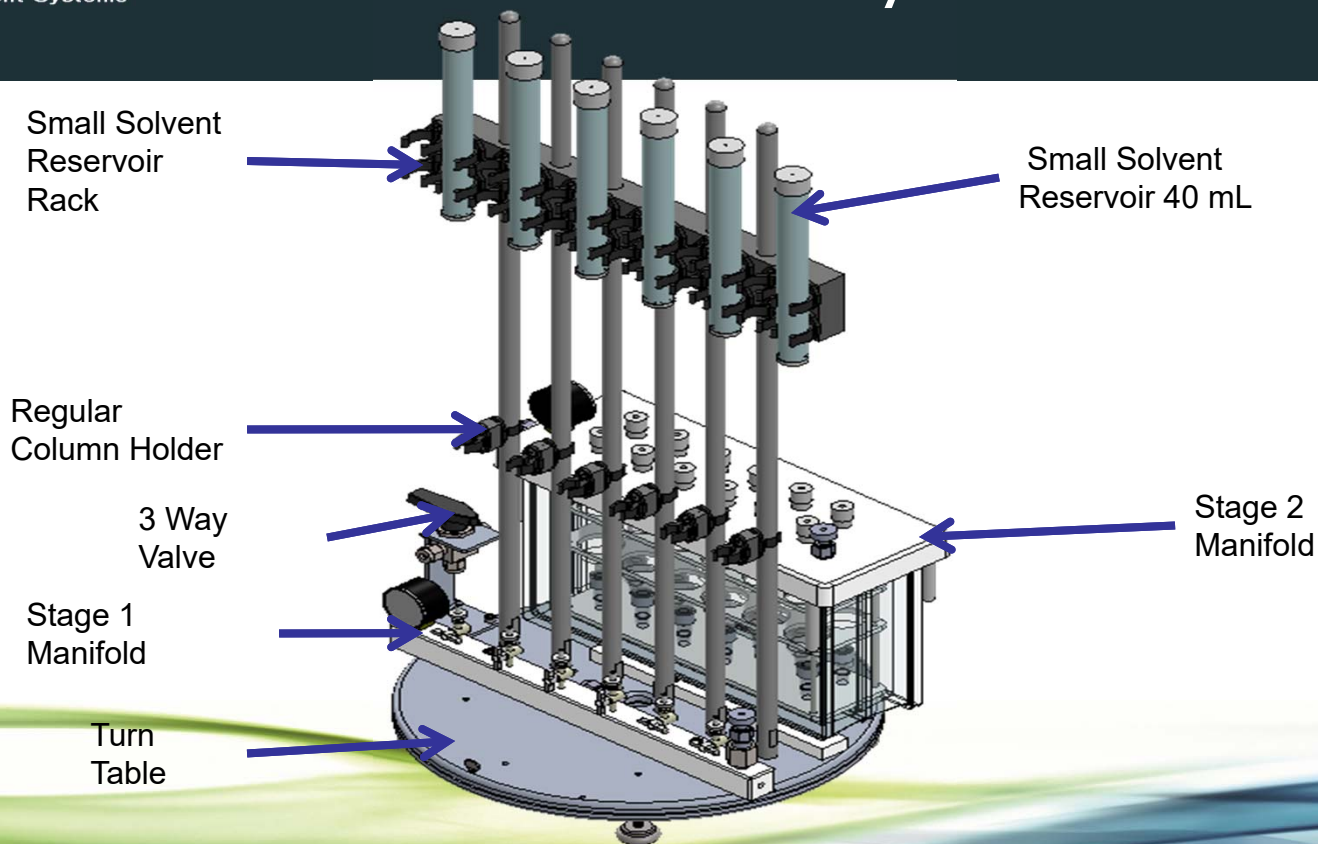
Semi-Automated System

Specification:

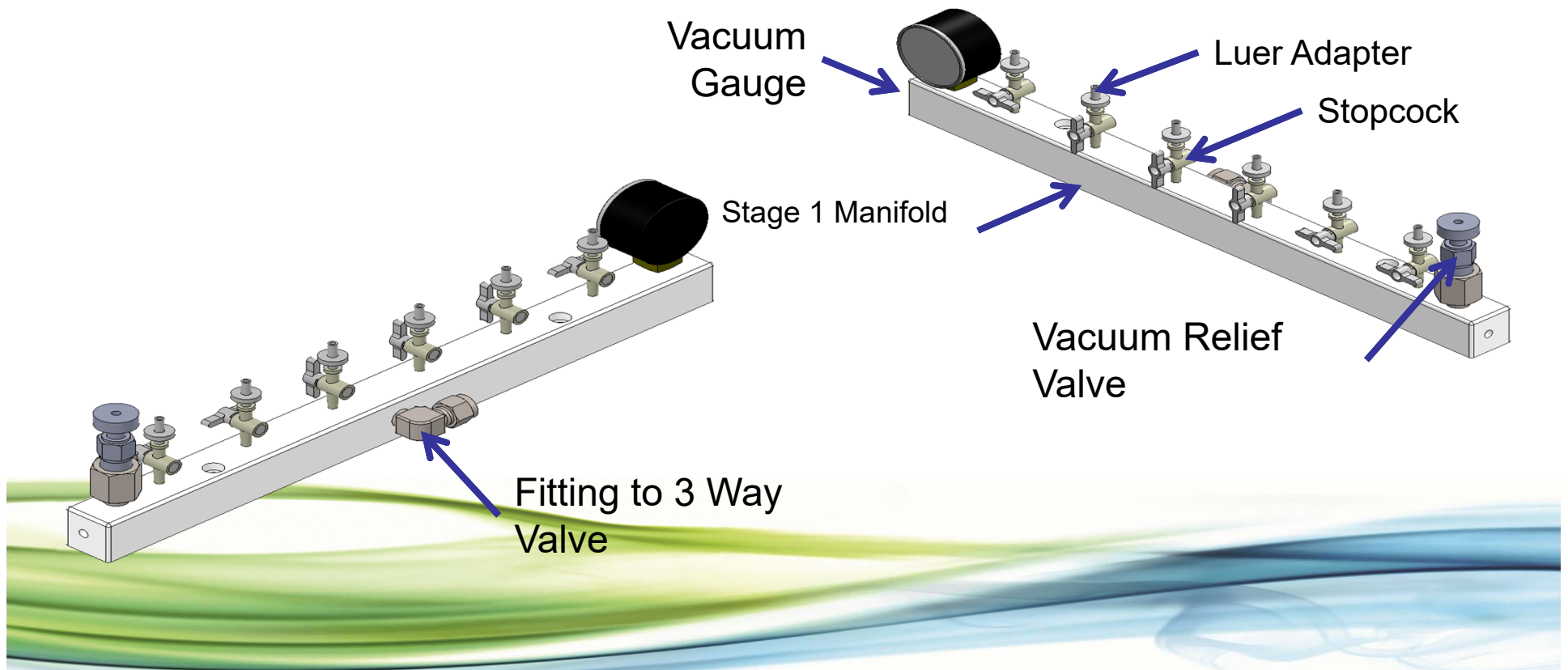
- Simple to run, no computerized instrumentation
- Fast: 20 min
- Closed loop system to give a clean background, low level detection
- Use certified columns
- One column per sample
- No capital equipment cost
- No electronics or mechanical equipment to fail
- No downtime



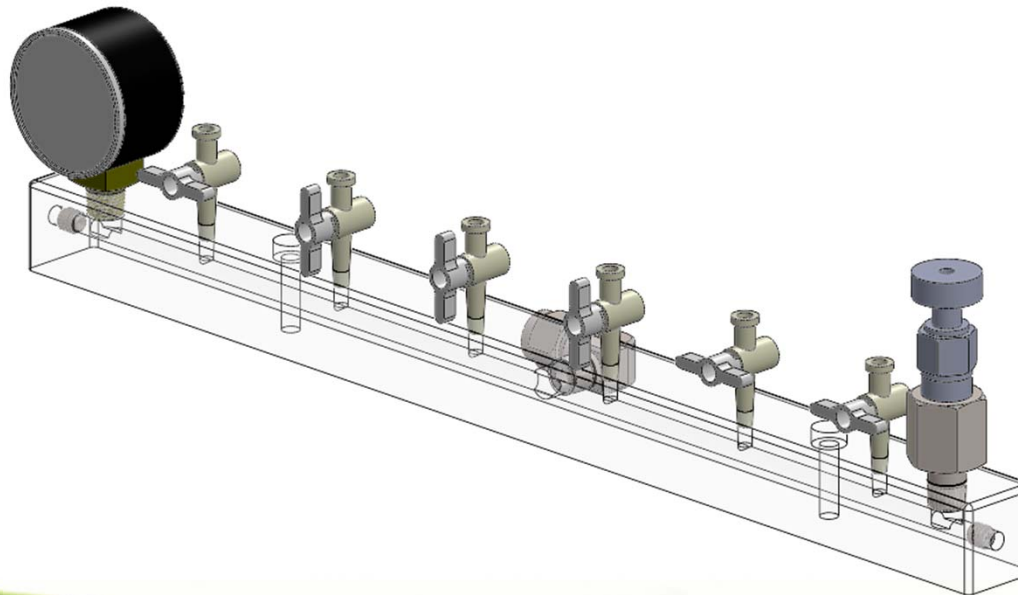
Semi-Automated System for EPH



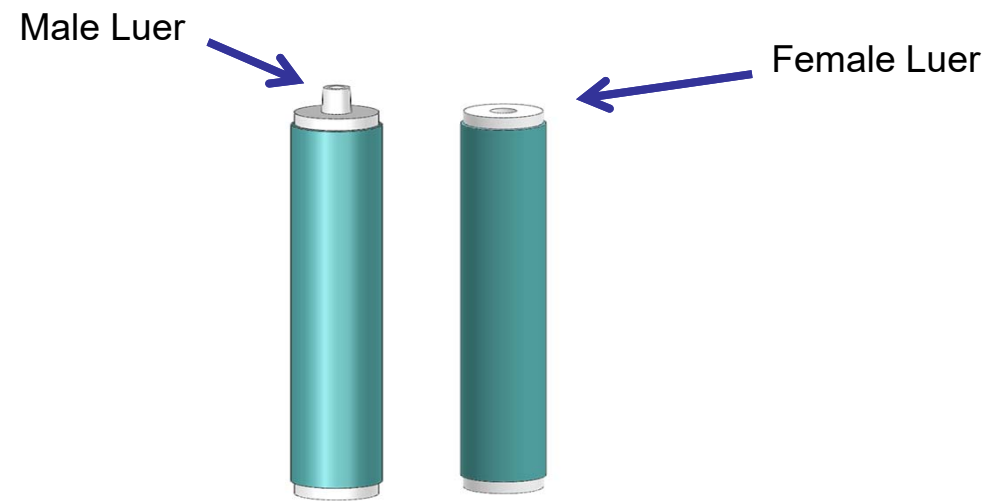
Stage 1 Manifold



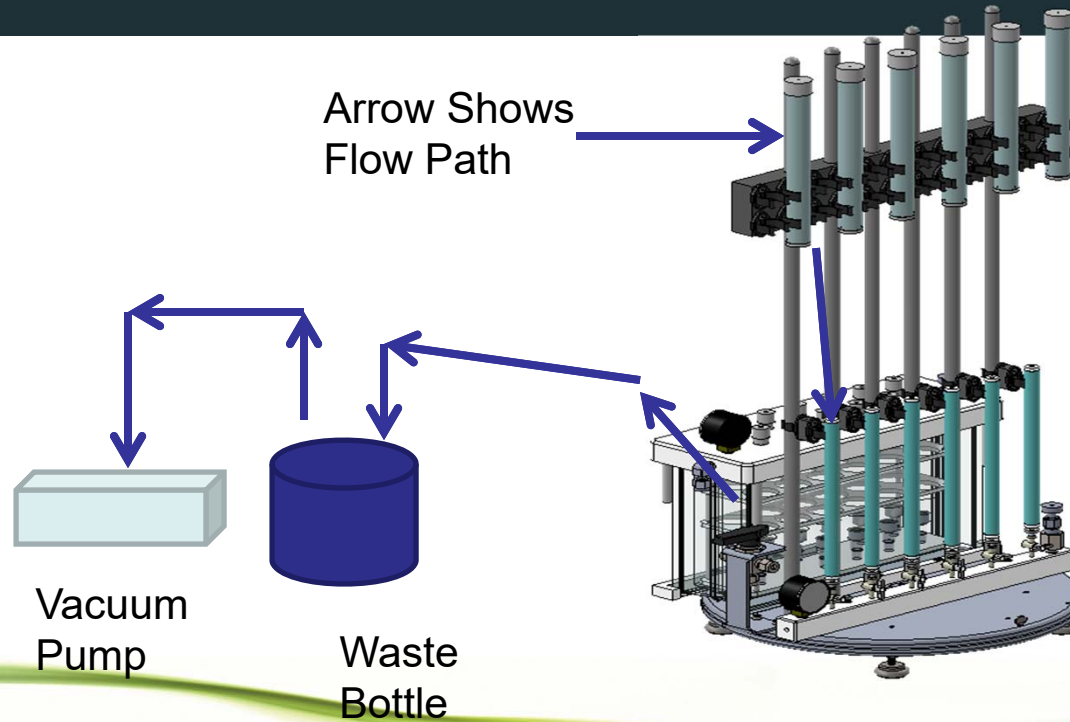
Stage 1 Manifold Transparent View



Neutral silica columns



Flow thru system (Stage 1)



Collection (Stage 2)

Small Solvent
Reservoir

Column

Male Luer Adapter

Stage 2 Manifold

Sample
Vial



Procedure (1)

- 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 dichloromethane (vacuum, waste)
- Condition silica column with 30 mL hexane (vacuum, waste)



Procedure (2)

- 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





12 position evaporator 50 mLs



Evaporation and Analysis

- 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



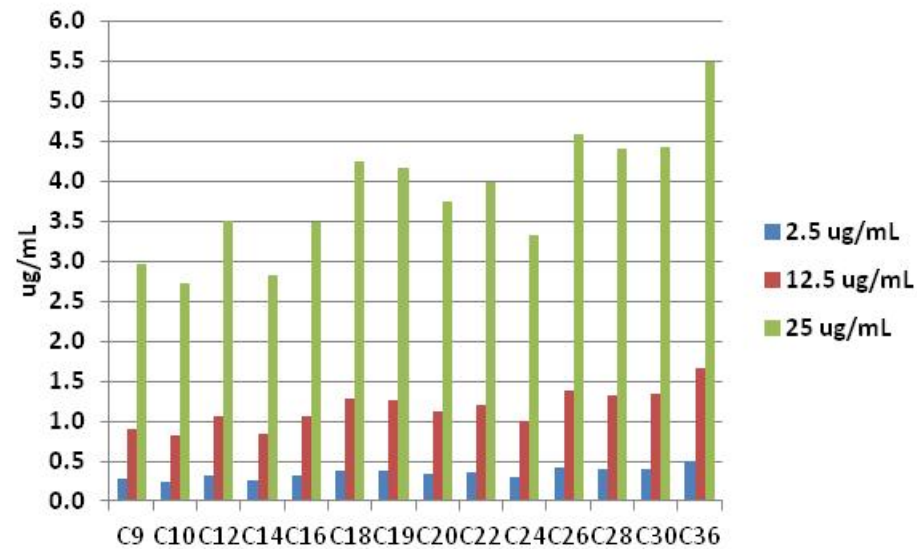
Aliphatic recoveries (25 ug/mL)

	Average Recoveries (%)	RSD (%)	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

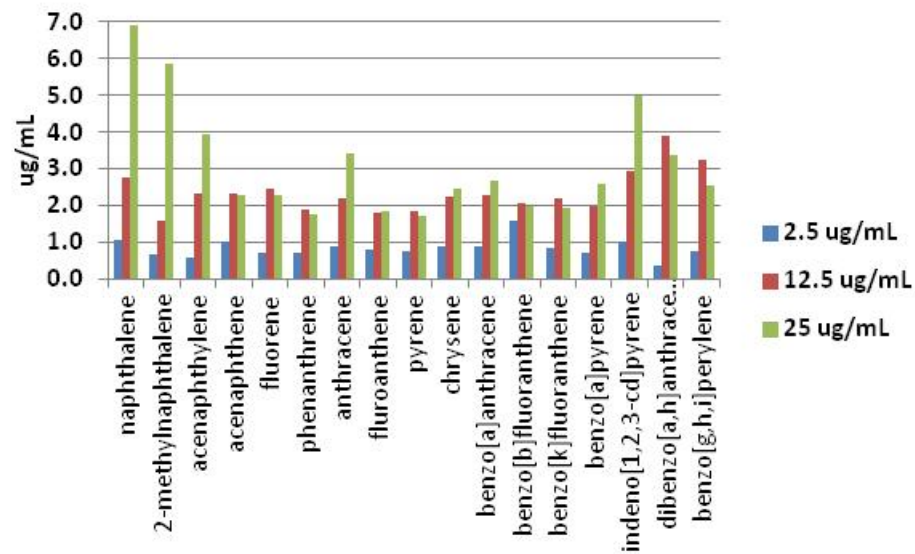
Aromatic recoveries (25 ug/mL)

	Average Recoveries (%)	RSD (%)	Limit (%)
naphthalene	110.5	6.7	40-140
2-methylnaphthalene	104.2	6.3	40-140
acenaphthylene	94.4	3.5	40-140
acenaphthene	99.3	2.5	40-140
fluorene	107.4	1.8	40-140
phenanthrene	109.0	1.9	40-140
anthracene	103.1	2.4	40-140
fluroanthene	104.8	1.8	40-140
pyrene	103.0	1.7	40-140
chrysene	97.1	2.2	40-140
benzo[a]anthracene	109.6	2.9	40-140
benzo[b]fluoranthene	111.9	1.9	40-140
benzo[k]fluoranthene	109.0	2.3	40-140
benzo[a]pyrene	98.0	2.3	40-140
indeno[1,2,3-cd]pyrene	111.6	3.1	40-140
dibenzo[a,h]anthracene	96.1	2.9	40-140
benzo[g,h,i]perylene	103.7	3.5	40-140

Method Detection Limit Aliphatics



Method Detection Limit Aromatics



Breakthrough

- 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)



Surrogates (limit 40-140%)

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

Comparison lab X vs EZPrep EPH

	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 FMS
lab
Data in
ug/mL**

Conclusions

- Excellent recoveries for aliphatics and aromatics with low RSDs
- All well within MA windows
- Very good MDL data
- Breakthrough of naphthalenes 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