


Advances in Sample Preparation for Semi-Volatile Analysis per EPA Method 625

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NEMC EMS
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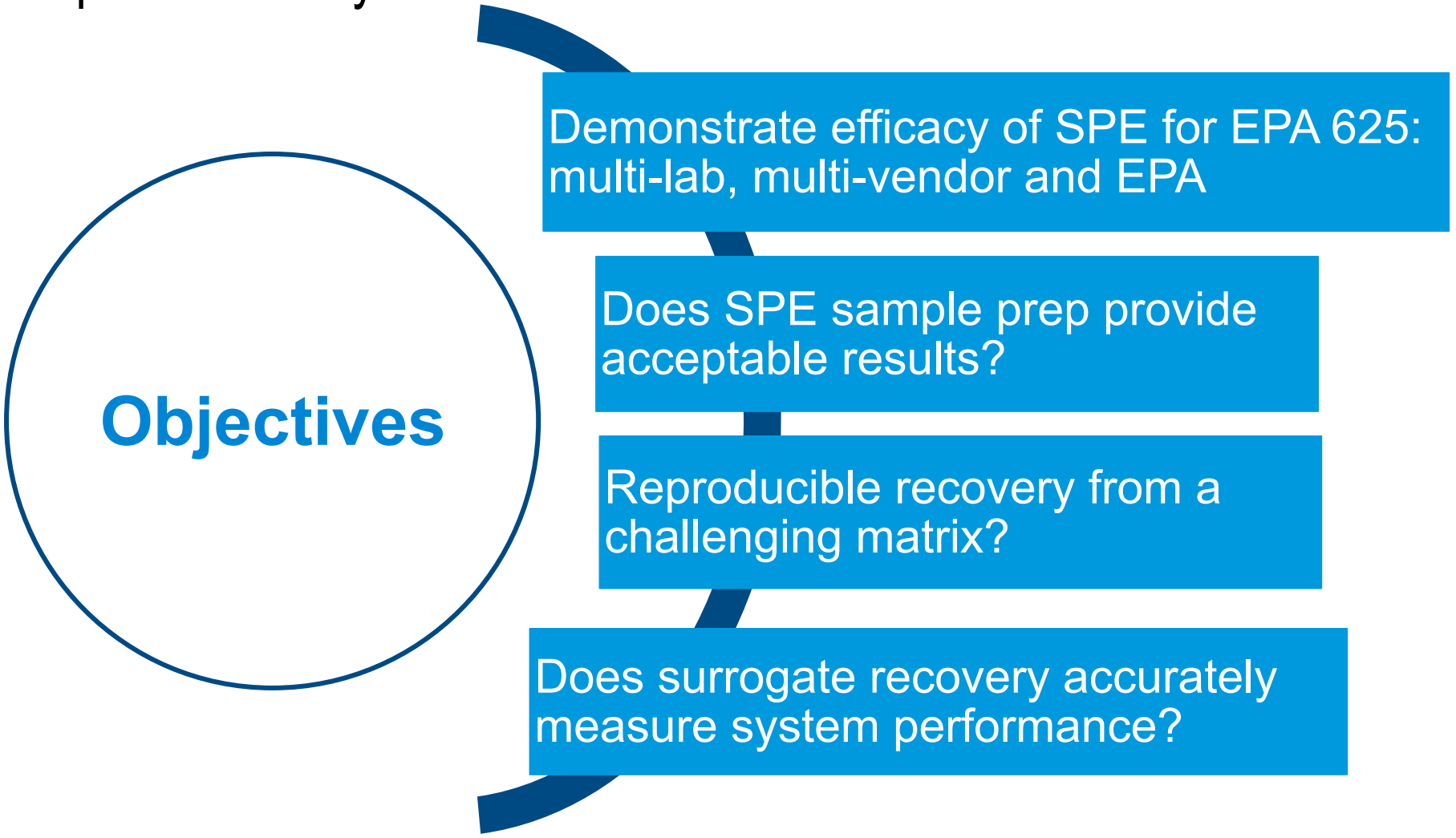
Revision to US EPA Method 625

Purpose of Study



Revision to US EPA Method 625
Round Robin Study

Test Criteria:

- Performance test in synthetic wastewater (triplicate analysis)
- Performance test in drinking water (i.e., Aquafina bottled water; triplicate analysis)
- LCS in laboratory reagent water (quadruple analysis)
- Wastewater, bottled water, and reagent water blanks
- MDL/LOQ check at three levels in reagent water

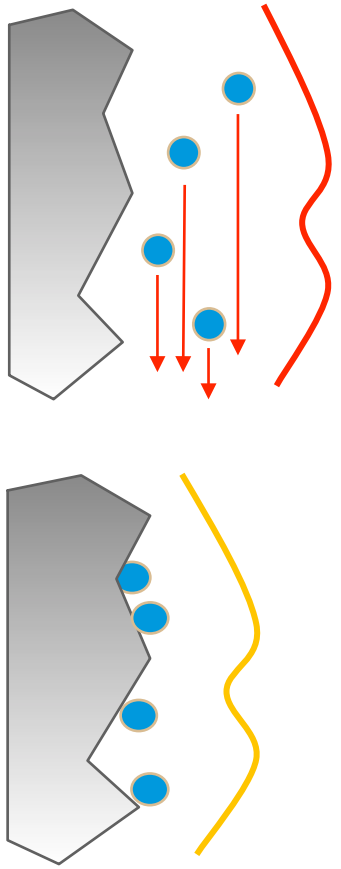
Revision to US EPA Method 625
Target Analytes

Base/Neutrals	Base/Neutrals	Acids	Surrogates
Chrysene	Hexachlorobutadiene	4-Chloro-3-methylphenol	Acenaphthylene-d8
Dibenzo(a,h)anthracene	Hexachlorocyclopentadiene	2-Chlorophenol	Anthracene-d10
Dibenzofuran	Hexachloroethane	2,4-Dichlorophenol	Benzo(a)pyrene-d12
1,2-Dichlorobenzene	Indeno(1,2,3, cd)pyrene	2,6-Dichlorophenol	Bis-(2-chloroethyl)ether-d8
1,3-Dichlorobenzene	Isophorone	2,4-Dimethylphenol	4-Chloroaniline-d4
1,4-Dichlorobenzene	2-Methylnaphthalene	2,4-Dinitrophenol	2-Chlorophenol-d4
3,3'-Dichlorobenzidine	Naphthalene	2-Methyl-4,6-Dinitrophenol	2,4-Dichlorophenol-d3
Diethyl phthalate	Nitrobenzene	2-Methylphenol (o-Cresol)	Dimethylphthalate-d6
Dimethyl phthalate	N-Nitrosodimethylamine	4-Methylphenol (p-Cresol) 14	4,6-Dinitro-2-methylphenol-d2
Di-n-butyl phthalate	N-Nitroso-di-n-propylamine	2-Nitrophenol	Fluorene-d10
2,4-Dinitrotoluene	N-Nitrosodiphenylamine	4-Nitrophenol	4-Methylphenol-d8
2,6-Dinitrotoluene	Phenanthrene	Phenol	Nitrobenzene-d5
Di-n-octyl phthalate	Pyrene	Pentachlorophenol	2-Nitrophenol-d4
Fluoranthene	1,2,4-Trichlorobenzene	2,4,5-Trichlorophenol	4-Nitrophenol-d4
Fluorene			Phenol-d5
Hexachlorobenzene			NDMA-d6

Solid Phase Extraction (SPE)
Basic Chromatography Theory

Mechanism of Action

- Similar to HPLC, its chromatography
- Higher affinity for the mobile phase, no retention
- Increased affinity for the stationary phase, retained stationary phase



Solid Phase Extraction (SPE)
Basic Chromatography Theory

SPE works because:

Oil And Water Do Not Mix, Like Dissolves Like

- Reversed phase
  - Van der Waals or hydrophobic interactions
- Normal Phase
  - Polar interactions (hydrogen bonding and dipole-dipole)

Opposite Charges Attract

- Ion Exchange
  - Electrostatic interactions

Select Phase based on these rules

Solid Phase Extraction (SPE)
Mechanisms of SPE

Hydrophobic

- Non-polar phases (reversed phase)

Polar

- Polar phases (normal phase)

Electrostatic

- Ion exchange phases

Mixed mode

- Can also introduce secondary interactions

Solid Phase Extraction (SPE)
Four Steps of SPE

Conditioning
- Preparation of the sorbent prior to sample addition

Retention
- Analytes of interest and other interferences adsorb onto the surface of the sorbent during sample addition

Washing
- Elimination of undesired interferences

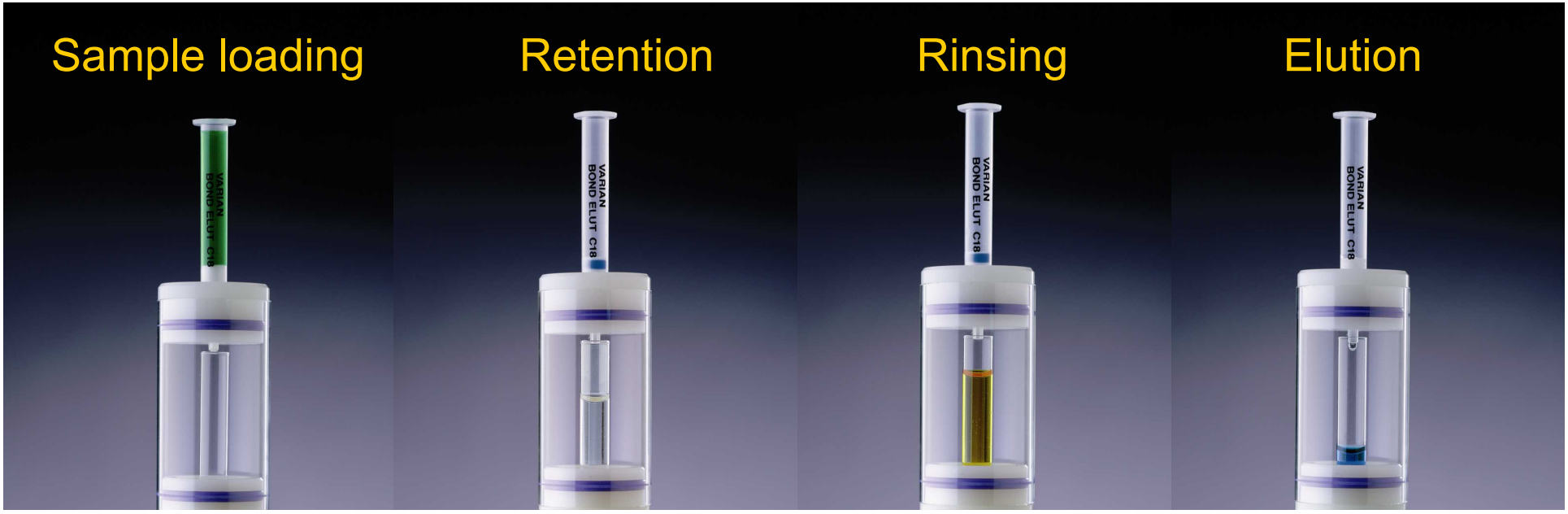
Elution
- Selective desorption and collection of desired analytes from the sorbent

Four Steps of SPE
Selective Elution

Green = Blue and Yellow

Blue is more non polar than yellow

Blue is retained



EPA 625.1 Update
Sample Preparation

Sample Pretreatment: 250 mL TCLP acetate buffer solution; bring to pH 2 with sulfuric acid.

↓

SPE: Bond Elut ENV – 6 mL, 500 mg
Bond Elut C18 – 6 mL, 1000 mg

Condition: 5 mL DCM, 5 mL MeOH, 5 mL water

↓

Load: Pass through cartridge bed at 10 mL/min; dry for 2 min

↓

Elution: 2 x 4 mL DCM, 1 x 4 mL ethyl acetate; dry over sodium sulfate

↓

Evaporation and Reconstitution: Reconstitute in 0.5 mL DCM

EPA 625: Base/Neutrals and Acids by GC/MS/MS
System configuration

Agilent 7000B GC/MS/MS in MRM mode

- Multi-mode injector
- 2mm dimpled liner
- Dual 15 m DB-5 columns with mid-point backflush

Offline SPE evaluation

- Bond Elut C-18, 6 mL, 1000 mg (silica)
- Bond Elut ENV, 6 mL, 500 mg (polymeric)

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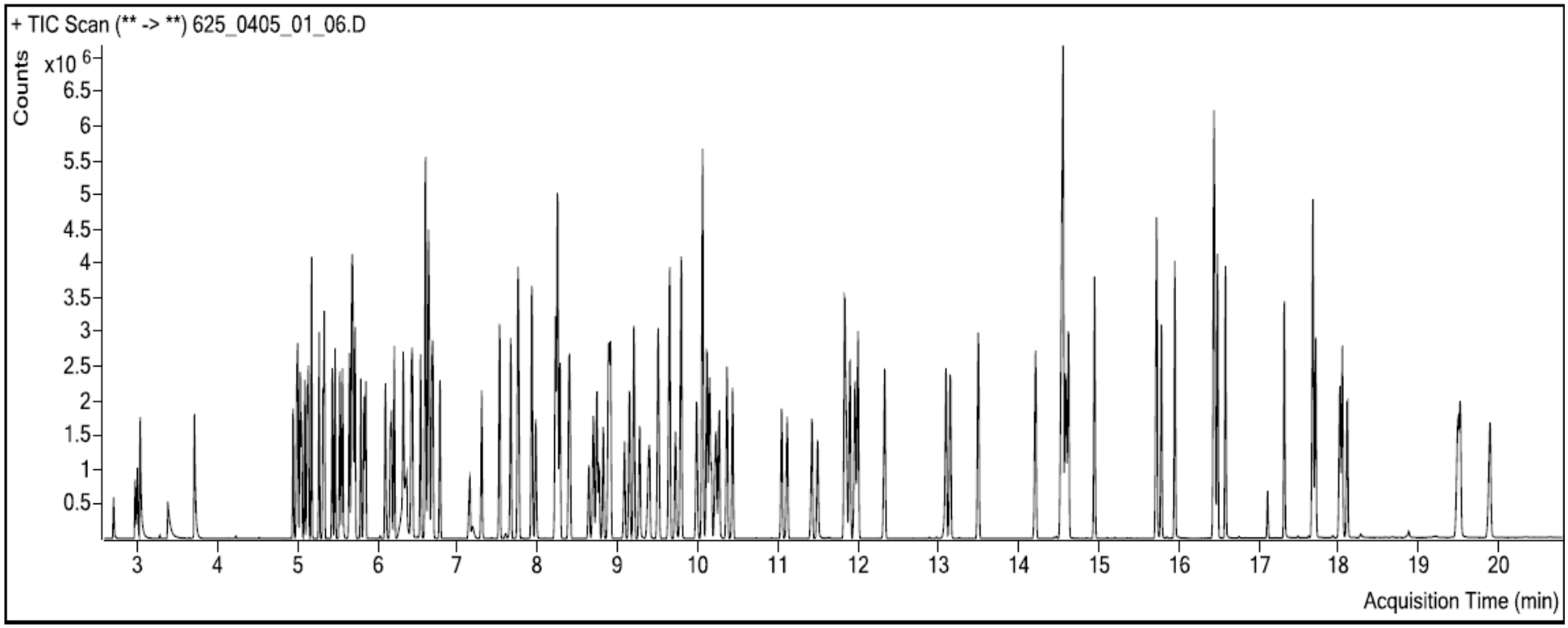
GC-MS (SIM) Chromatogram



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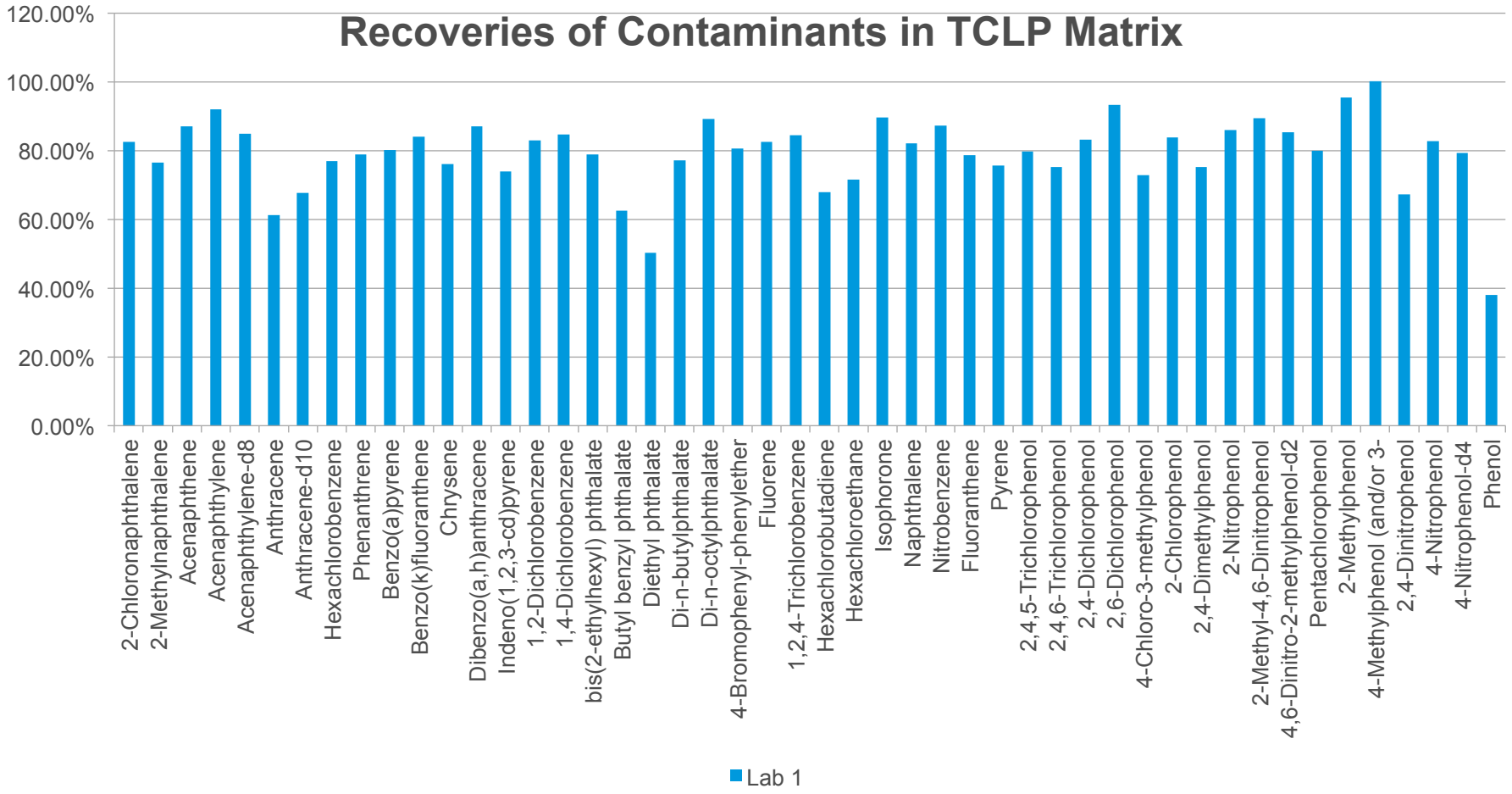
Recovery by Analyte, Bond Elut ENV (Laboratory 1)



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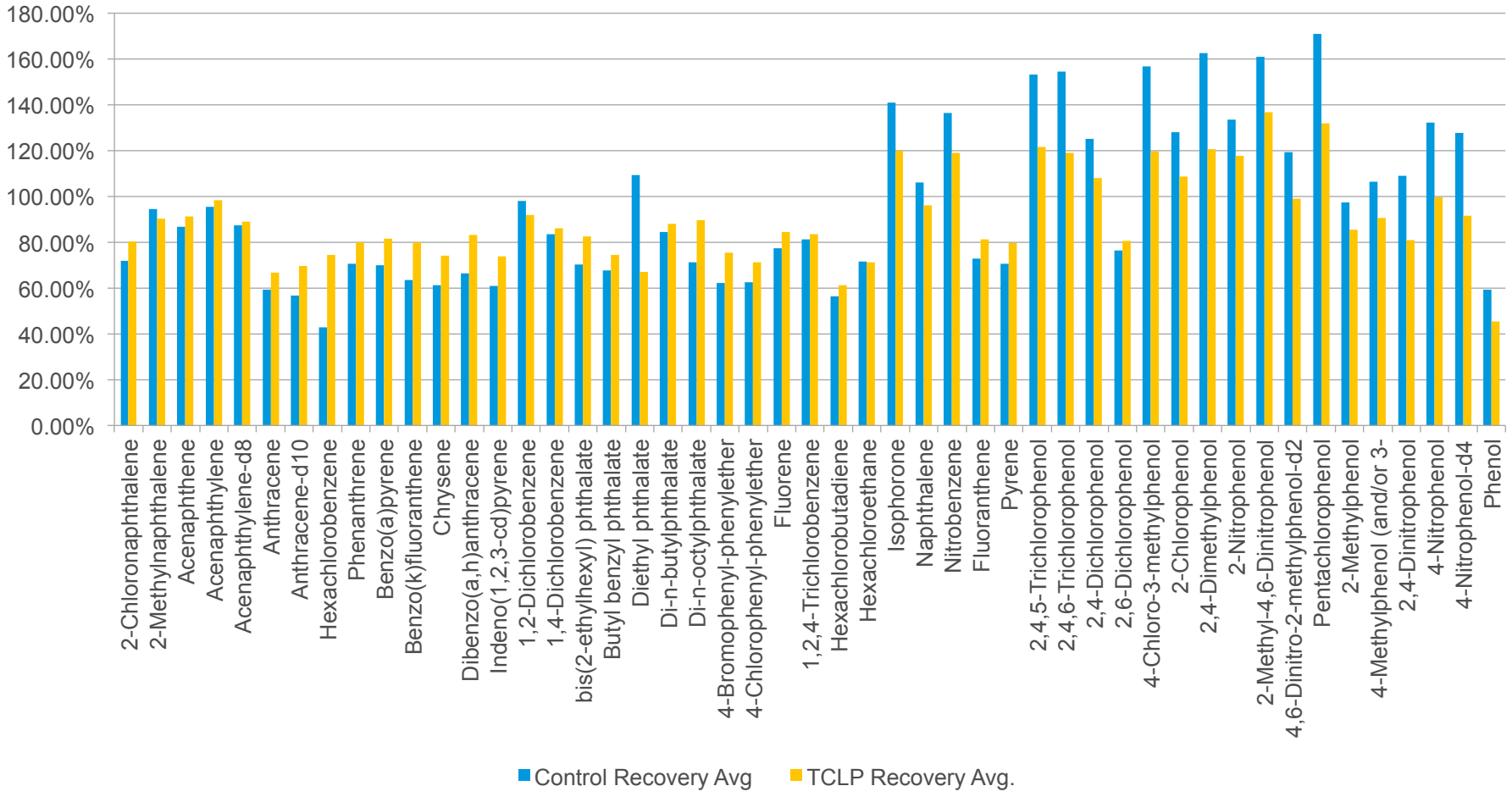
Recovery by Analyte, Bond Elut ENV – LCS versus TCLP Matrix



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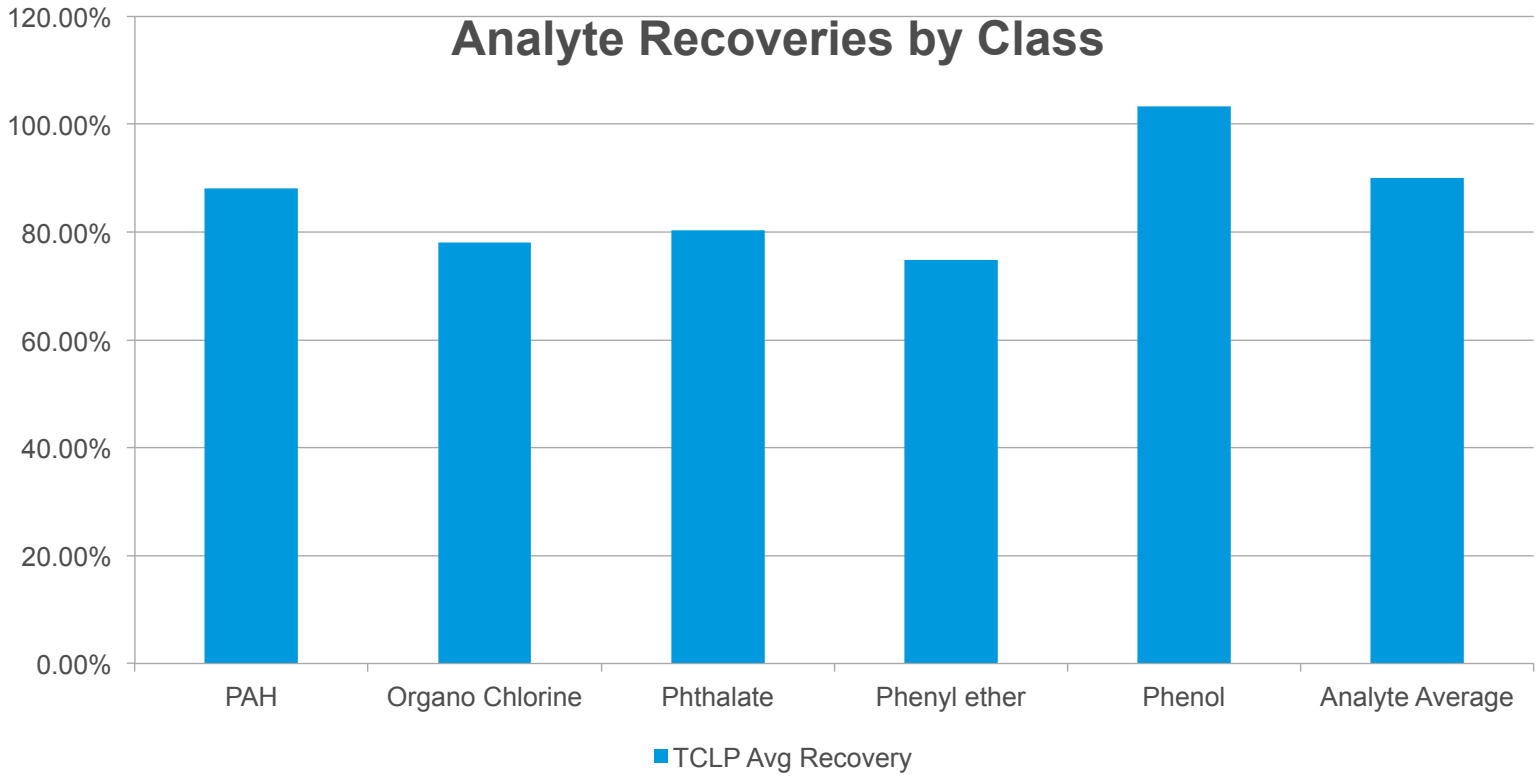
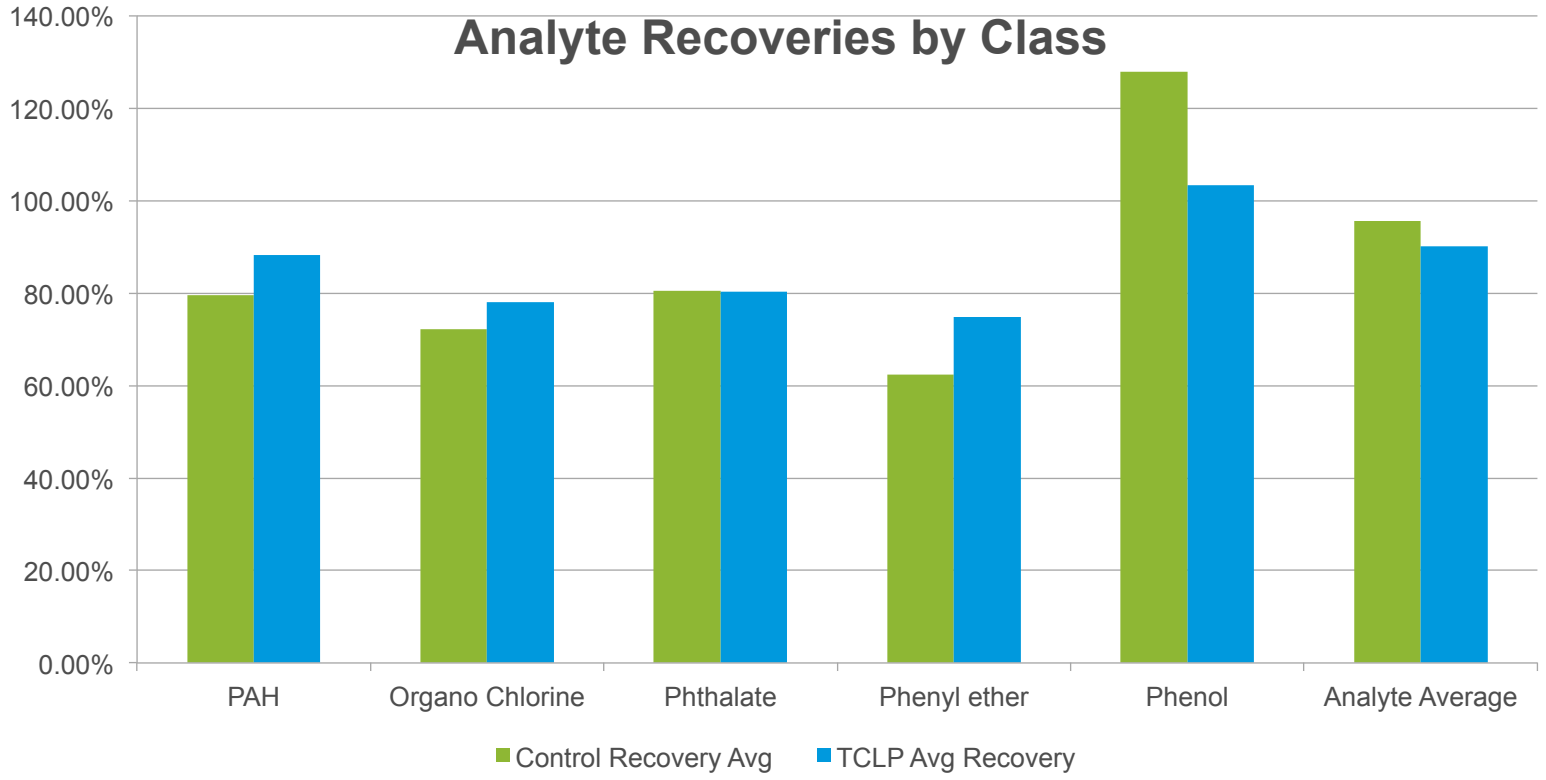
Recovery by Class, Bond Elut ENV – Laboratory Average



Recovery by Class, Bond Elut ENV – Control Avg. Versus TCLP Avg.



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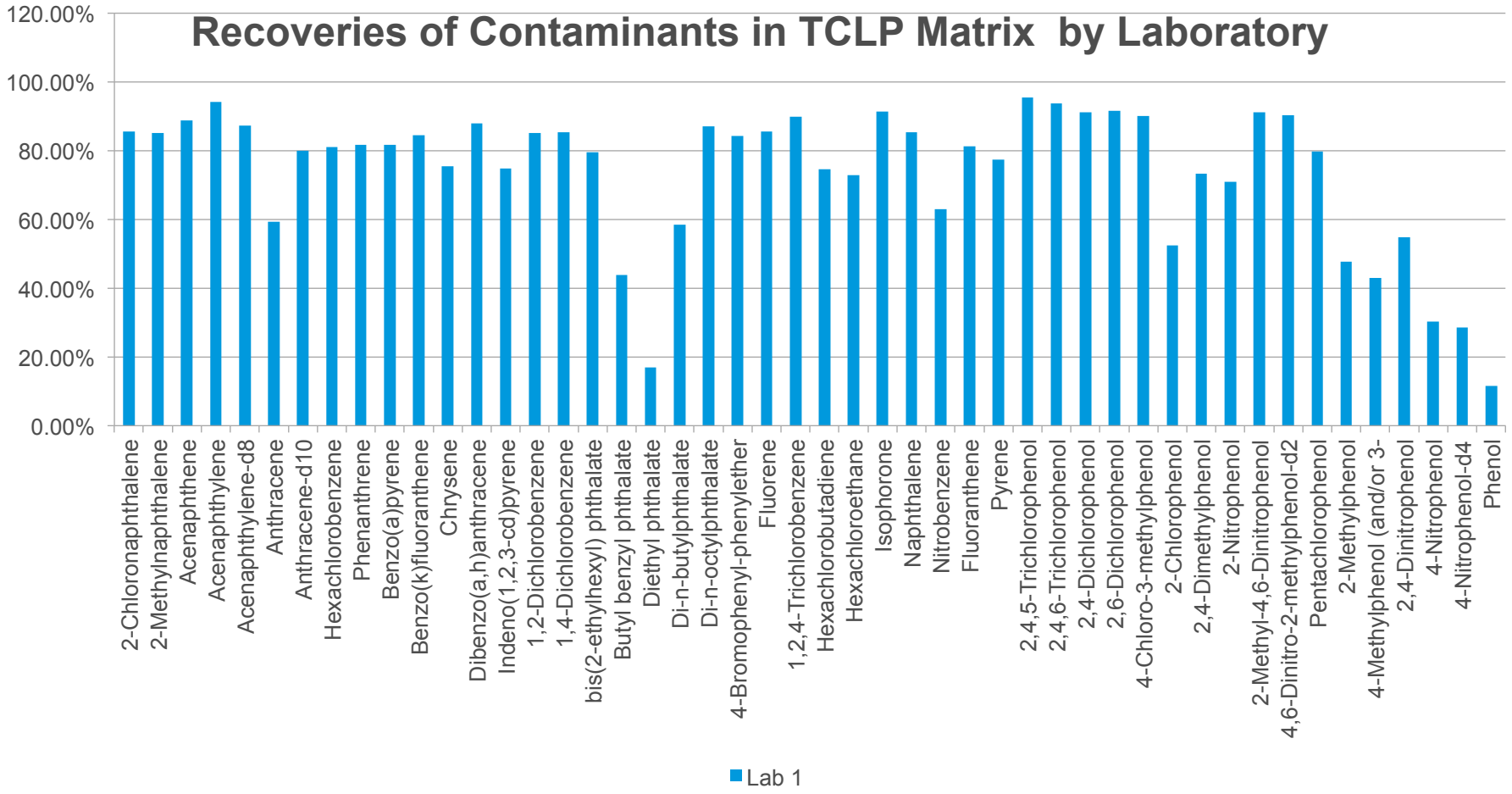
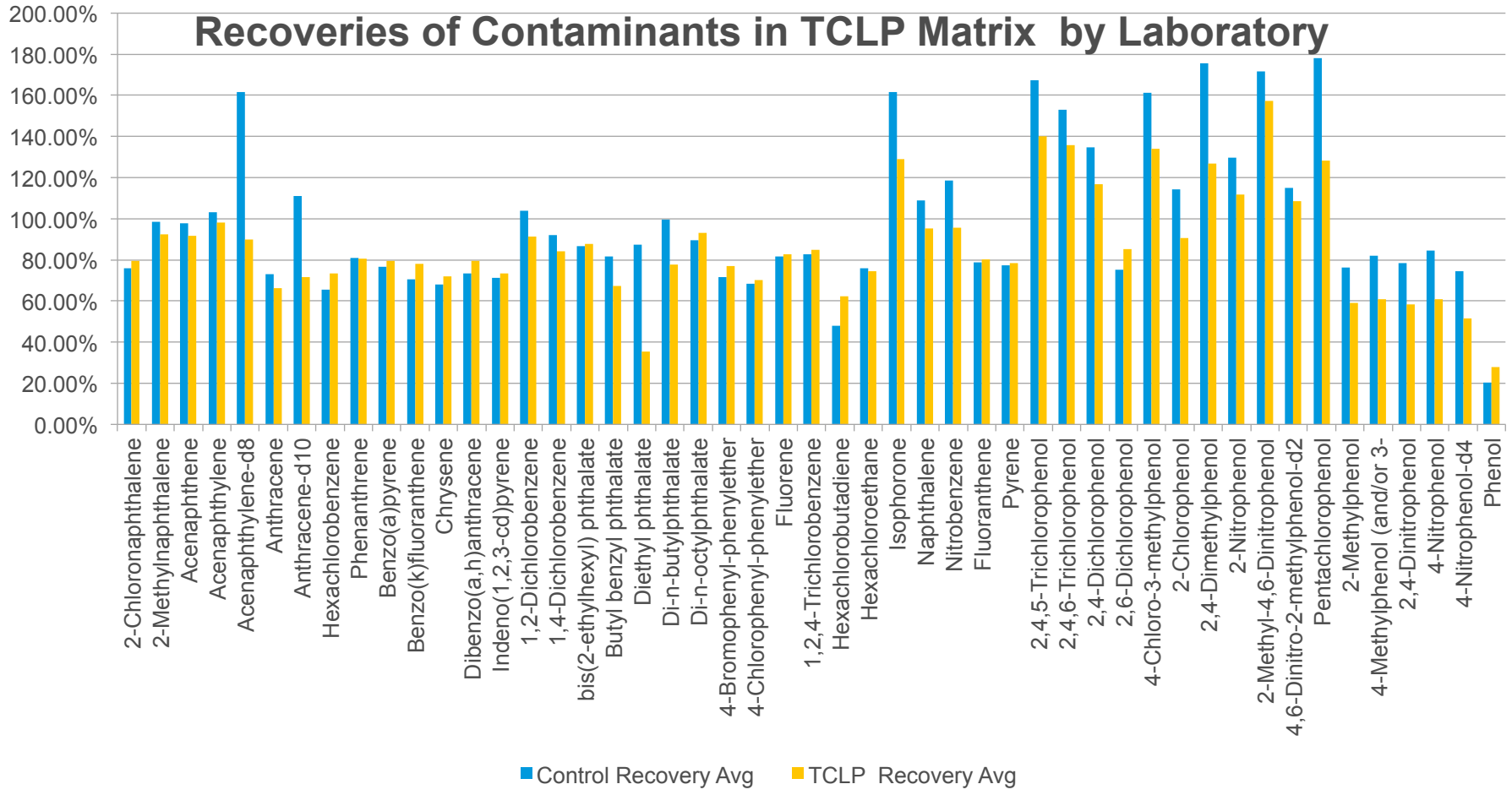
Recovery by Analyte, Bond Elut C18 (Laboratory 1)



Analyte Recovery by Analyte, Bond Elut C18 – Laboratory Control versus TCLP Matrix



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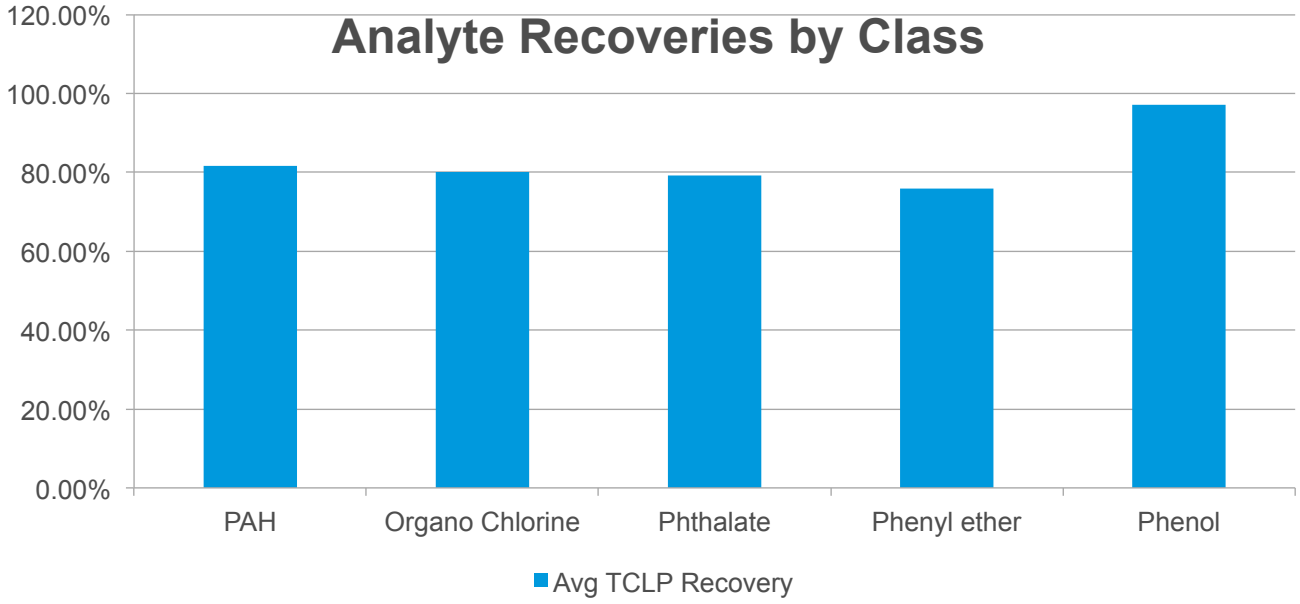
Recovery by Class, Bond Elut C18 – Laboratory Average



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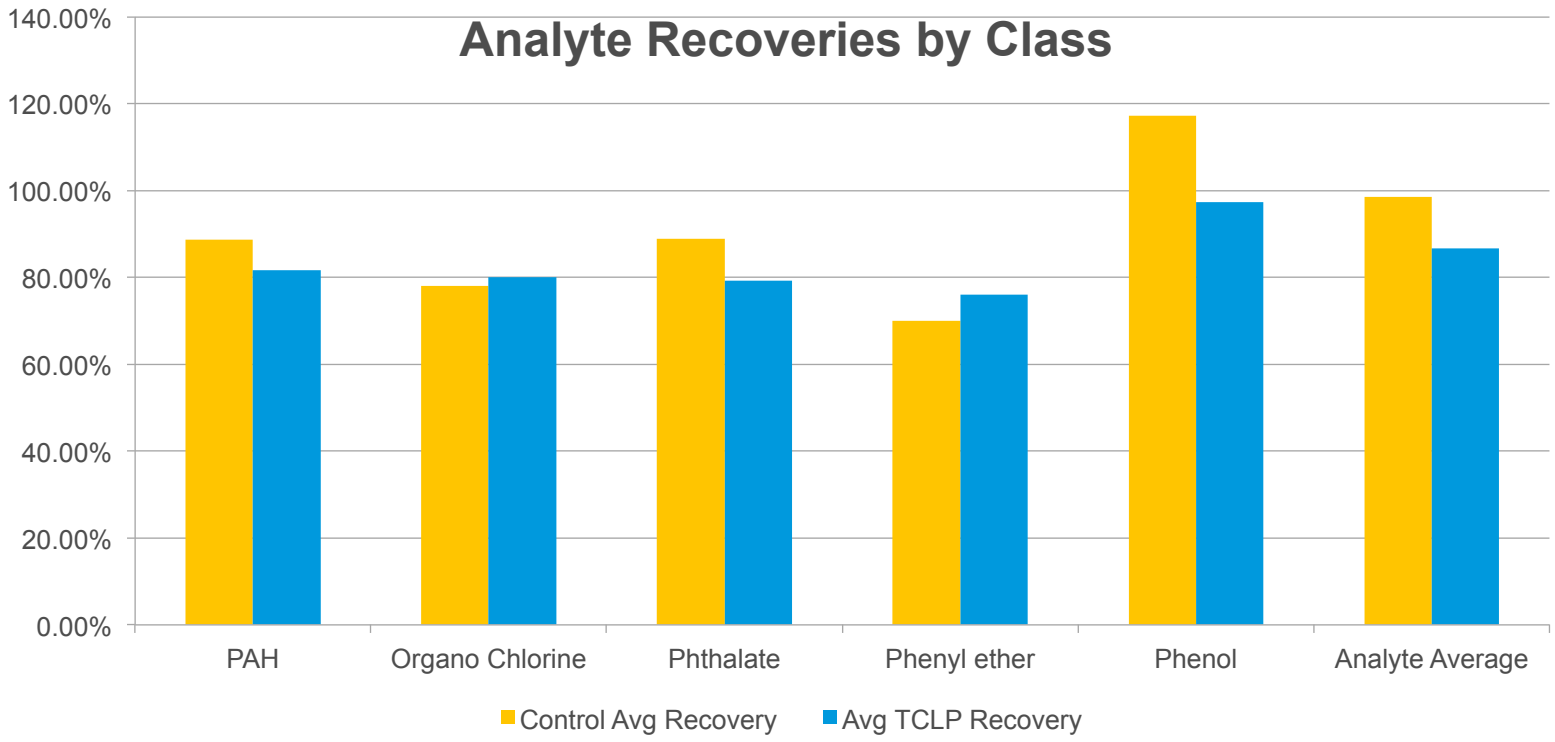
Recovery by Class, Bond Elut C18 – Control Avg. Vs TCLP Avg.



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Conclusions

Recovery

- Analyte recovery from ASTM Synthetic Wastewater samples and TCLP extract matrix within the acceptance limits for EPA Method 625.1 and TNI lab performance tests

Applicability

- SPE yields analytical results comparable to conventional liquid-liquid extraction.

Ruggedness

- Use of two different SPE products without prior optimization of the particular SPE products for the types of aqueous matrix or particular types of analytes demonstrates ruggedness of SPE technique itself.

Ease of Use

- Three commercial laboratories, with no prior experience with SPE, successfully prepared and analyzed

Thank you

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APPENDIX

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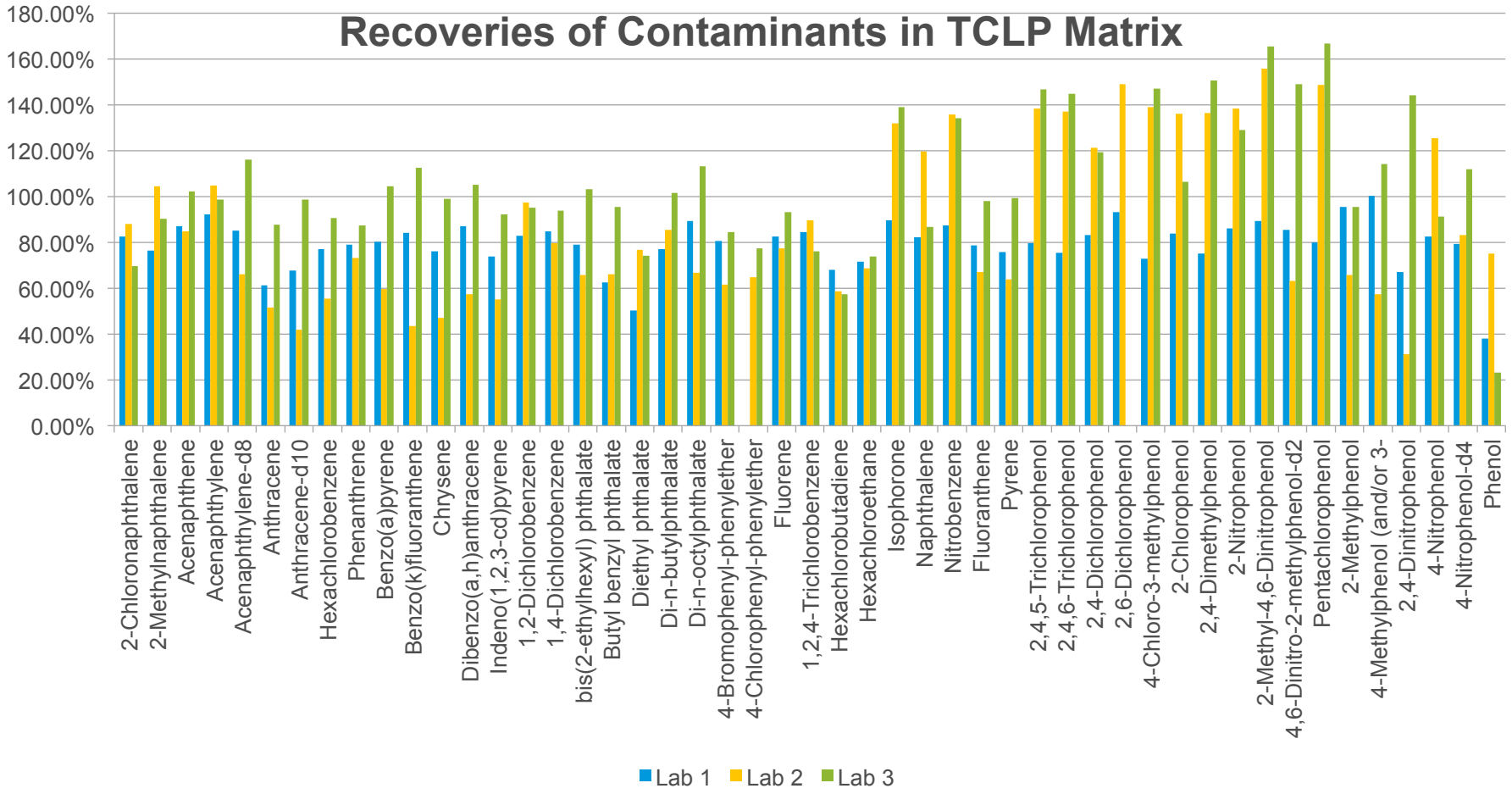
Recovery by Analyte, Bond Elut ENV – By Laboratory (n = 3)



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Recovery by Analyte, Bond Elut C18 – By Laboratory (n = 3)