EPA Method 625 SPE Validation Study – A New Approach

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Study Participants

Under a program organized and supported by the Independent Laboratory Institute (ILI), a broad coalition representing government, the commercial analytical laboratory community, the technology innovation community and academia worked together to develop a generic protocol for the use of Solid Phase Extraction (SPE) as a technique for concentrating chemical contaminants in aqueous samples for organic chemical analysis.
Study Objectives

- Establish a generic SPE protocol for the validation of Solid Phase Extraction for test methods

- Have embed into the protocol, the proper QC elements necessary to flag any individual sample or product failings.

- Apply that protocol in a blind feasibility study involving multiple segments of the laboratory and vendor community.

- Evaluate that data suitability and study parameters for usage to validate Solid Phase Extraction in test methods.

- Develop a fluid protocol to be used as a template in the application of future methods.
Study History

- Coalition began meeting in 2012

- Began a comprehensive review of existing Vendor SPE applications and EPA method procedures

- Examined the analyte lists found in EPA 625 and cross referenced those individual analytes with optimal sorbent types, pH requirements and other extraction requirements.

- Examined the various different SPE platforms and technologies available on the market.
Study Overview

- The complete study was comprised of two different Phases.

- Each Phase was designed to improve efficiency and the performance for EPA Method 625.
SPE Product Types
Study Participant Contribution

- Over 18 individual products/techniques tested
- 27 Contributing Labs
- Over 100 different extractions and analyses completed
- Hours of data analysis and review
Study Protocol

- Focusing on the analytes from Tables #1 and #2 from EPA 625
  - Additionally OCPs were an optional add on
- Establish a blind Round Robin study
- Require 3 participating labs per product tested
- RR samples to be analyzed in both a clean matrix (DI), TCLP Extraction Fluid #1 and a synthetic waste water matrix (ASTM D5905)
- Surrogate spikes provided (P2)
Phase 1
Phase One Objectives

- Determine the performance of a board spectrum of market available SPE products in a standardized waste water matrix.
- Compare data from SPE products to current Liquid-Liquid Extraction (LLE) performance.
- Evaluate the data – Does SPE work as well as LLE
Phase 1 Analyte Category Data

- PAHs: 59.4
- Acids/Phenols: 66.6
- BN's: 69.7
- OCPs: 70.9

SPE
CLLE
PAHs Waste Water vs. DI Water

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Phenol/Acids
Waste Water vs. DI Water

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Phthalates
Waste Water vs. DI Water

Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
bis(2-ethylhexyl) phthalate

DI Water
Wastewater
Lower Limit
Upper Limit

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Base/Neutrals

Waste Water vs. DI Water

Lower Limit
Wastewater
DI Water
Upper Limit

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Phenol Variability

- Phenol (D = 59.5%)
- 4-Nitrophenol (D = 44.9%)
- 2,4,5-Trichlorophenol (D = 36%)
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Phase 1 Conclusions

- Data demonstrates the across the wide variety of analytes SPE products tested are as accurate as traditional LLE.

- Study results were within the current method criteria for EPA 625 and within the acceptance limits in the TNI FoPT tables.

**HOWEVER....**

- Issues were noted with the surrogates that did not demonstrate the failure of an extraction or product.

- Rigorous quality control to allow laboratories to know of a potential issue was need provided with the current surrogate list.

- Answer – Phase 2
Phase 2
Phase 2 Objectives

- Provide more vendors to participate in the study.
  - ASTM Waste Water matrix provided again.
- Provide a second challenge matrix
  - EPA Method 1311 (Toxicity Characteristic Leaching Procedure or TCLP)
  - Evaluate the results of the new challenge matrix
- Provide a new set of surrogate compounds for evaluation.
  - Evaluate the new surrogate list to analyte recovery
  - Do the surrogates provide the intended quality assurance?
Surrogate Analyte Recoveries
Matrix Comparison
Aromatic Surrogate Analyte Recoveries

Matrix Comparison

Percent Recovery

2-Chloronaphthalene
2-Methylnaphthalene
acenaphthene
acenaphthylene
Anthracene
Anthracene-d10
Benzo[a]pyrene
Benzo(a)pyrene-d12
benzo(k)fluoranthene
Benzo(k)fluoranthene-d12
Benzo(a)pyrene
Chrysene
Dibenzo(a,h)anthracene
Indeno(1,2,3-cd)pyrene
4-Bromophenol-phenylether
4-Chlorophenol-phenylether
Fluorene
Fluorene-d10
1,2,4-Trichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorobutane
Hexachloroethane
Isophorone
Naphthalene
Nitrobenzene
Nitrobenzene-d5
Fluoranthene
Pyrene
Pyrene-d10

TCLP Matrix
ASTM Matrix
LCS DI Water
Phthalate Surrogate Analyte Recoveries
Matrix Comparison

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Surrogate Analyte Recoveries
Delta Across Matrix Comparison
<table>
<thead>
<tr>
<th>Substance</th>
<th>Percent Recovery</th>
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<tbody>
<tr>
<td>2-Chloronaphthalene</td>
<td>-20.00%</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>-10.00%</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.00%</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>10.00%</td>
</tr>
<tr>
<td>Anthracene</td>
<td>20.00%</td>
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<tr>
<td>Hexachlorobenzene</td>
<td>30.00%</td>
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<tr>
<td>Phenanthrene</td>
<td>40.00%</td>
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<tr>
<td>Benzo(a)pyrene</td>
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</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
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</tr>
<tr>
<td>Chrysene</td>
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</tr>
<tr>
<td>Dibenz(a,h)anthracene</td>
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</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
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</tr>
<tr>
<td>4-Bromophenyl-phenylether</td>
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</tr>
<tr>
<td>4-Chlorophenyl-phenylether</td>
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<tr>
<td>1,2,4-Trichlorobenzene</td>
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<tr>
<td>Hexachlorobutadiene</td>
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<tr>
<td>Hexachlorocethane</td>
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<td>Nitrobenzene</td>
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<tr>
<td>Fluoranthene</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td></td>
</tr>
<tr>
<td>Percent Recovery</td>
<td></td>
</tr>
</tbody>
</table>

**Graphs**

- **Aromatic Surrogate Analyte Delta**
- **Percent Recovery**
  - TCLP Matrix
  - ASTM Matrix
  - LCS DI Water
Halogenated Hydrocarbon Surrogate Analyte Recovery Delta
Phthalate Surrogate Analyte Recovery Delta

Phthalate Surrogate/Analyte Delta

-40.00%
-30.00%
-20.00%
-10.00%
0.00%
10.00%
20.00%

TCLP Matrix
ASTM Matrix
LCS DI Water

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Surrogates Selected

- Acenaphthylene-d8
- Anthracene-d10
- Benzo(a)pyrene-d12
- Bis(2-chloroethyl)ether-d8
- 4-Chloroaniline
- Dimethylphthalate-d6
- Fluorene-d10
- Nitrobenzene-d5
- N-Nitrosodimethylamine-d6
- Pyrene-d10

- 2,4-Dichlorophenol-d3
- 2-Chlorophenol-d4
- 2-Nitrophenol-d4
- 4,6-Dinitro-2-methylphenol-d2
- 4-Methylphenol-d$_8$
- 4-Nitrophenol-d4
- Phenol-d5
Phase 2 Conclusions

- Data demonstrates the across the wide variety of analytes SPE products tested are as accurate as traditional LLE.
- Study results were within the current method criteria for EPA 625 and within the acceptance limits in the TNI FoPT tables.
- With the exception of Phthalate Surrogates the new batch of analytes were a significant improvement.
- SPE Products perform equivalent to LLE performance across difficult matrices.
Acknowledgements

• SPE Vendors
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Questions?

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