Analysis of Polycyclic Aromatic Hydrocarbons in Polyurethane Foam (PUF) and Diethylene Glycol/Water Samples using Automated Pressurized Liquid Extraction, Cleanup and Solid Phase Extraction

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Introduction

- PAHs analyzed worldwide: air, sediment, soil, water.
- Industrial sources: coal gasification, municipal solid waste incineration, petroleum refining.
- PAHs result of incomplete combustion.

PAHs

- Can be found in incinerator emissions, dust, fly ash, bottom ash
- Subject to monitoring and regulations in most countries
- Stack emissions can be collected with sampling using poly-urethane foam (PUF) and solvent impingers (diethylene glycol-water)

Pressurized Liquid Extraction

- An automated Extraction technique can be used for PAHs collected on PUF

- The Technique Incorporates:
  - Solvent
  - Pressure
  - Heat
  - Time

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Why is PLE so effective?

- Performed near the solvent's supercritical region
- Under Programmable Pressure
- Creates a high degree of analyte solubility releasing PAHs from the solid matrix

Extraction

- A solid or semi-solid sample is placed in the Pressurized Extraction Cell 5mL to 200mL

- The Extraction cell is capped and placed into the extraction device which can be pressurized to up 2500psi

Extraction

- The Extraction cell is filled with the extraction solvent put under pressure and depressurized
  - PAHs (suitable for lots of other analytes too)
- The Extract is flushed with Nitrogen into a collection vessel

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The PLE®
Pressurized Liquid Extraction

PLE - Pressurized Liquid Extraction

- High Speed
- Modular and expandable from 1 to 8
- Process 1 to 8 samples in 10 to 15 min
- Extraction cell size 5 mL to 200 mL
- Real time plot of temperature and pressure
- Reduced Solvent Consumption
- Lower Energy Consumption
- In Cell Sample Cleanup

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Economical Extraction Cells

Easy to Use End Caps

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Modular and Expandable

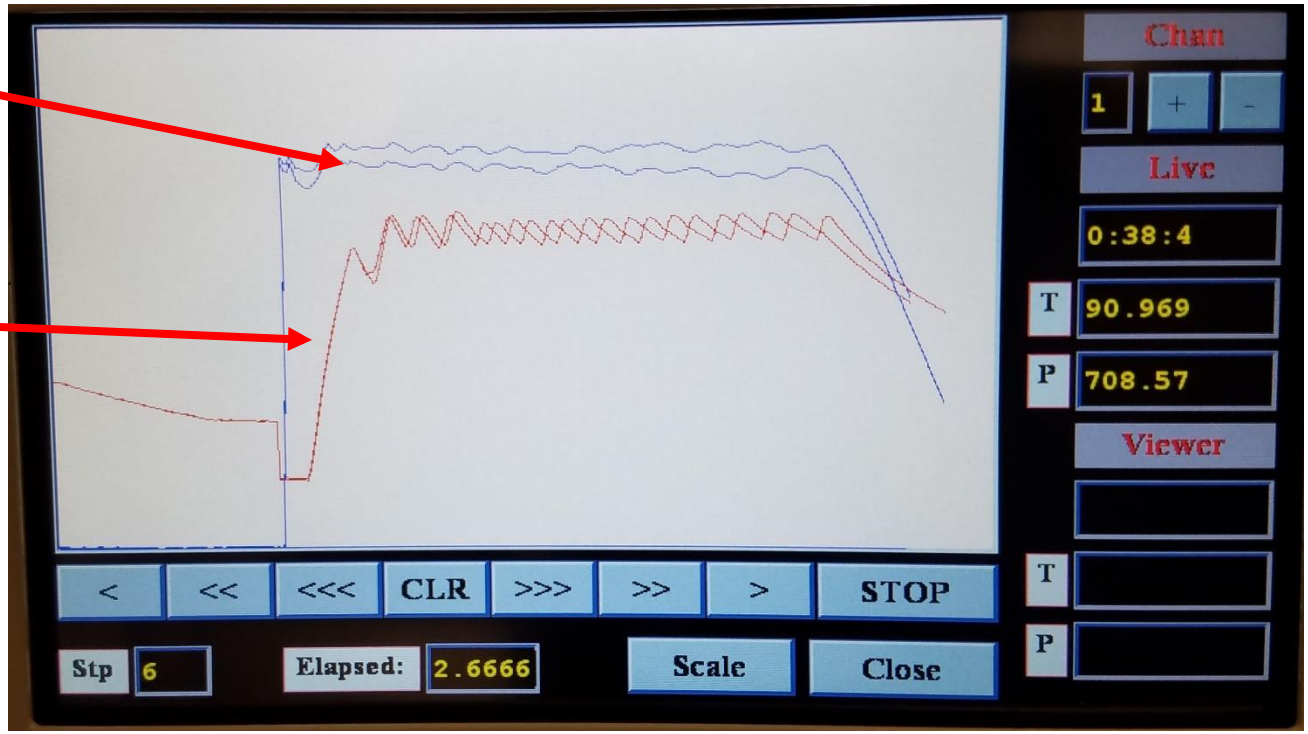
Expandable from 1 to 8 Modules

Parallel Extraction

Method Documentation

Pressure

Temperature



Pressurized Liquid Extraction for PAHs in PUF

- Large PUF plug (ca 6 cm OD x 7 cm length) spiked with native PAH standards
- Sample placed in 40 mL extraction cell and void space filled with Ottawa Sand
- Capped with disposable Teflon end caps
- 50% Dichloromethane/50% Hexane for 15 min at 100 ^{o}C and 1500 psi
- 15 min cool down
- Nitrogen flush to transfer analytes and extract to 50 mL collection tubes

Concentration of PLE extract

Extract after Cleanup

- System pre-heated to 40 ºC.
- Samples evaporated at stable T under 5-6 psi nitrogen.
- Solvent exchange to hexane.
- Reduce volume to 1 mL.

Automated EZprep/+ for cleanup

EzPrep/+ Features (1)

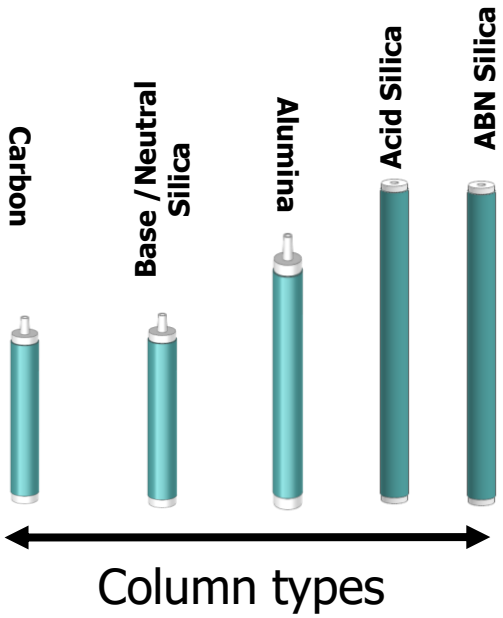
Features:

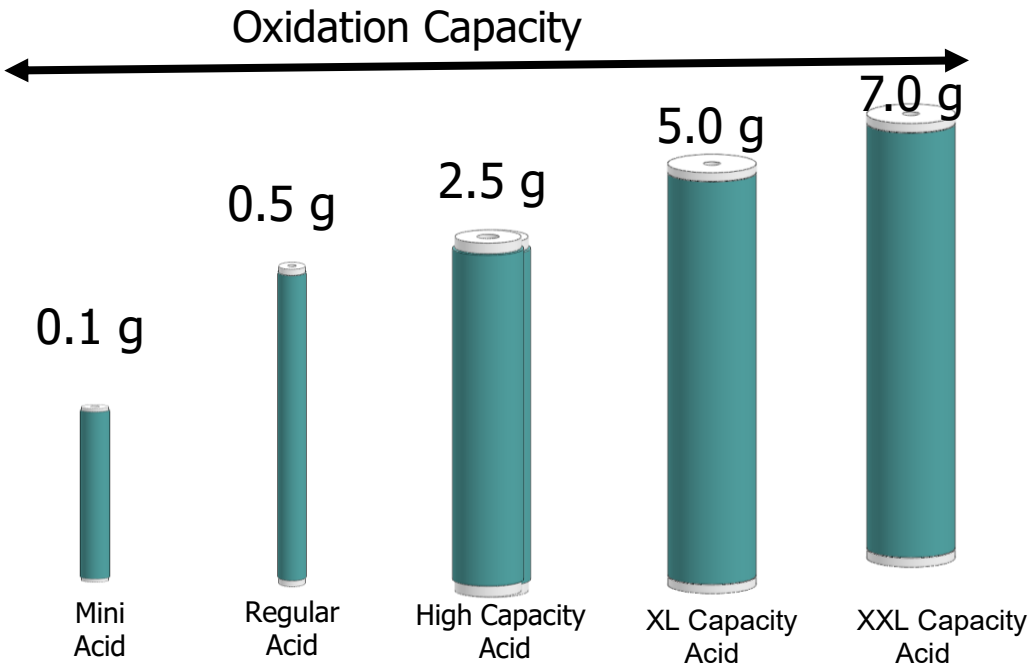
- Programmable Flow rate and Volume
- Pressure indicator and over pressure alarm
- Real time read-out for dispensed volume and pressure
- Ability to select from 1 to six samples
- Can accommodate up to 4 solvents
- Economical & less expensive automation

EZPrep/+ Features (2)

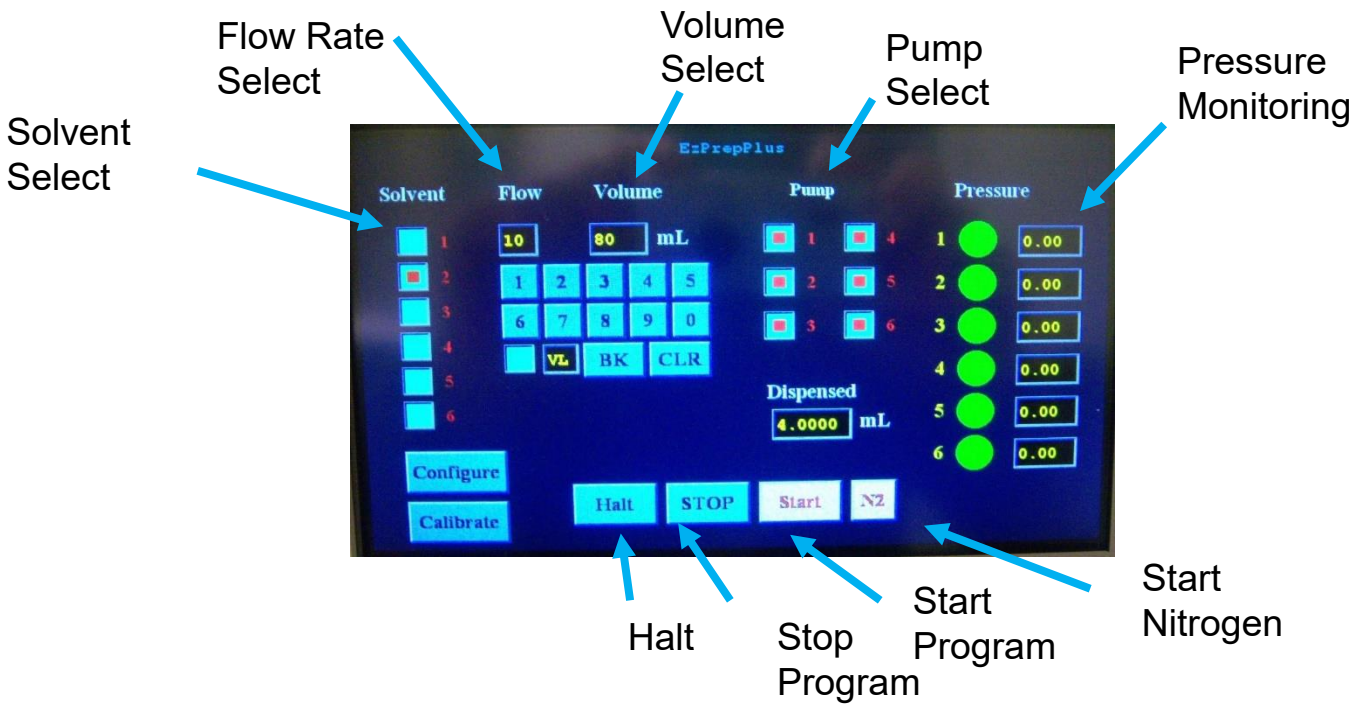
- Closed loop system, eliminates background contaminants & exposure to chemicals
- Optimized for solvent reduction while obtaining highest possible recoveries
- Certified disposable Columns with guaranteed low contaminants background and Excellent Recoveries
- Quick connect SNAP columns simplifies system set up
- Multi pump Solvent Delivery system brings convenient automated solvent selection & dispense with controllable flow & volume
- EzPrep/+ designed with Minimum number of electronics and Electromechanical valve to lower cost and simplify the maintenance

Columns/ Oxidation Capacity





EzPrep /+ Control Panel



PAHs Cleanup

- Assemble 6 g neutral silica columns with EZPrep +
- Syringe vial at top is used for sample loading.
- **Stage 1:**
- Dilute sample extract with 9 mL hexane.
- Load sample extract onto silica column
- Elute column with 10 mL hexane (waste)
- **Stage 2:**
- Elute columns with 35 mL dichloromethane, collecting aromatic fraction (PAHs).

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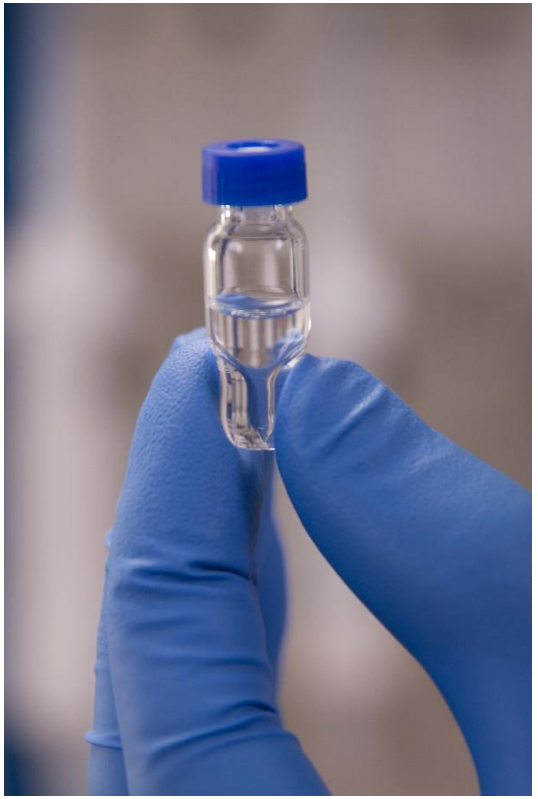
Glass Evaporation tube



GC vial

Final Concentration

- Reduce volume to 1 mL.
- 24 positions in parallel.
- T = 25 °C for most volume reductions.
- Nitrogen flow 1-2 psi.

Impinger w/PAHs: use SPE (1)

LLE/CLE	Automated SPE
Open to laboratory background	Closed system
Uses >360mls solvent	Uses <60mls solvent
Shaking / Continuous process	Filtration process
Forms emulsions requiring centrifuging	No emulsions formed
Little Selectivity	Wide Selectivity (adsorbent)
Requires water removal	In-line water removal

Comparison of LLE/CLE vs SPE Methods (2)

LLE/CLE	Semi-Automated SPE
No Separation of waste	Separates Aqueous and Organic Waste
More volume to evaporate	<60mls solvent to evaporate
Massive solvent emission	6 times less solvent emission
CLE uses a lot of solvent	Easily Capture Solvent
Requires lots of solvent for cleaning	Lower solvent costs
	Lower Disposal Costs

Automated SPE system

TurboTrace® SPE

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System Features

- **Simultaneous Processing:** Modular, processes up to six samples in parallel.
- **Versatile Sample Handling:** Compatible with beverages, blood, milk, urine.
- **Sample Size:** Handles sample volumes from 2 mL to unlimited.
- **Programmable Operations:** Built-in computer.
- **Precise Delivery:** Positive pressure pumping for accurate solvent delivery.
- **Loading:** Incorporates vacuum or positive pressure pumps for efficient sample loading.
- **On-line evaporation:** Concentrates up to 250 mL directly into a GC vial for analysis.

SPE for PAHs (1)

- Acidify 10% Diethylene glycol/water samples with 6 N Hydrochloric Acid to pH < 2
- Add surrogates if so desired
- Load samples on automated system
- Install C-18 cartridges
- Fill rinse bottles with 35 mL dichloromethane
- Condition catridges:10 mL dichloromethane, 20 mL methanol and 35 mL water (waste)
- Load samples under vacuum across cartridges (waste)

SPE for PAHs (2)

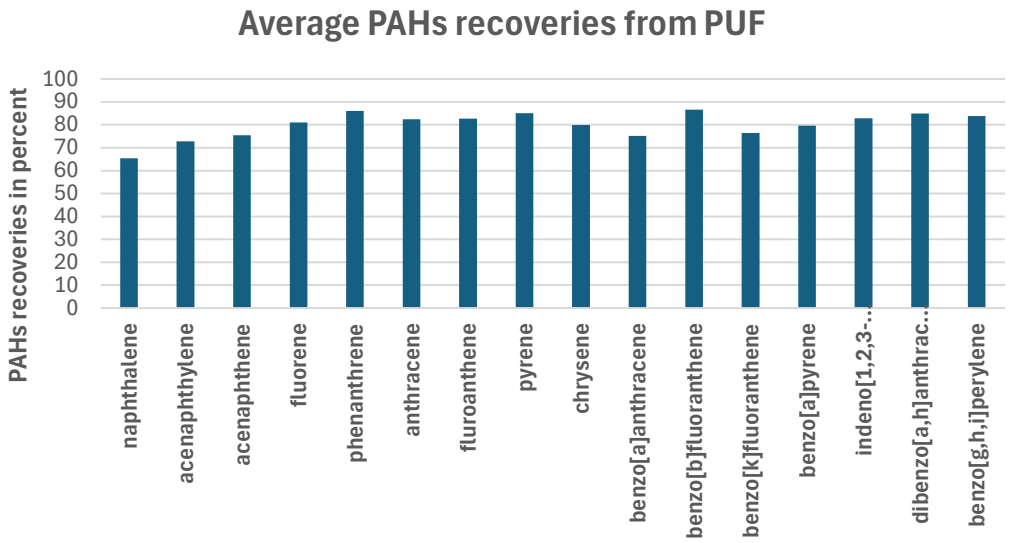
- Dry with nitrogen for 3 min
- Rinse sample bottles with 35 mL dichloromethane and load across cartridges for elution and collect
- Elute 5 mL, another 5 mL, and another 2 mL of dichloromethane for soaking and elute and collect
- Blow out fraction lines with nitrogen and collect
- Dry samples over sodium sulfate (can be in-line cartridges)

- Concentration in 12-position evaporator as described.

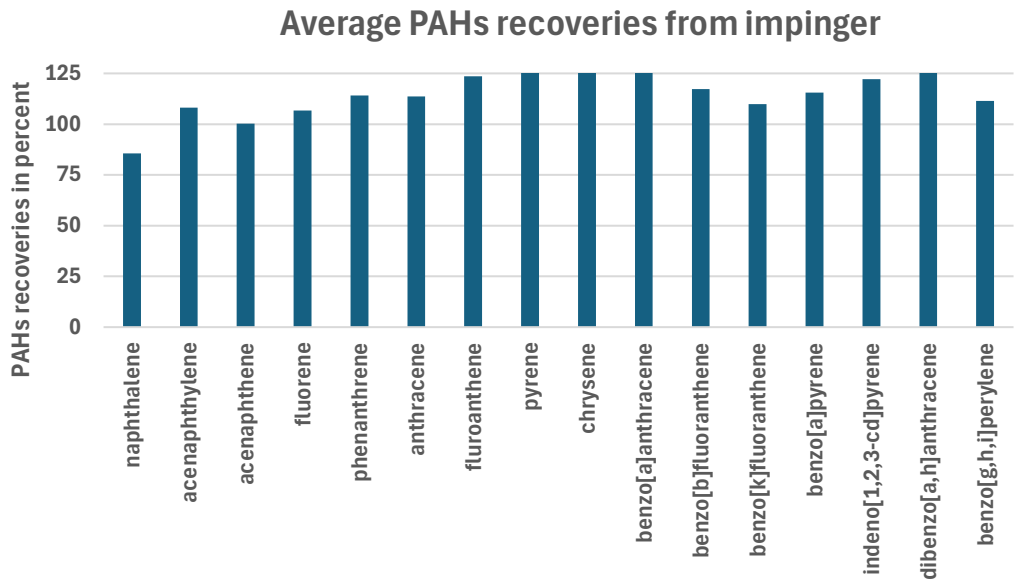
Analysis

Agilent 7010 B Triple Quad GC/MS/MS

PAHs recoveries from PUF



PAHs recoveries from impinger



Conclusions (1)

- Work illustrates use of Sample Prep automation in monitoring stack emissions
- Solid matrices used for collection can be easily processed with Pressurized Liquid Extraction, automated cleanup with column chromatography and automated sample concentration
- PLE is green technique compared to Soxhlet because of fast process ~ 1 h, less power use
- Automated Solid Phase Extraction can provide quick processing of emissions collected in liquids using impingers. No additional cleanup is necessary.
- Automation reduces errors and produces consistent, reproducible results.
- Increased productivity.

Conclusions (2)

- Faster and easier operator training
- Automatic documentation of extraction and cleanup and concentration conditions
- Reduced errors due to mistakes eliminating manual steps and conditions.
- Reduced solvent usage and disposal costs.

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Come see us at our booth

Questions?

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