

Semi-Automated Clean Up for Persistent Organic Pollutants Analysis in Environmental Samples - Complete Separation of PCDD/Fs and PCBs for Sample Extracts in Toluene

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Introduction

- POPs (PCDD/Fs, PCBs) continue to attract interest around the world due to strict regulations enforced in many countries
- Rapid and quality sample clean up and analysis is needed for many laboratories processing samples
- Processing times and cost are important considerations
- In US EPA methods 1613 and 1668 are used

Challenges of POPs Sample Prep

- ▶ Labor intensive, prone to error
- ▶ Compliance with regulatory procedures and accreditation (lengthy method validation)
- ▶ Strict QA/QC requirements
- ▶ Sample matrix complexity
- ▶ Native background and interferences (can be orders of magnitude higher than analytes)
- ▶ Pico/femto-gram analyses require ultra pure extract and excellent instrument sensitivity

Automated Sample Prep

► **Advantages of Automated Sample Prep**

- Rapid Turn Around Time: 60 Minutes for 6 Samples
- Cleaner Background Interferences: Closed Loop System
- Quality Results: Certified Prepacked Columns
- Green Technology: Often lower solvent use
- QA/QC & Accreditation Requirements: Easier to Manage
- Computerized Method: Instrumentation based prep

Manual Sample Prep

► **Advantages of Manual Sample Prep**

- Most labs use a Manual Methods for the following reasons:
 - No electronics or mechanical components to fail
 - No down time due to the system failure
 - No service contract
 - No capital equipment cost

Automated System Attributes

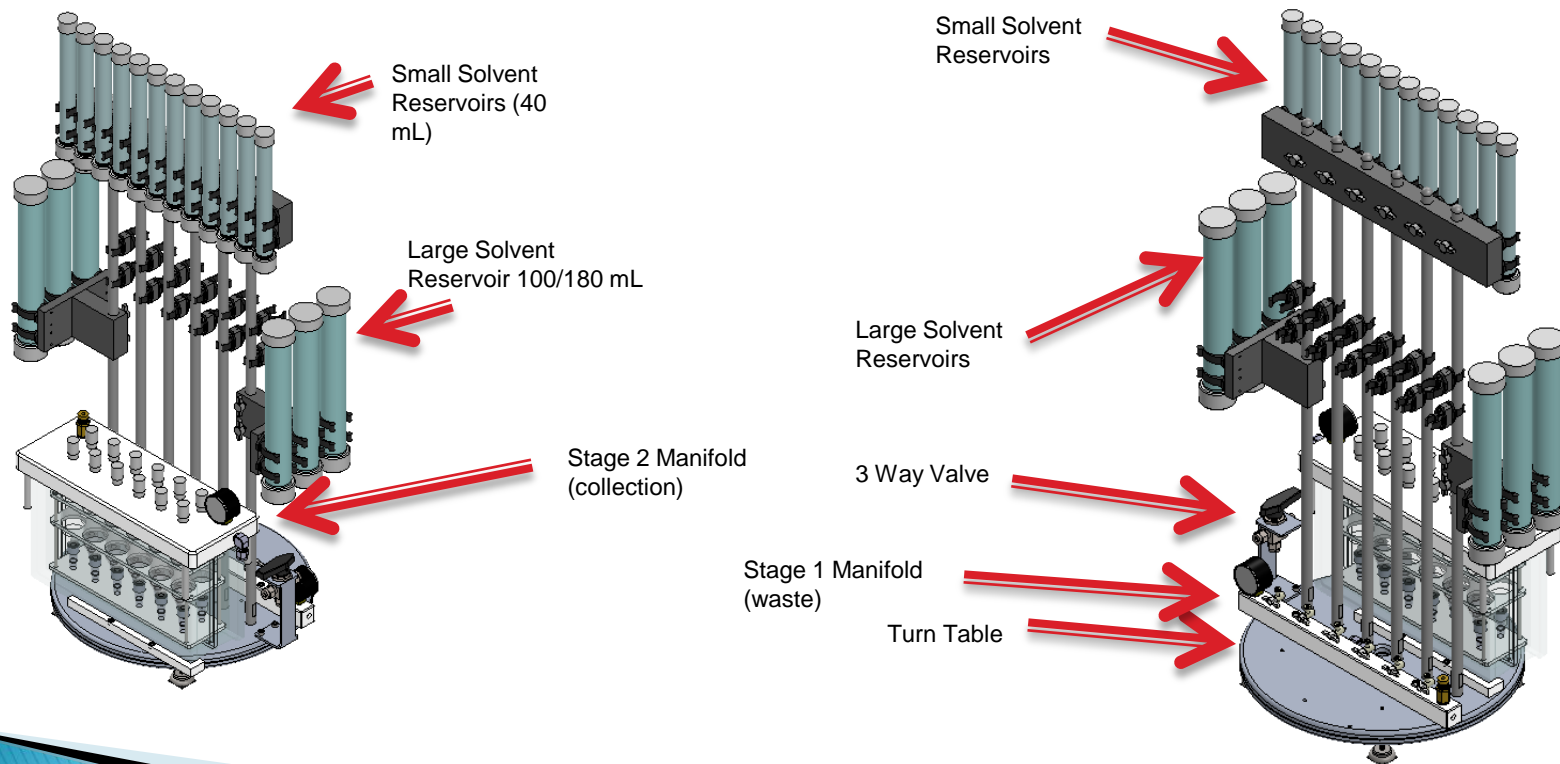
- Fully automated: From sample loading to elution and fraction collection
- Closed loop system: Cleaner background, lower detection limit
- High recoveries & Excellent precision: Certified columns
- Green Technology: Low power usage
- Fast: Total Clean Up time 60 min.
- Low volumes: varies, as low as 100 -250 mLs

Semi-Automated System

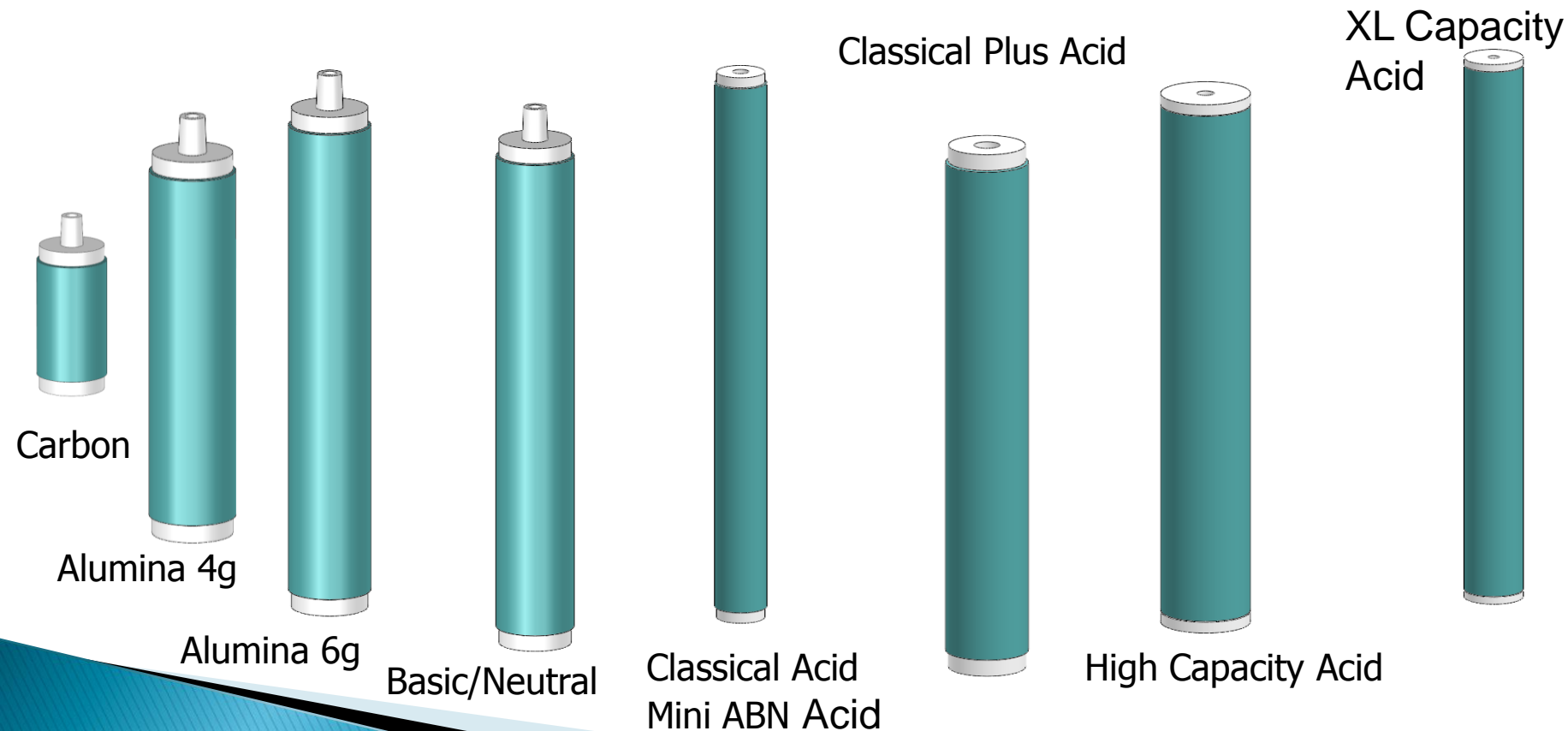
Specification:

- Simple to run, no computerized instrumentation
- Fast: 60 min
- Closed loop system to give a clean background, low level detection
- Use certified columns
- Green technology, only vacuum pump uses power
- Low solvents, as low as 90ml for serum
- Economical column kits, choice of low fat and high fat column kits
- No capital equipment cost
- No electronics or mechanical equipment to fail
- No downtime

Characteristics of Semi-Automated System (EZPrep)

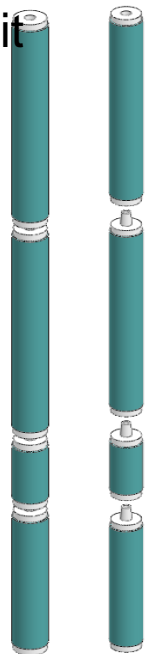


Columns (1)

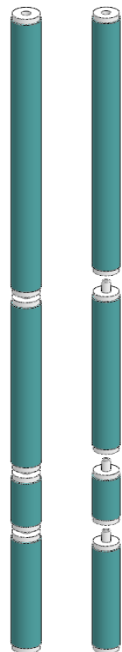


Columns (2)

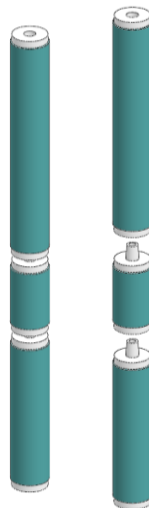
Classical
Kit



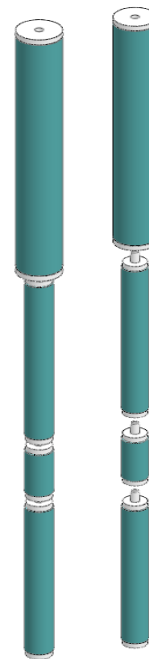
Classical Plus
Kit



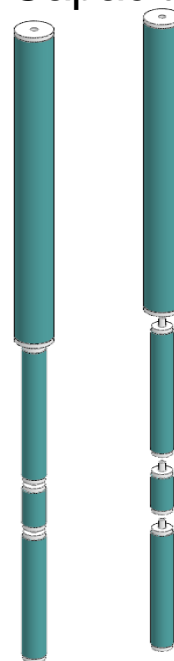
Mini Kit



High Capacity
Kit

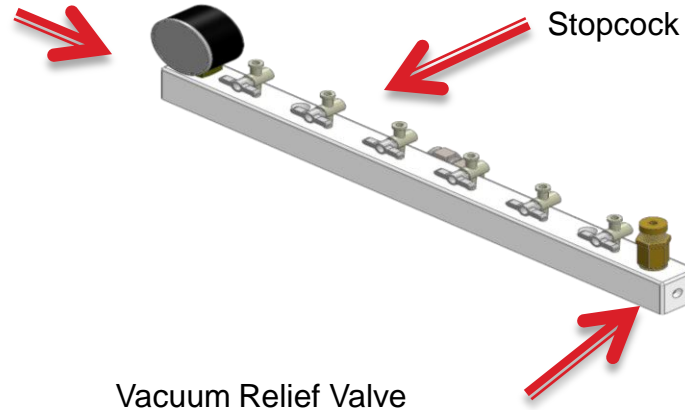
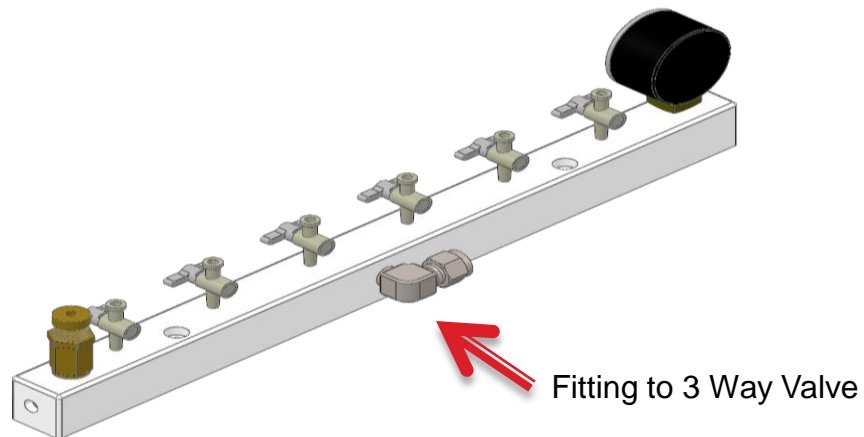


XL Capacity
Kit

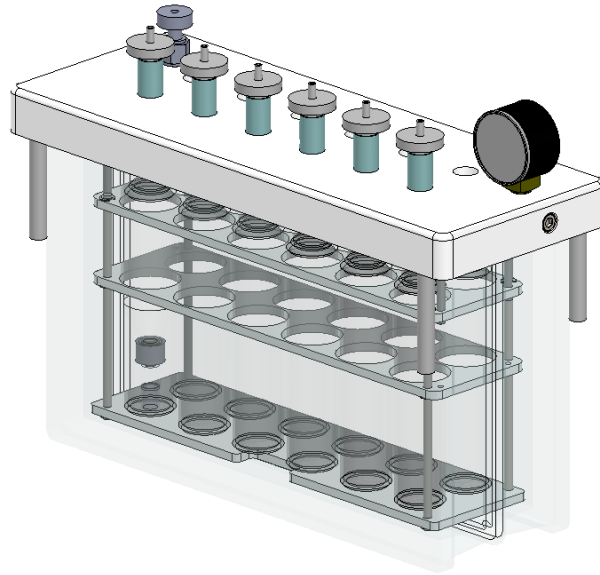


Vacuum

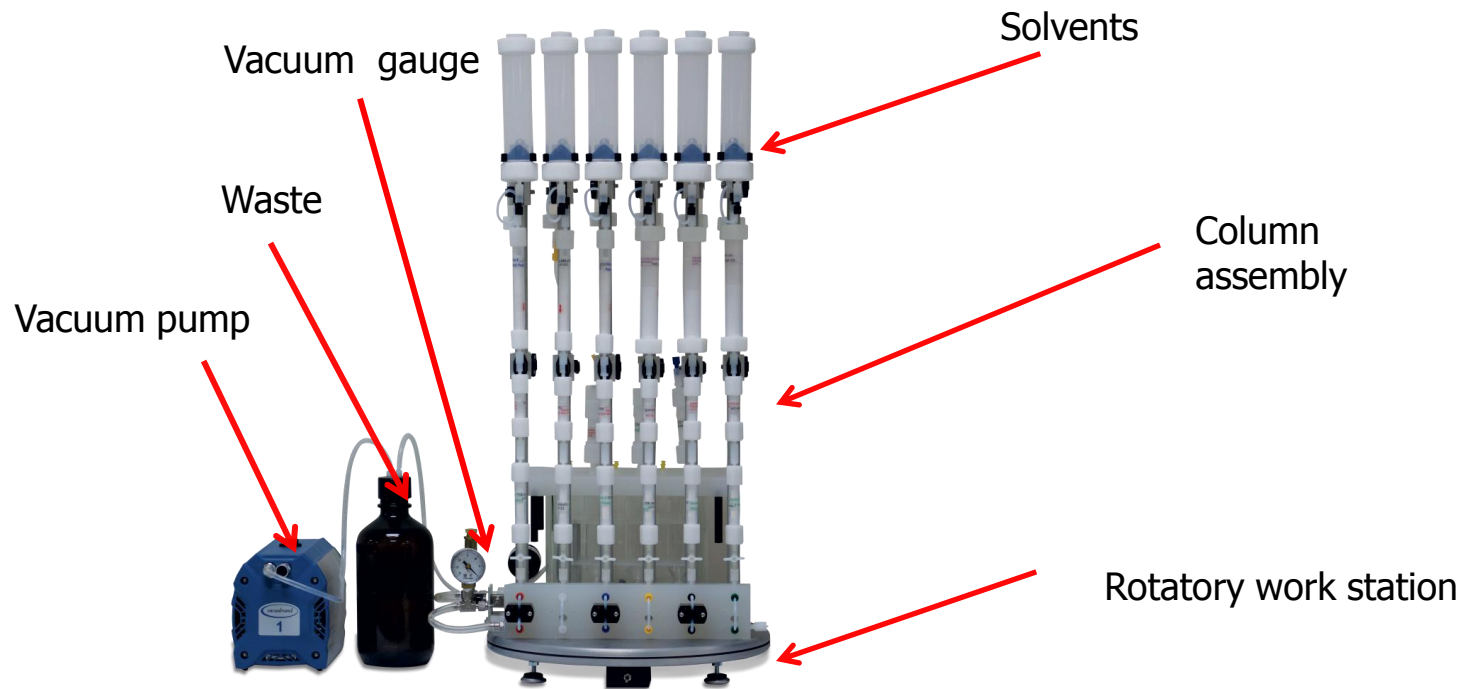
Vacuum Gauge



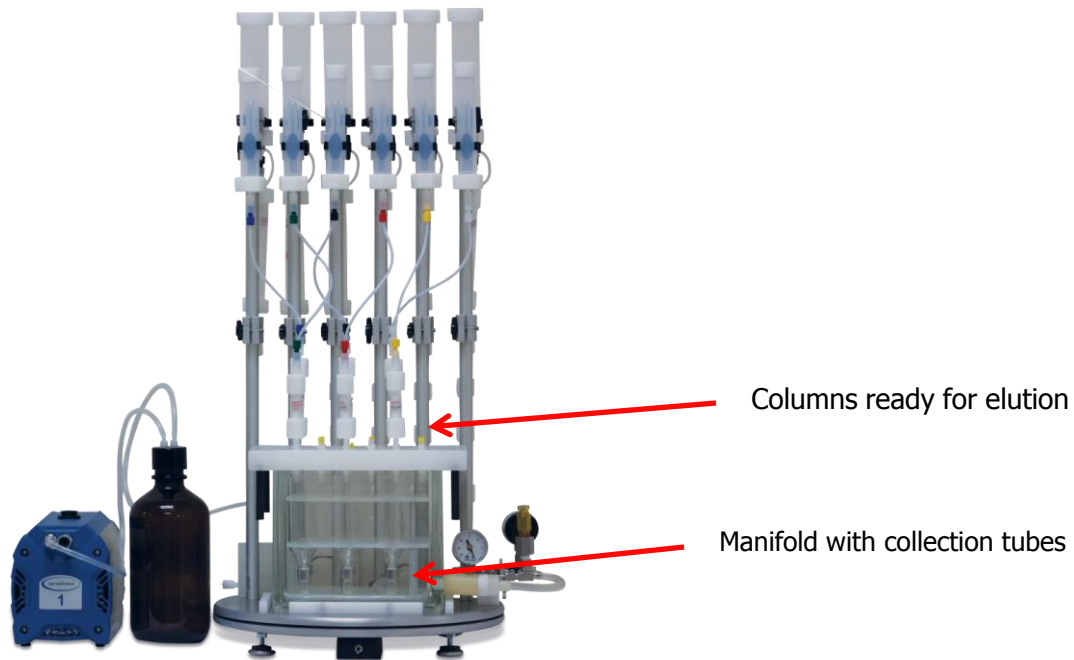
Manifold



Stage 1: to waste



Stage 2: collect



Attributes

- Closed loop system:
 - Eliminates background contaminants
 - No washing needed.
 - Capped solvent reservoirs
- Optimized for solvent reduction while obtaining highest possible recoveries
- Easy sample loading on top of silica column via injection or syringe vial
- Columns connect easy with SNAP connections

Program for samples (1)

- Stage 1: Connect High Capacity Acid Silica and Alumina (no Carbon) and condition with 60 mL of hexane (vacuum, waste)
- Stage 2: Load sample (in 2-10 mL toluene, collect Fraction # 1), rinse loading vials with hexane, elute with 60 mL hexane (collect Fraction # 1), remove acid silica, elute alumina with 30 mL 10% dichloromethane/hexane (collect Fraction # 1)
- All PCBs are now in Fraction # 1, PCDD/Fs have remained on alumina

Program for samples (2)

- Stage 1: Connect Alumina to Carbon and elute with 50 mL of dichloromethane (vacuum, waste); the PCDD/Fs will now be on carbon column
- Stage 2: Turn Carbon column upside down and elute in reverse direction with 60 mL toluene (Fraction # 2). This fraction now contains all PCDD/Fs.
- This method is suitable for samples in 2-10 mL of toluene. This ideal for environmental labs with extracts in toluene.

12 position evaporator 50 mLs



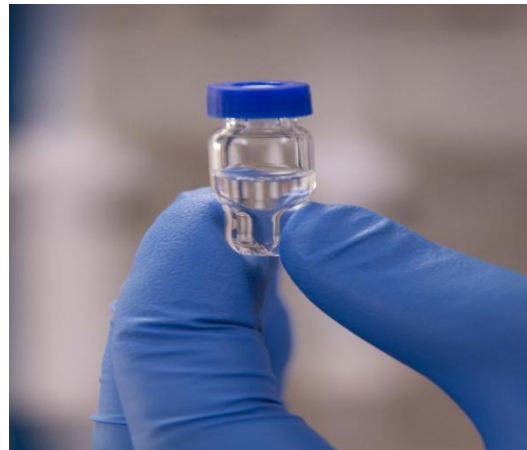
SuperVap Evaporation

- System pre-heated to 45-60 °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).
- Recovery standards added (nonane/dodecane).
- Extract taken to 10 uL volume with a gentle stream of nitrogen at ambient temperature.

24 position vial evaporator



Direct-to-Vial

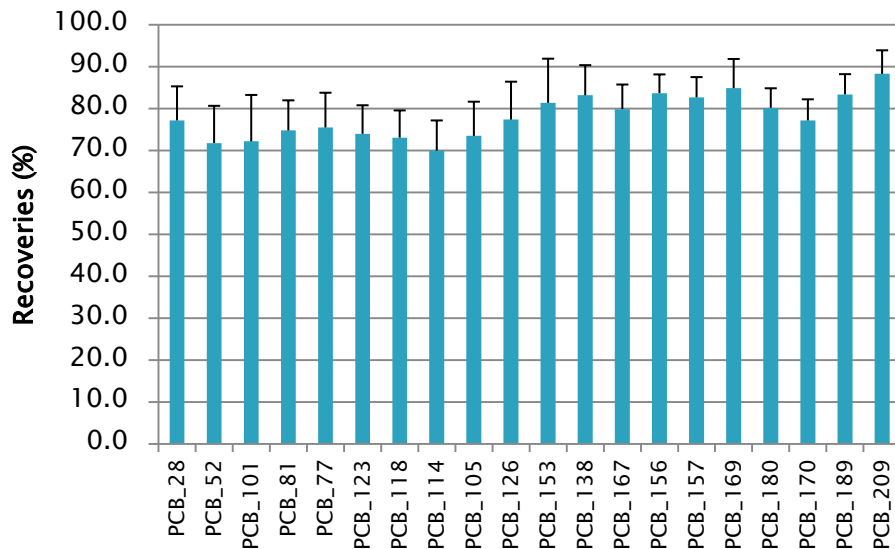


GC vial

DFS HRGC/HRMS

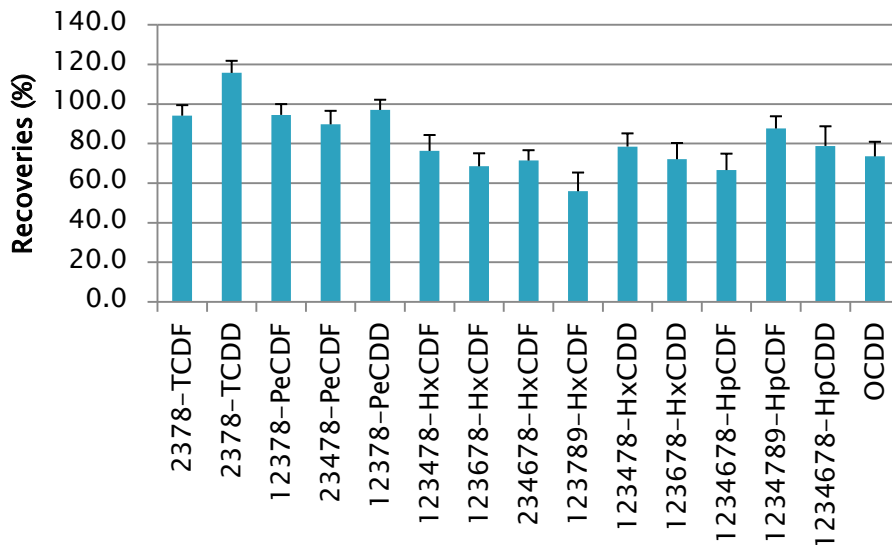


13C recoveries PCBs soil



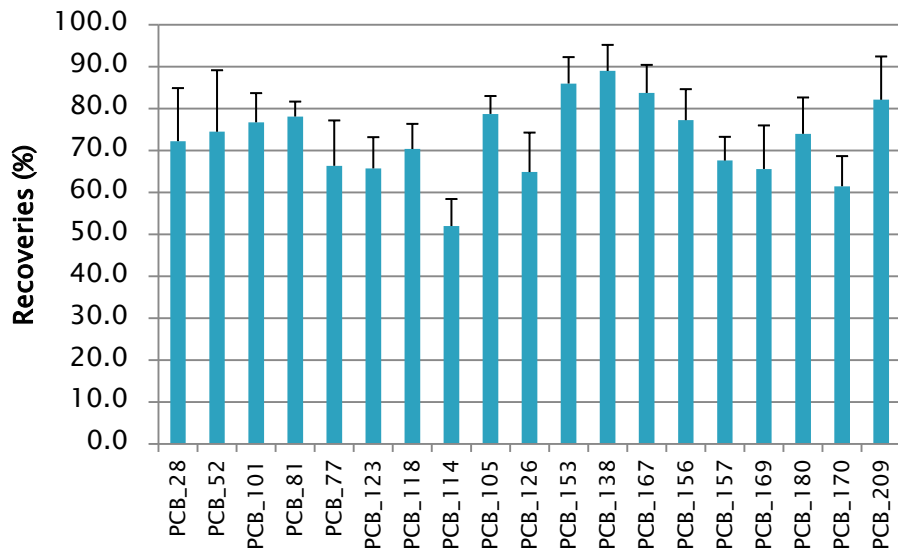
10 g soil in
toluene, n = 10

13C recoveries PCDD/Fs soil



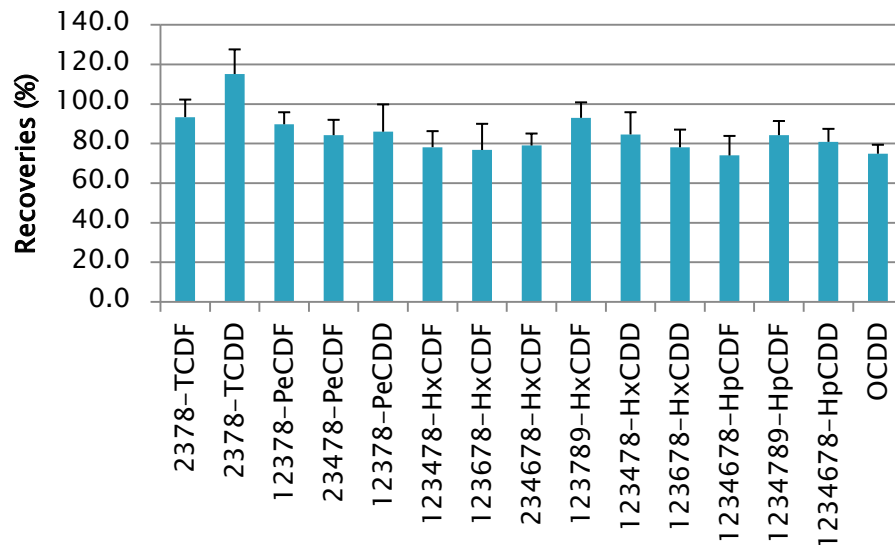
10 g soil in
toluene, n = 10

13C recoveries PCBs salmon



10 g salmon in
toluene, n = 12

13C recoveries PCDD/Fs salmon

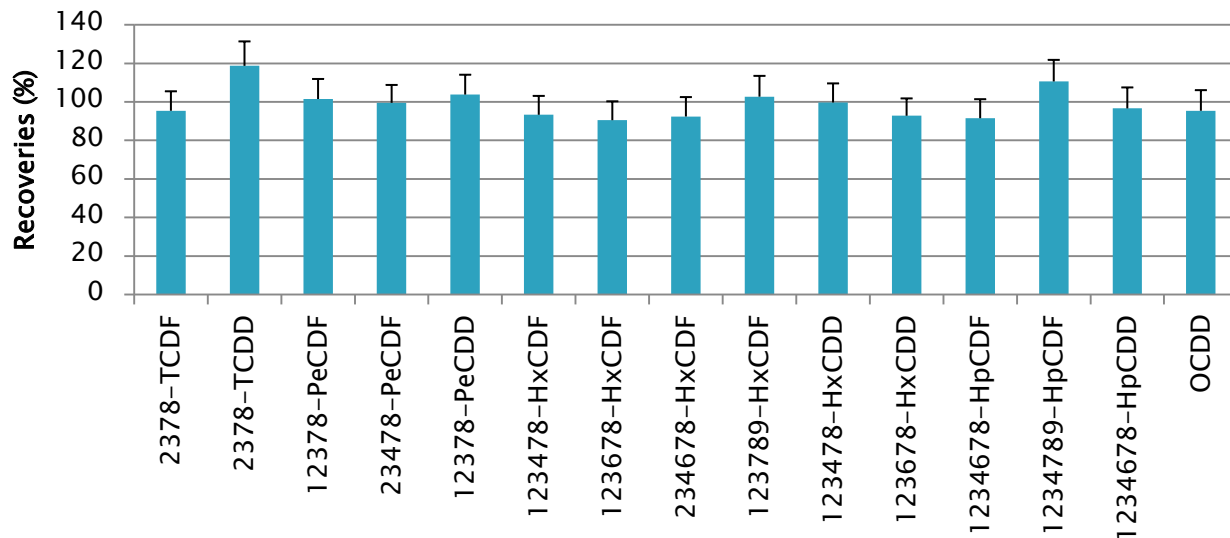


10 g salmon in
toluene, n = 12

Program for samples in toluene (PCDD/F only)

- Stage 1: Connect High Capacity Acid Silica, Alumina and Carbon and condition with 40 mL of hexane (vacuum, waste)
- Stage 1: Load sample (vacuum, waste), rinse loading vials with hexane, elute with 180 mL hexane (vacuum, waste), remove acid silica
- Stage 1: all analytes are now on alumina. Elute alumina-carbon assembly with 50 mL dichloromethane (vacuum, waste; if collected contains mono- and di-ortho PCBs)
- Stage 2: Turn Carbon column upside down and elute in reverse direction with 60 mL toluene (Fraction # 1). This fraction now contains all PCDD/Fs (and co-planary PCBs if present)

13C recoveries PCDD/Fs fish



10 g fish in
toluene, n = 12

Conclusions (1)

- Samples in toluene (environmental, food): 2-10 mL toluene, separate PCBs and PCDD/Fs completely using hexane and 10% DCM/hexane, followed by DCM and toluene
- Reduced hexane volume needed for silica column because of presence toluene
- Alternative for samples in toluene: use hexane, DCM and toluene to have mono- and di-ortho PCBs in one fraction, PCDD/F/co-planary PCBs in other fraction
- Works also for samples in hexane but more hexane needed in that case for silica elution ("toluene effect" not present)

Column Kits with various fat removal capacities for samples in hexane

		Stage 1 (volumes in mLs)			Stage 2 (volume in mLs)		Total time (min)
					PCBs/PBDEs	PCDD/Fs	
Column kits	Fat Removal Capacity	Hexane Conditioning	Hexane Sample loading	Hexane Elute silica	DCM Alumina-carbon	Toluene Reverse carbon	
Classical Plus	1.0 g	20 mL	30 mL	100 mL	50 mL	50 mL	50
High Capacity	2.5 g	40 mL	30 mL	180 mL	50 mL	50 mL	70
Extra high Capacity	5.0 g	60 mL	30 mL	220 mL	50 mL	50 mL	80

Conclusions (2)

- EZPrep suitable for environmental and food analyses in toluene as solvent. Also suitable for samples in hexane
- Can keep PCBs and PCDD/Fs completely separate if so desired. Alternatively have co-planary PCBs in with PCDD/Fs
- High sample throughput → 18 samples/hour
 - 6 samples in parallel per station
 - 3 stations fit in one hood
- System gives excellent recoveries for PCDD/F and PCBs and PBDEs comparable to our automated system
- Use of certified pre-packaged columns guarantees low native background

Conclusions (3)

- No worries about breakdown or downtime
- No washing needed
- No cross-contamination
- Low cost

Questions

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