Toxic Reports™

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

R. Addink
Toxic Report LLC
Watertown MA

Toxic Reports™

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

Toxic Reports™

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

Toxic Reports™

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

Toxic Reports™

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

Toxic Reports™

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

Toxic Reports™

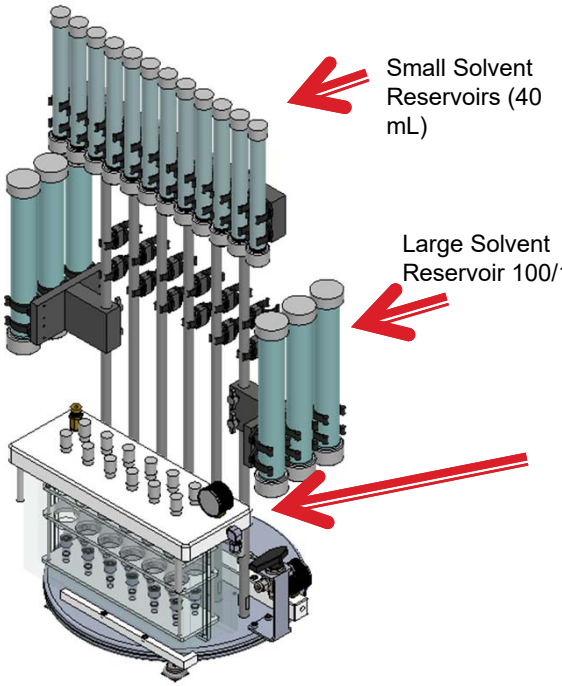
Semi-Automated System

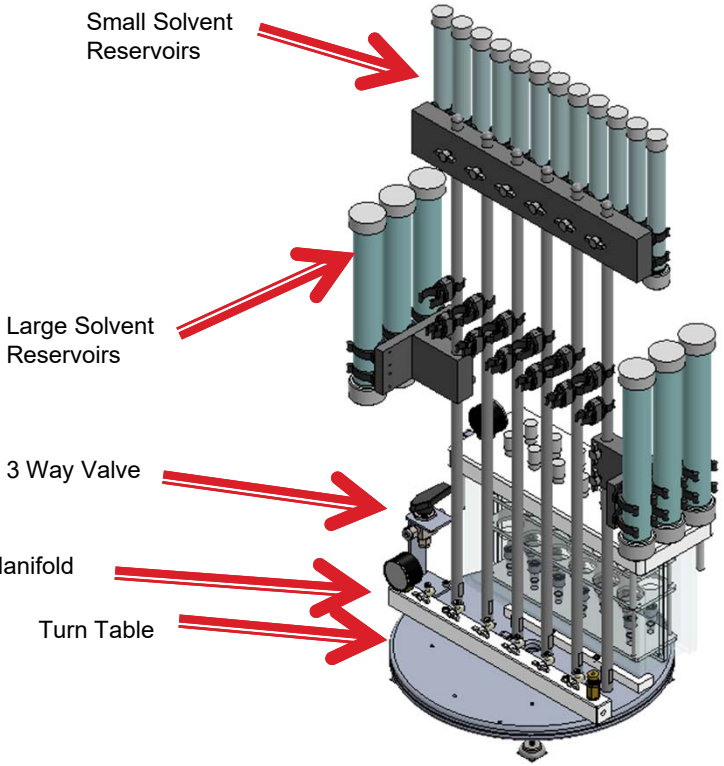
Specification:

- 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

Toxic Reports™

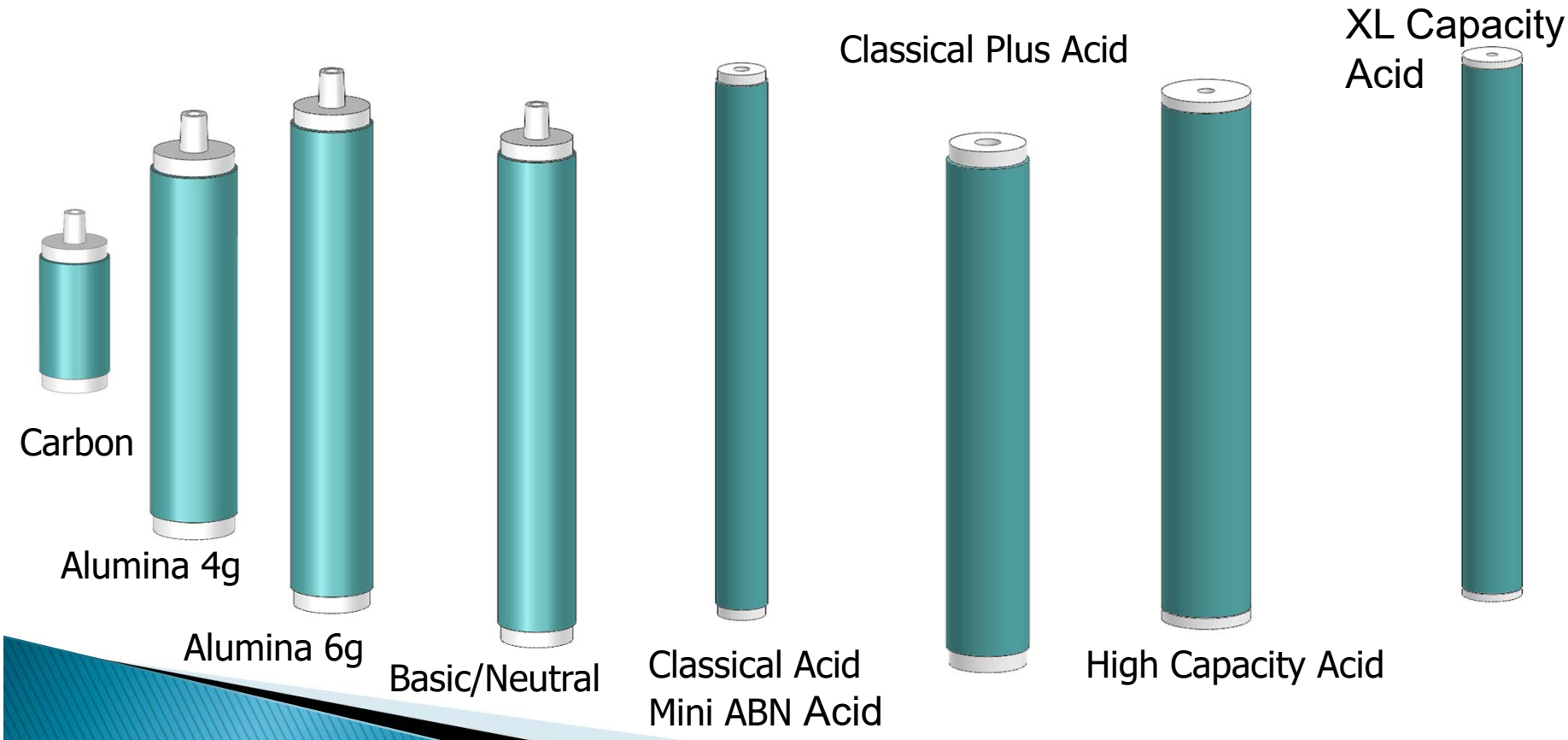
Characteristics of Semi-Automated System (EZPrep)





Toxic Reports™

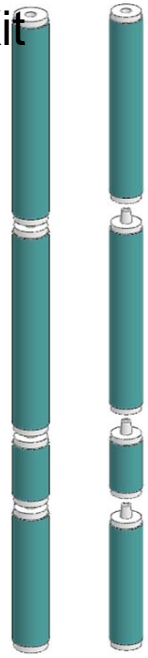
Columns (1)



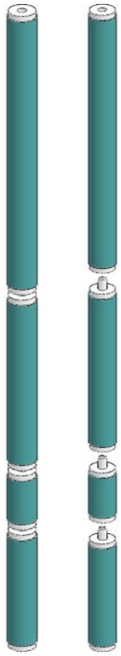
Toxic Reports™

Columns (2)

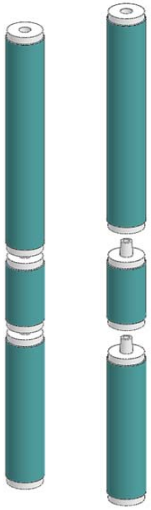
Classical Kit



Classical Plus Kit

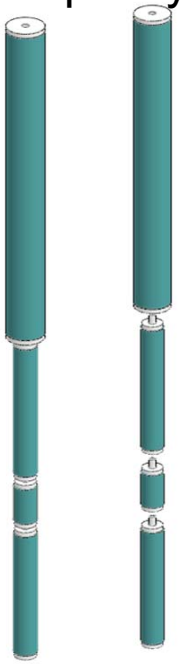


Mini Kit



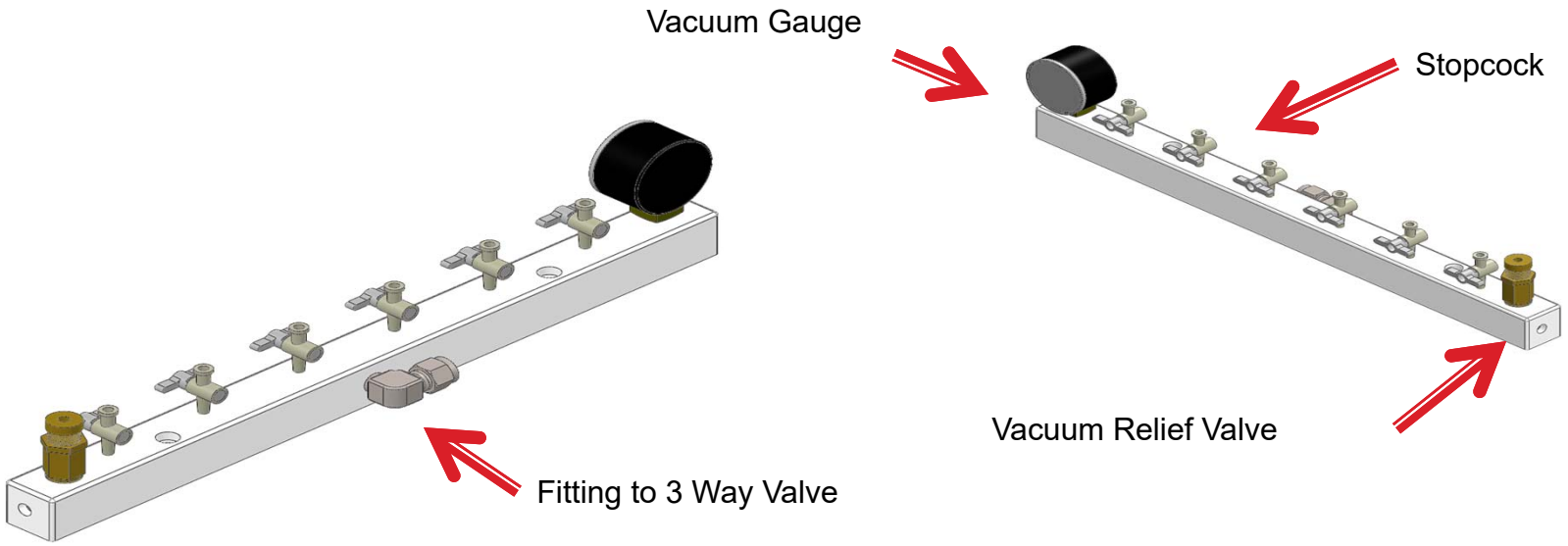
High Capacity Kit

XL Capacity Kit



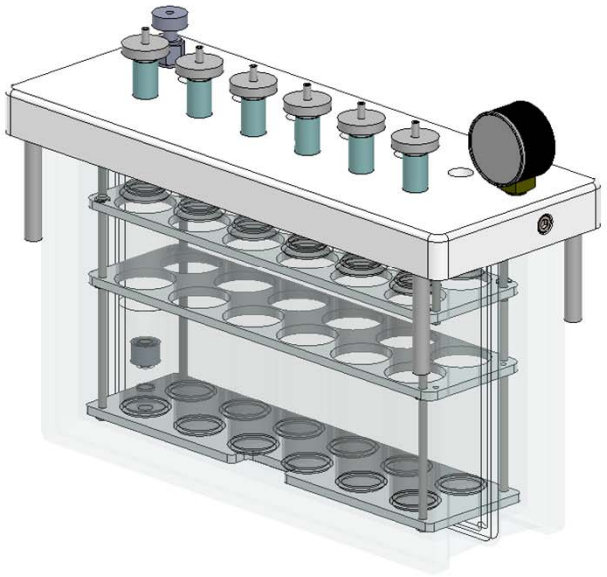
Toxic Reports™

Vacuum



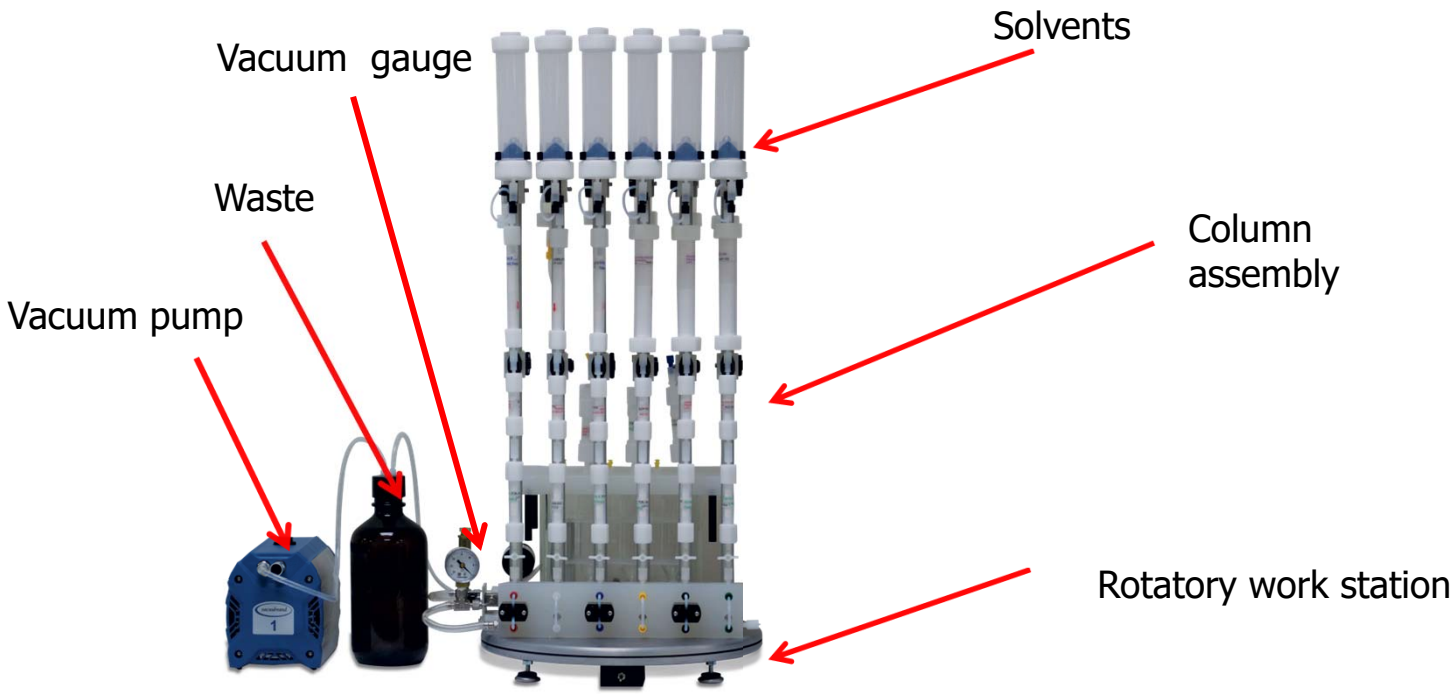
Toxic Reports™

Manifold



Toxic Reports™

Stage 1: to waste



Toxic Reports™

Stage 2: collect

Columns ready for elution

Manifold with collection tubes

Toxic Reports™

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

Toxic Reports™

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

Toxic Reports™

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.

Toxic Reports™

12 position evaporator 50 mLs

SuperVap Evaporation

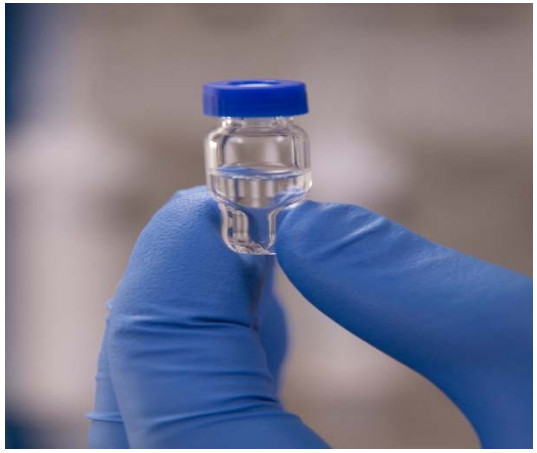
- System pre-heated to 45-60 ºC.
- Samples evaporated at stable T under 5-6 psi nitrogen.
- 1 mL extract vial transferred to GC vial (can have direct-to-vial feature).
- Recovery standards added (nonane/dodecane).
- Extract taken to 10 uL volume with a gentle stream of nitrogen at ambient temperature.

Toxic Reports™

24 position vial evaporator

Toxic Reports™

Direct-to-Vial



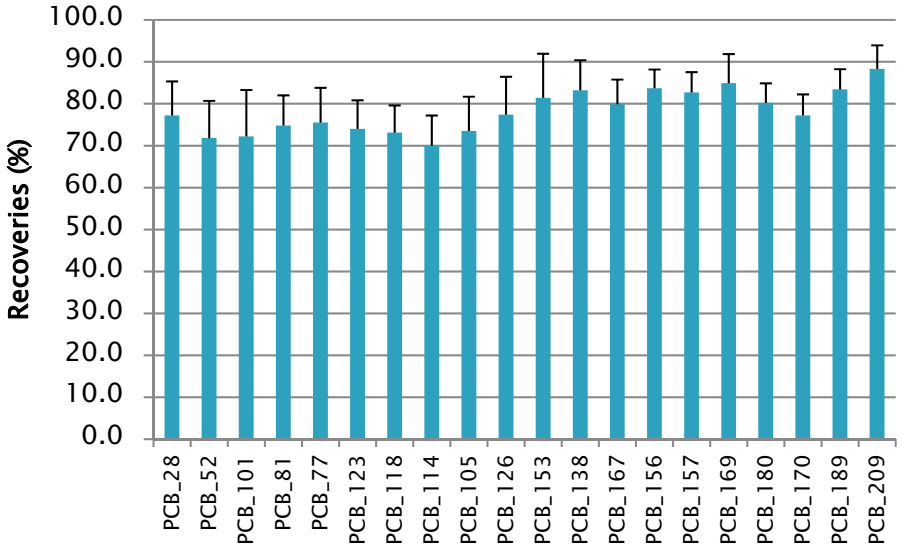
GC vial

Toxic Reports™

DFS HRGC/HRMS

Toxic Reports™

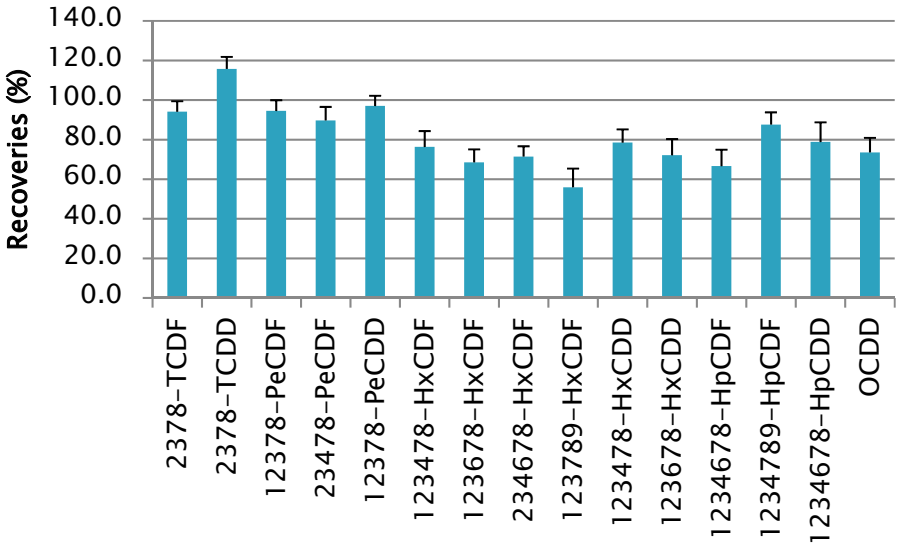
13C recoveries PCBs soil



10 g soil in toluene, n = 10

Toxic Reports™

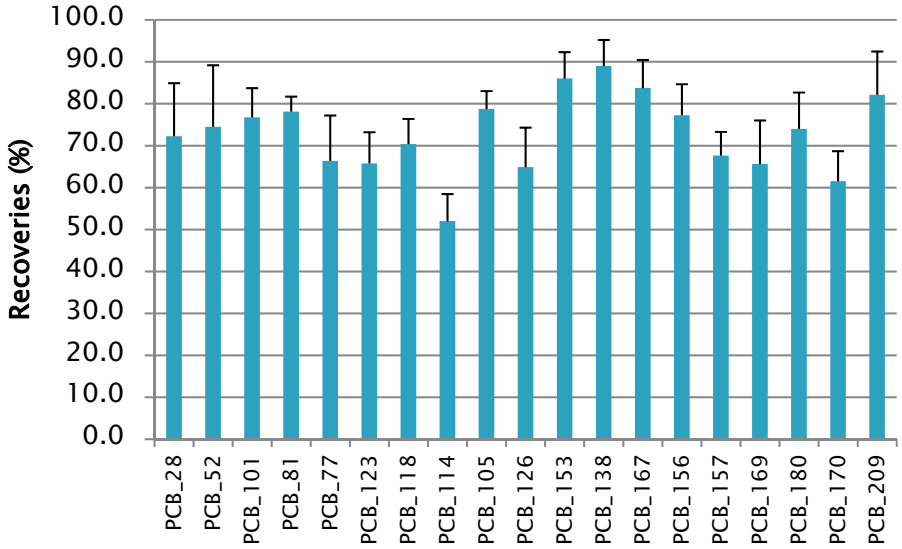
13C recoveries PCDD/Fs soil



10 g soil in toluene, n = 10

Toxic Reports™

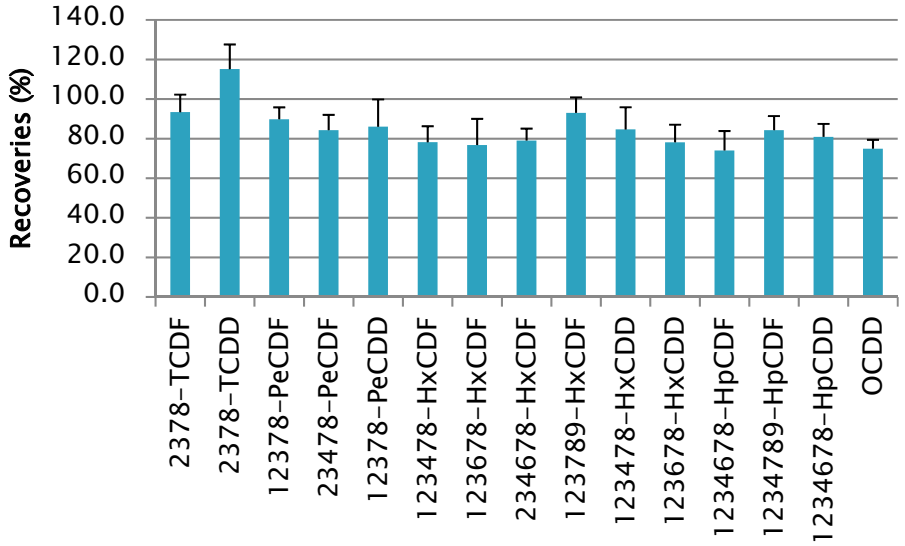
13C recoveries PCBs salmon



10 g salmon in toluene, n = 12

Toxic Reports™

13C recoveries PCDD/Fs salmon



10 g salmon in toluene, n = 12

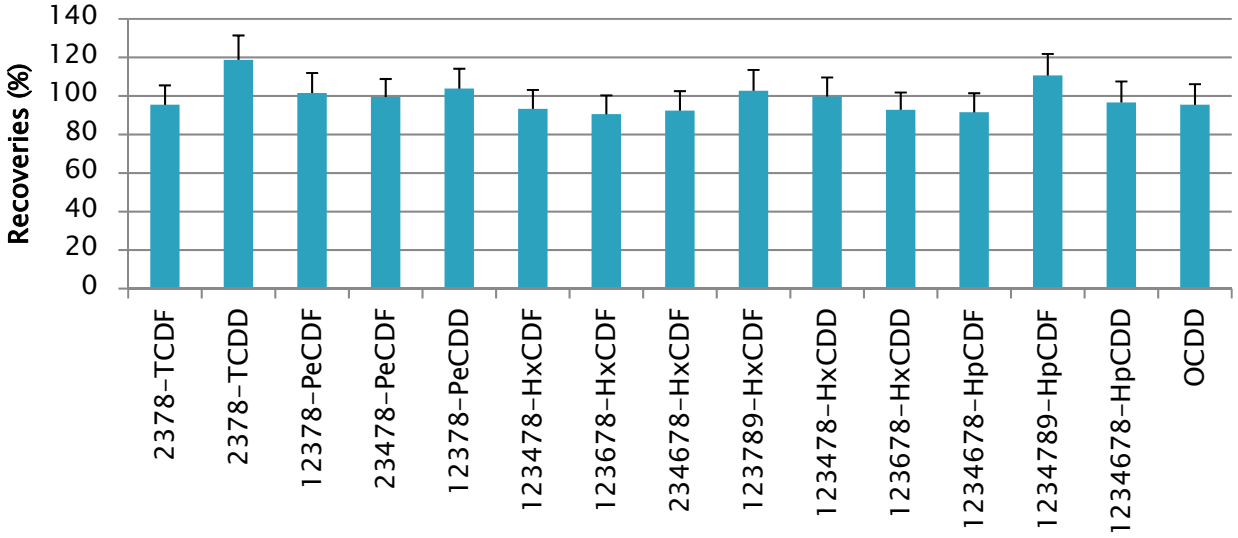
Toxic Reports™

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)

Toxic Reports™

13C recoveries PCDD/Fs fish



10 g fish in toluene, n = 12

Toxic Reports™

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)

Toxic Reports™

Column Kits with various fat removal capacities for samples in hexane

		Stage 1 (volumes in mLs)				Stage 2 (volume in mLs)			
						PCBs/PBDEs	PCDD/Fs		Total
	Fat Removal	Hexane	Hexane	Hexane		DCM	Toluene		time
Column kits	Capacity	Conditioning	Sample loading	Elute silica		Alumina-carbon	Reverse carbon		(min)
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

Toxic Reports™

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

Toxic Reports™

Conclusions (3)

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

Toxic Reports™

Questions

Contact us at:
raddink@fms-inc.com (Ruud Addink)
thall@fms-inc.com (Tom Hall)
nkaurin@fms-inc.com (Nem Kaurin)