

Optimized Workflow of POPs Analysis in Environmental and Food Matrices Using Semi-Automated Cleanup and GC-MS/MS

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Overview

- Introduction
- Automated Hyphenated System Configurations for different Matrices and Extractions
- Semi Automated Systems
- GC/MS/MS Data



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: 30 to 45 Minutes for 6 Samples
- Cleaner Background Interferences: Closed Loop System
- Quality Results: Certified Pre-packaged Columns
- Green Technology: Lower solvent and power use
- QA/QC & Accreditation Requirements: Easier to Manage
- Computerized Method: Instrumentation based prep

Sample Processing Workflow

- Analysis of various matrices for PCDD/Fs and PCBs using extraction, cleanup and concentration.
- Soxhlet extraction (typically up to 16-24 h).
- Concentration step
- Preparative multi-column chromatography involving various solvents and steps.
- Can include acid-base-neutral silica, pure acidified silica, alumina, Florisil and carbon columns. Use of H₂SO₄ acid mixed with silica; NaOH mixed with silica Neutral Silica
- Fractionation and Concentration

Automation

- Advantages of automated sample prep are:
- Reduced time:
 - Automated Pressurized Liquid Extraction (PLE) takes 60 min start-to-finish
 - Manual Soxhlet up to 24 h.
- Reduced cost: less labor involved, shorter turnover time per sample, less electricity use for PLE than Soxhlet.
- Reduced volume: less solvent used.

Automating the Workflow

- Automated Pressurized Liquid Extraction (PLE) for sample extraction is fast (60 min), efficient (120 °C, 1500 psi), green (less power), reliable (long track record).
- Users' choice of fully automated or semi automated clean up system: fast (30-45 min), low solvent usage



Automated Cleanup

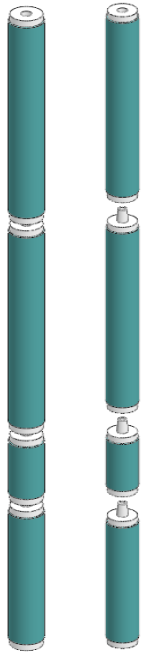
- Fully automated sample load and elution.
- Load Sample Extracts in hexane directly onto the system with no Manual Pretreatment
- Easy to perform QC sample simultaneously with a Real sample.
 - 2 samples per module
- Different column configuration: silica-carbon-alumina.
- Uses no DCM, only Hexane and Toluene.
- Total Clean Up time 30-45 min.
- Low volumes

Columns

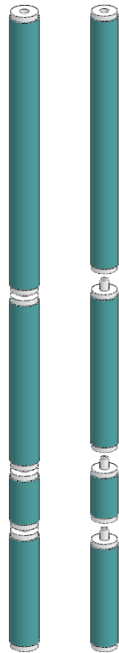
- Silica - PCB/PBDE-free Acid, Base and Neutral silica gel column (mini, classical, classical plus, high capacity, XL).
- Alumina – PCB/PBDE-free basic alumina column.
- Carbon – PCB/PBDE-free carbon/celite column.
- Packed in disposable Teflon tubes; individually sealed in Mylar packaging; production in clean room environment.

Column Kits

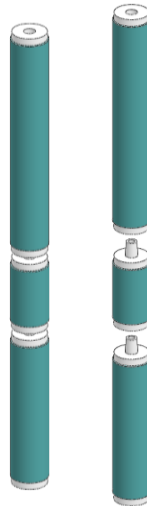
Classical
Kit



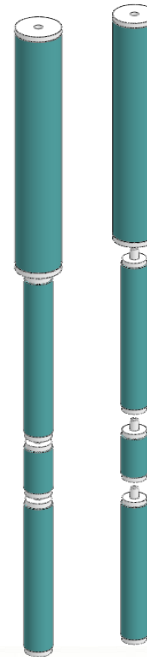
Classical Plus
Kit



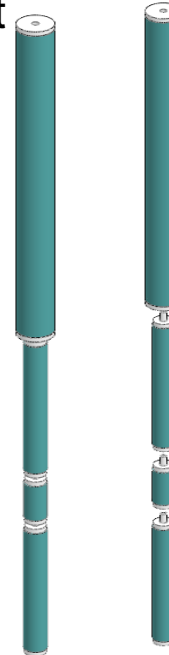
Mini Kit



High-Capacity
Kit



XL Capacity
Kit



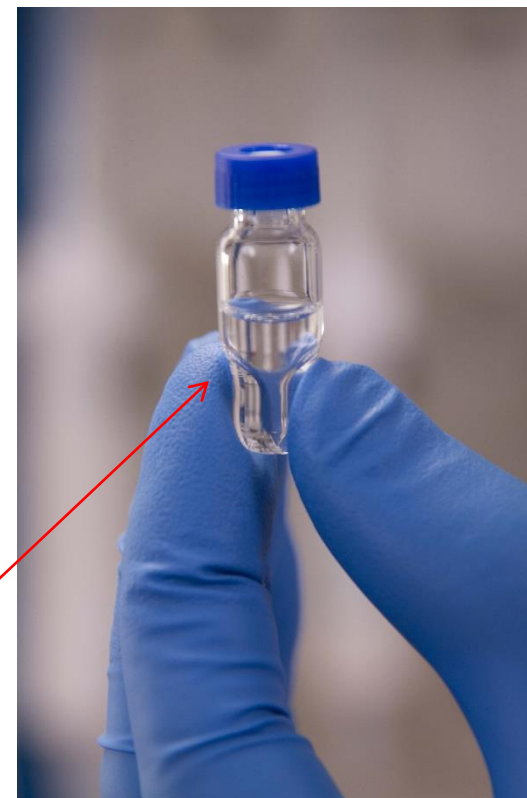
SuperVap Concentrator



SuperVap Evaporation

- System pre-heated to 45-60 °C.
- Samples evaporated at stable T under 8 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.

Glass Evaporation tube



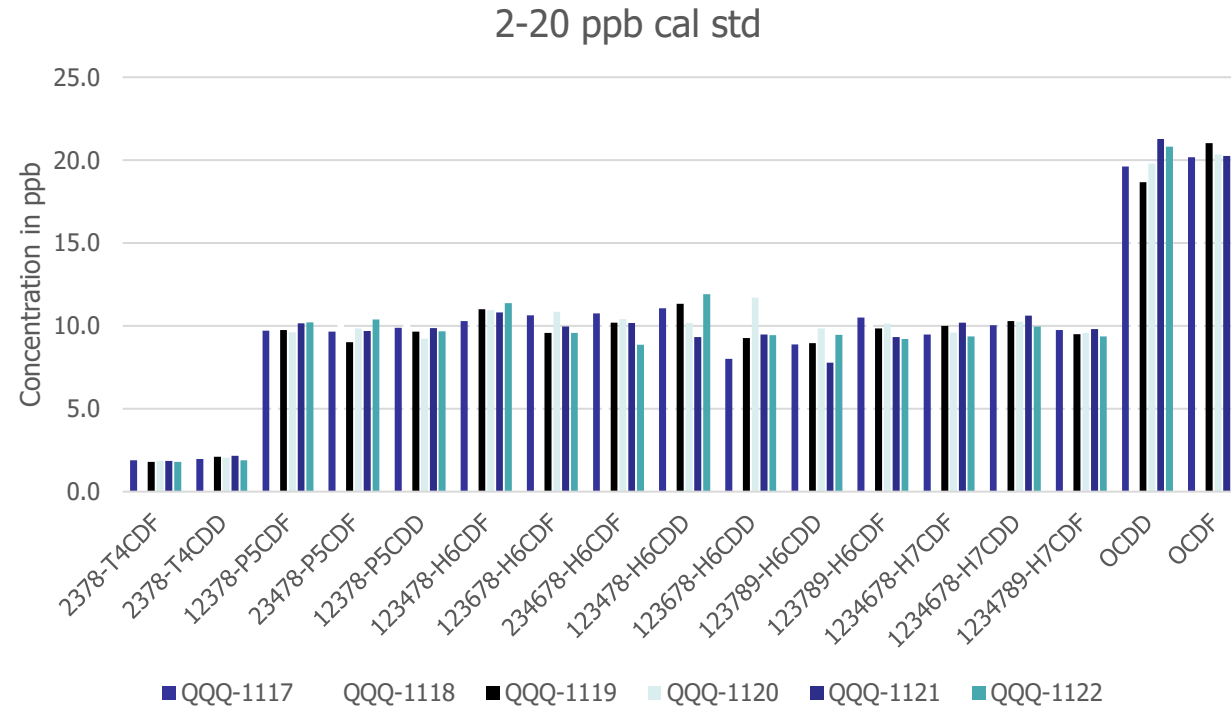
GC vial

Using the GC-MS/MS

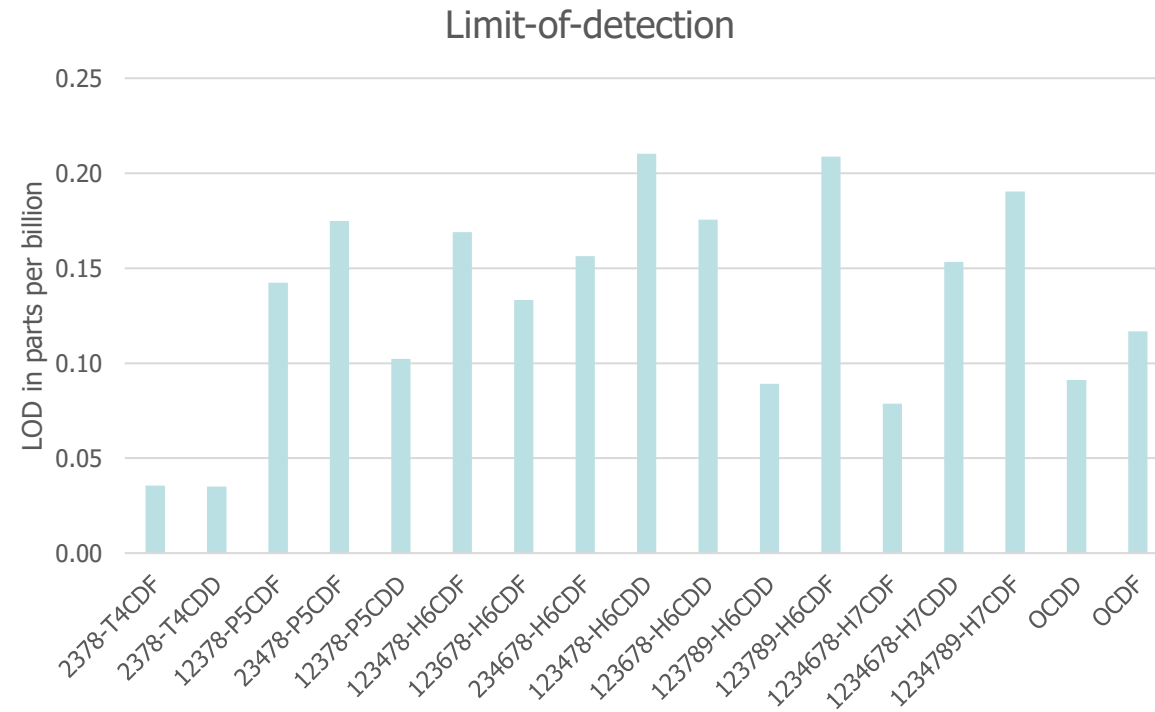


Agilent 7010

GC-MS/MS Precision



GC-MS/MS Limit of Detection

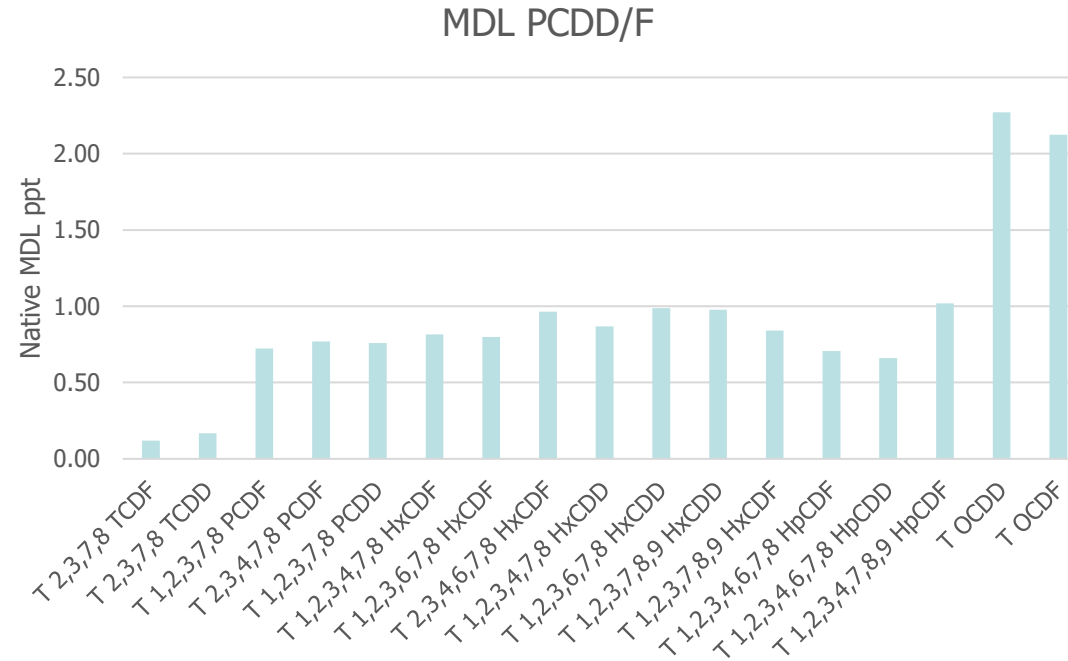


Method Validation (1)

						Acceptable
natives in pg	IDC-1	IDC-2	IDC-3	IDC-4	spike	window
T 2,3,7,8 TCDF	367.2	388.9	385.6	373.8	400.0	280-520
T 2,3,7,8 TCDD	372.0	389.7	381.4	378.8	400.0	280-520
T 1,2,3,7,8 PCDF	1898.2	1997.0	1903.7	1934.1	2000.0	1400-2600
T 2,3,4,7,8 PCDF	1838.9	1937.6	1894.3	1888.8	2000.0	1400-2600
T 1,2,3,7,8 PCDD	1926.0	2000.2	2030.7	1965.0	2000.0	1400-2600
T 1,2,3,4,7,8 HxCDF	1983.3	2037.2	1996.9	2074.7	2000.0	1400-2600
T 1,2,3,6,7,8 HxCDF	1976.6	2034.5	2045.5	1940.1	2000.0	1400-2600
T 2,3,4,6,7,8 HxCDF	1992.6	2033.8	2013.5	2039.3	2000.0	1400-2600
T 1,2,3,4,7,8 HxCDD	2124.4	2009.0	1996.5	1960.9	2000.0	1400-2600
T 1,2,3,6,7,8 HxCDD	1890.6	2153.7	2139.1	2122.3	2000.0	1400-2600
T 1,2,3,7,8,9 HxCDD	2118.9	2331.2	2231.8	2154.1	2000.0	1400-2600
T 1,2,3,7,8,9 HxCDF	1943.1	2035.8	1989.1	2008.9	2000.0	1400-2600
T 1,2,3,4,6,7,8 HpCDF	1883.6	1986.2	1911.5	1871.0	2000.0	1400-2600
T 1,2,3,4,6,7,8 HpCDD	1935.7	1981.0	1978.0	1958.7	2000.0	1400-2600
T 1,2,3,4,7,8,9 HpCDF	1880.2	1945.3	1942.1	1902.9	2000.0	1400-2600
T OCDD	3893.5	4057.9	4132.2	4043.0	4000.0	2800-5200
T OCDF	4026.2	4175.0	4156.9	4080.2	4000.0	2800-5200

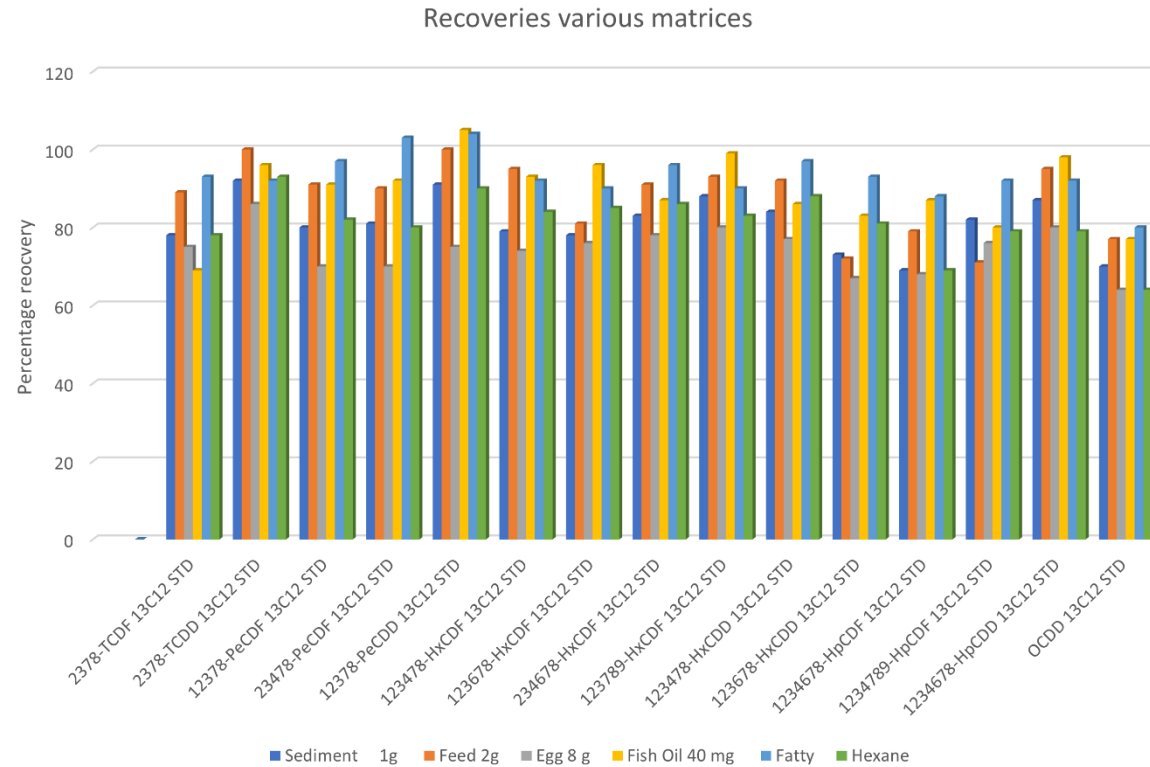
PLE + EZPrep

Method Validation (2)

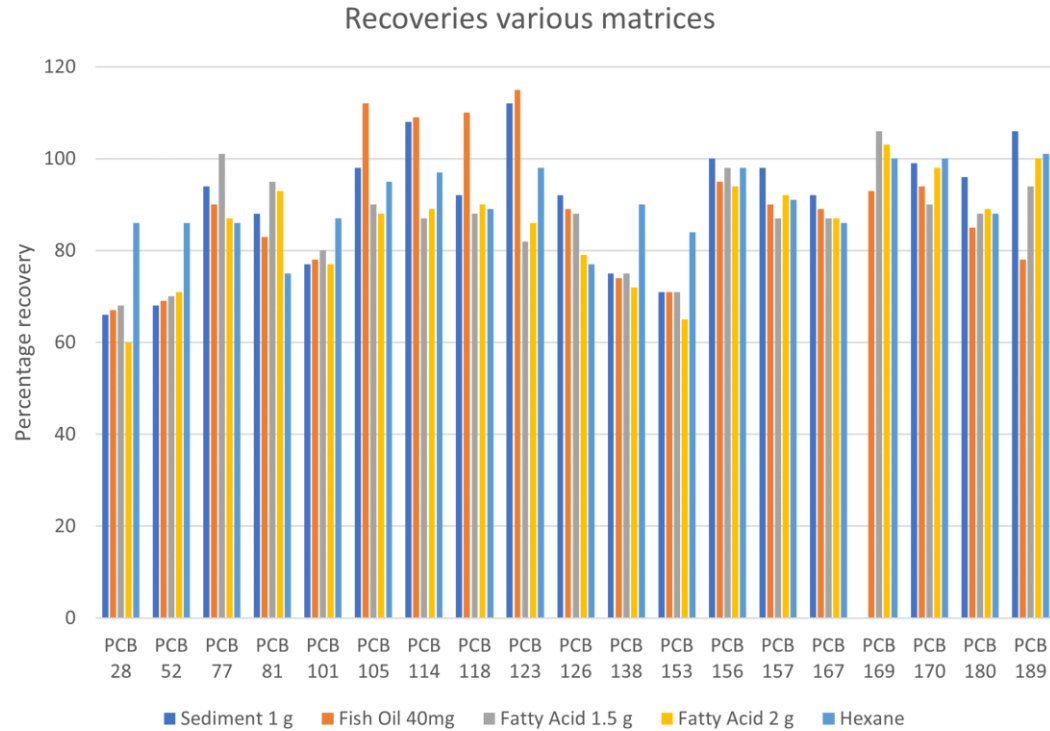


PLE + EZPrep

EP-110 13C Recoveries DD/F Matrices



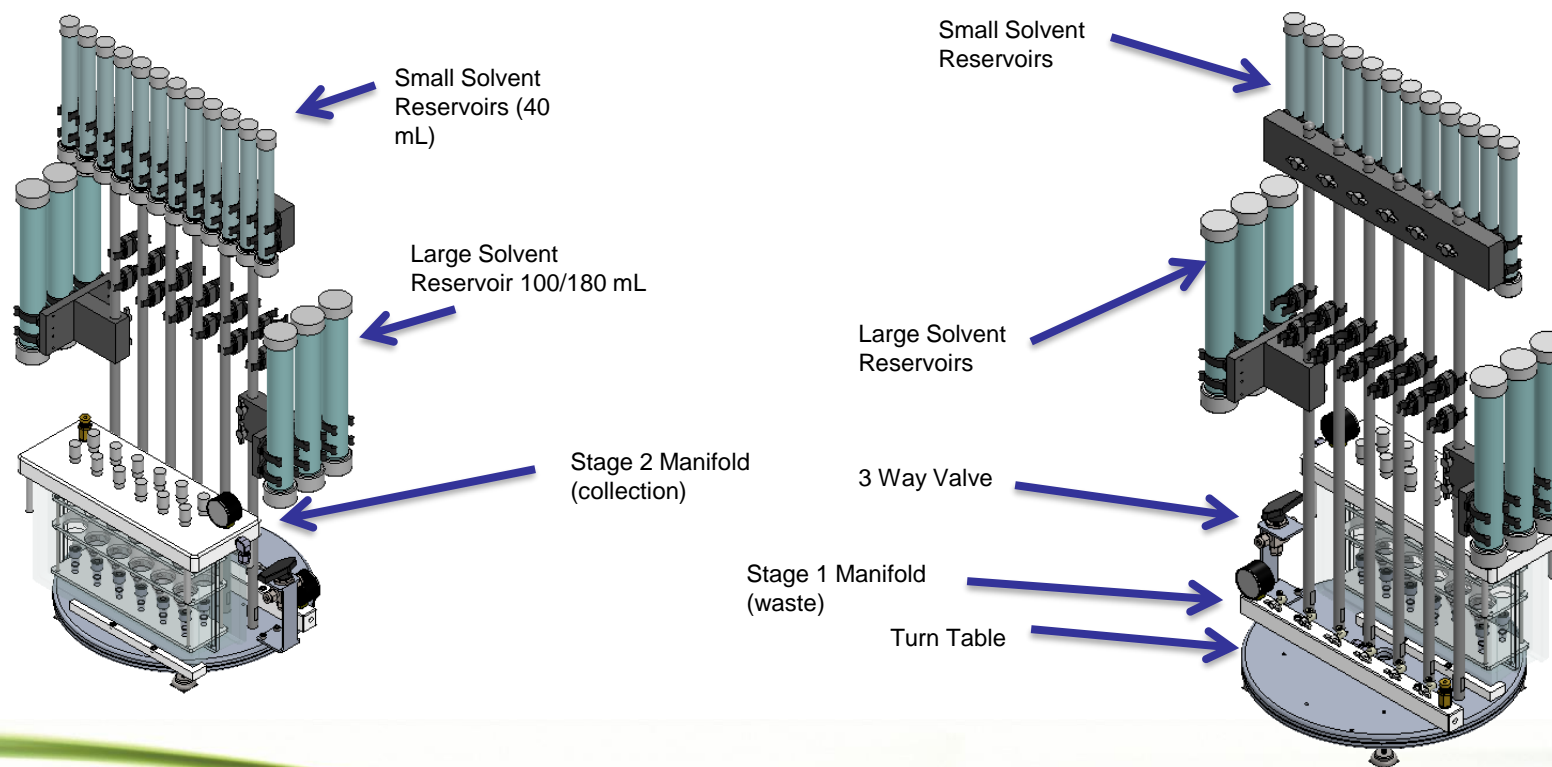
EP-110 13C PCBs Recoveries Matrices



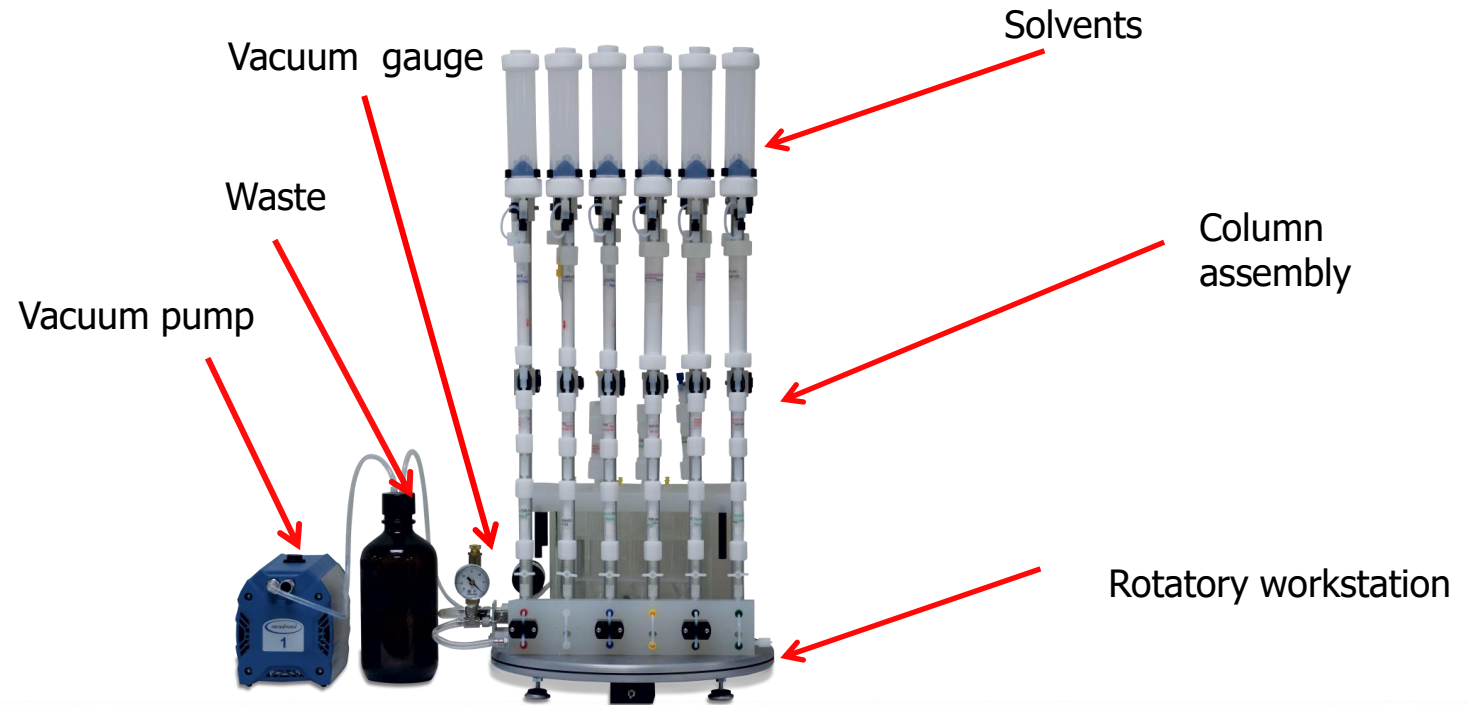
Semi-Automated Sample Cleanup

- Simple to run, no computerized instrumentation
- Fast: 30 - 45 min
- Closed loop system to give a clean background, low level detection
- Use certified pre-packaged columns
- Green technology, only vacuum pump uses power
- Economical column kits, choice of low fat and high fat column kits
- No electronics or mechanical equipment to fail

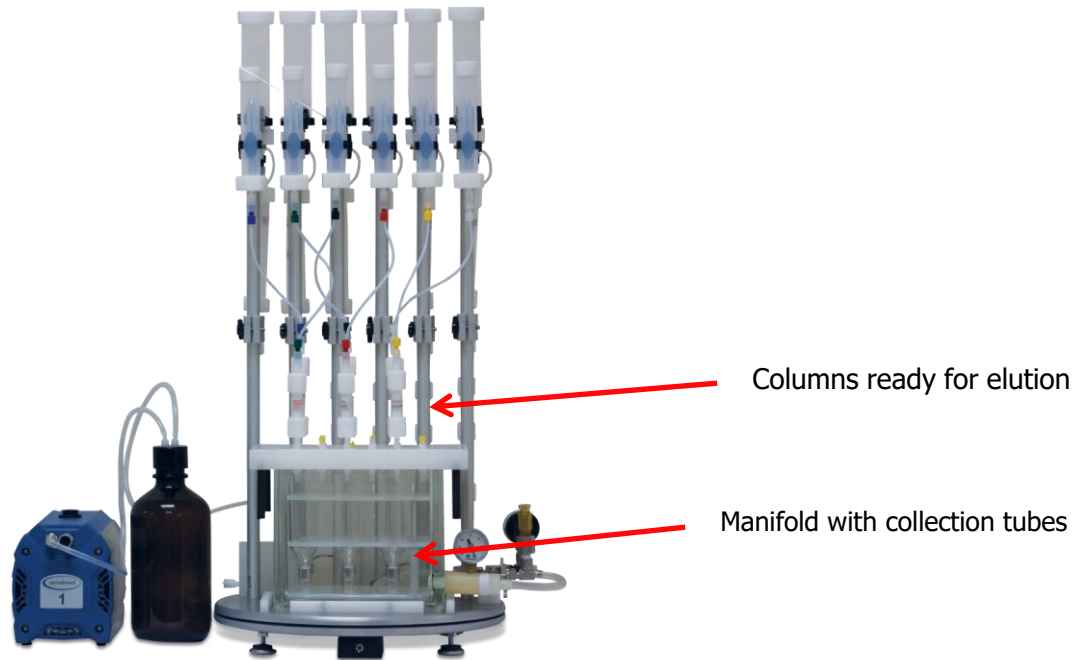
Characteristics of Semi-Automated System (EZPrep)



Stage 1: to waste



Stage 2: collect



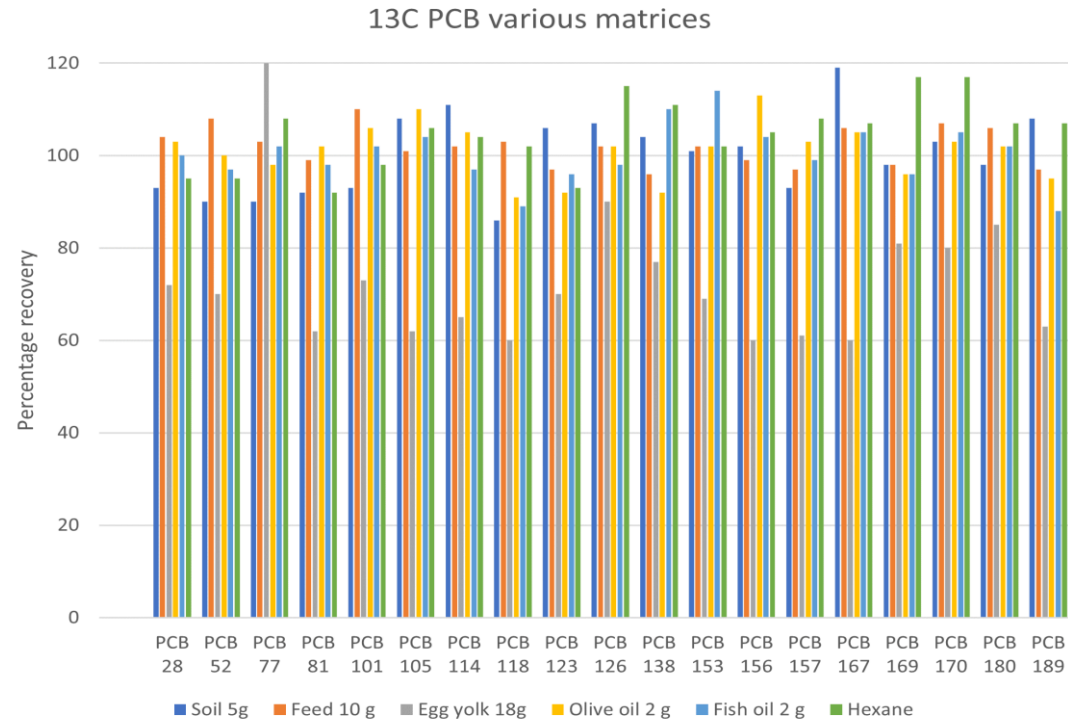
Attributes

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

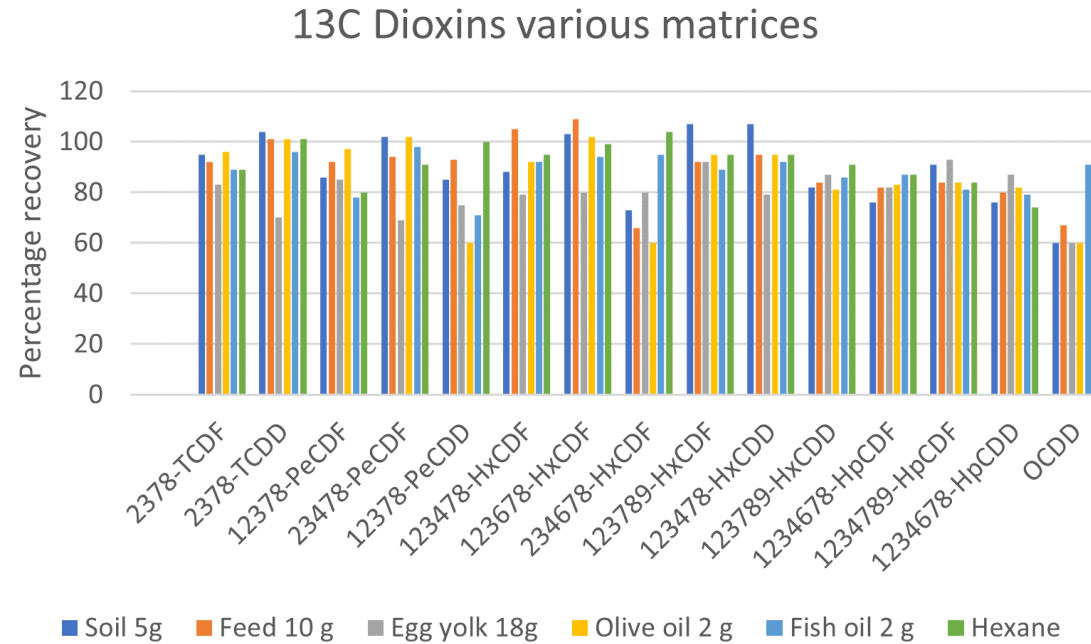
Procedure

- **Order of column assembly: Acid Silica-Carbon-Alumina**
- **Conditioning all columns with hexane (waste)**
- **Load sample**
- **Elute columns with hexane and transfer all target compounds to carbon and alumina (waste)**
- **Discard silica columns and remove carbon and alumina columns**
- **Elute carbon and alumina individually with toluene (reverse)**
- **Collect carbon fraction (PCDD/F and co-planary PCBs) and alumina fraction (mono- and di-ortho PCBs)**

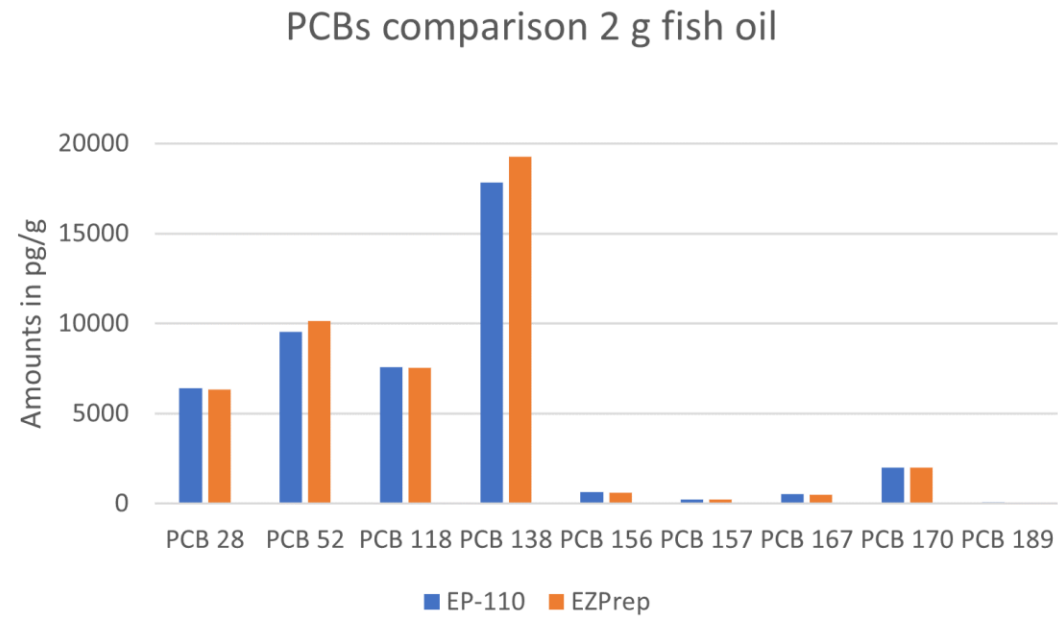
^{13}C PCBs Recoveries EZPrep (%)



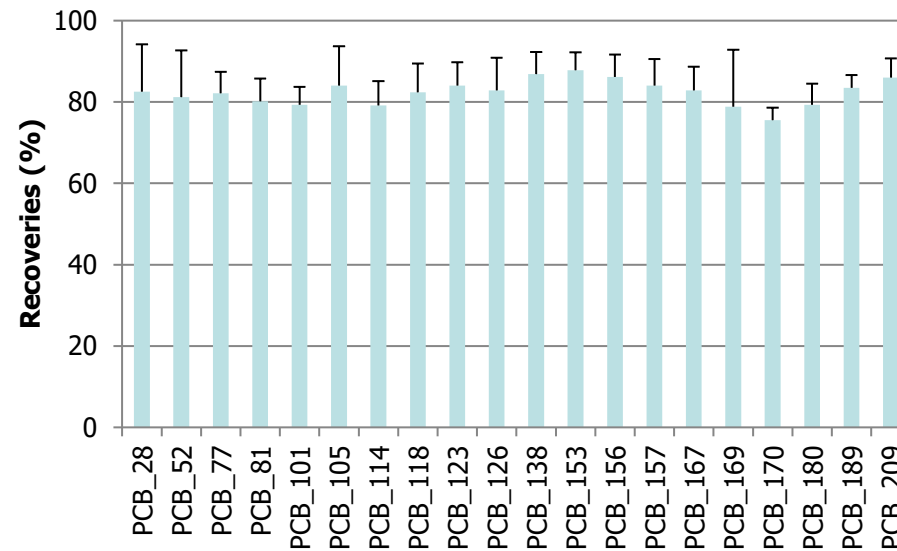
^{13}C PCDD/F Recoveries EZPrep (%)



Comparison of Native Data with Automated System



13C PCBs recoveries in soil



10 g soil in
toluene, n=6

Conclusions (1)

- Combination of PLE, SuperVap and EP-110/EZPrep give flexibility to (semi-) automate extraction, concentration and cleanup for a wide variety of compounds.
- **PLE** (Pressurized Liquid Extraction)
 - Reduced time:
 - Automated Pressurized Liquid Extraction (PLE) takes 60 min start-to-finish
 - Manual Soxhlet up to 24 h.
 - Up to 8 samples in Parallel
 - Reduced cost: less labor involved, shorter turnover time per sample, less electricity use for PLE than Soxhlet.
 - Reduced volume: less solvent used.
- **EP110**
 - Uses No DCM
 - Low solvent use 100-250 mL
 - Total time from sample till data between 3-4.5 h
 - Clean up step time between 30 and 45 min
 - Modular 2 to 8 sample configurations in parallel
- **PLE and EP-110 can be configured in one system**

Conclusions (2)

- **Ezprep Semi-Automated Sample Cleanup**
 - Is a low solvent and fastest clean up system for Dioxins and PCBs (30 - 45 min)
- 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, PCB and PBDEs comparable to automated systems
- Use of certified pre-packaged columns guarantees low native background

Agilent 7010 MS/MS Dioxin Analysis

- **Provides a complete Dioxin/PCB workflow with FMS Sample Prep Systems**
- **Easy to Use and Implement**
- **Cost Effective Alternative to High-Res Mass Spec**
 - Lower instrumental purchase cost
 - Lower cost of real estate
 - Lower operational cost from lower training requirements and lower maintenance costs

Come see us at booth G-2

Questions?

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