Simple, Quick Analysis of Dioxins, PCBs & PBDEs in Vegetable Oils and Fats

Fluid Management Systems

Billerica MA

Introduction

- Stockholm Convention on Persistent Organics Pollutants 2004.

- Compounds of interest: polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs) and poly brominated diphenyl ethers (PBDEs).

- Known toxicity.

- Strict environmental regulations in force in most countries.

- US EPA and EU methods and regulations; other countries have their own.

- 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 (sometimes orders of magnitude higher than analytes)
- Pico-/femto-gram analyses require ultra-pure extract and excellent instrument sensitivity

Advantages of Manual Sample Prep

- ➢ Flexibility
- ➢ Low initial Capital equipment Cost
- ➢ Easier to implement
- ➢ No electronics or mechanical failure No down time due to system failure
- ➢ No service contract cost

Disadvantages of Manual Sample Prep

- ➢ Human Error
- ➢ Less Efficiency
- ➢ Increased workload
- ➢ Inconsistency
- ➢ Risk of Cross contamination
- ➢ Human Exposure to Chemical
- ➢ Lack of Traceability
- ➢ Difficult to Scale up

Automated Sample Prep

Advantages Automated Sample Prep

- Efficiency & Speed
- Accuracy & Consistency
- Repeatability & Reproducibility
- Reduction of Manual Labor
- Documentation & Traceability
- Less exposure to Hazardous
- Cleaner Background Interference
- Simpler QA/QC & Accreditation

Disadvantages Automated Sample Prep

- High Initial Cost
- Maintenance & Service contract Cost
- Technical Knowledge required
- System Limited Flexibility
- Down time due to failure
- Sample size limitation

Design of the Ideal Sample Clean-up
Combining The Best Features of Manual & Automated

FMS
Fluid Management Systems

Advantages of Manual Sample Prep

- ➤ Flexibility
- ➤ Low initial Capital equipment Cost
- ➤ Easier to implement
- ➤ No electronics or mechanical failure
  No down time due to system failure
- ➤ No service contract cost

+

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- ➤ Repeatability & Reproducibility
- ➤ Reduction of Manual Labor
- ➤ Documentation & Traceability
- ➤ Less exposure to Hazardous
- ➤ Low Background Interferences
- ➤ Simpler QA/QC & Accreditation

Features:

➢ Rapid Turn Around Time: 45 to 60 Minutes for 6 Samples

➢ Simple to operate   Resemble Manual Sample Clean-up

➢ Cleaner Background Interferences: Closed Loop System

➢ Quality Results: Certified Pre-packaged Columns

➢ Green Technology: Low solvent and power use

➢ QA/QC & Accreditation Requirements: Easy to manage

➢ Reliable   Little electronic or Electro-Mechanical to fail

➢ Affordable Automation: Low cost

Combine both features:

- Fast: 30-40 min
- Simple to run, touch screen programming
- Closed loop system with clean background, low detection limits
- Use certified pre-packaged columns
- Green technology, uses multi-pump to do cleanup
- Low solvent volumes
- Economical column kits, five choices of low fat to high fat column kits
- Low capital equipment cost
- Little electronics or mechanical equipment to fail
- Little cleaning and no cross-contamination
- Minimal downtime
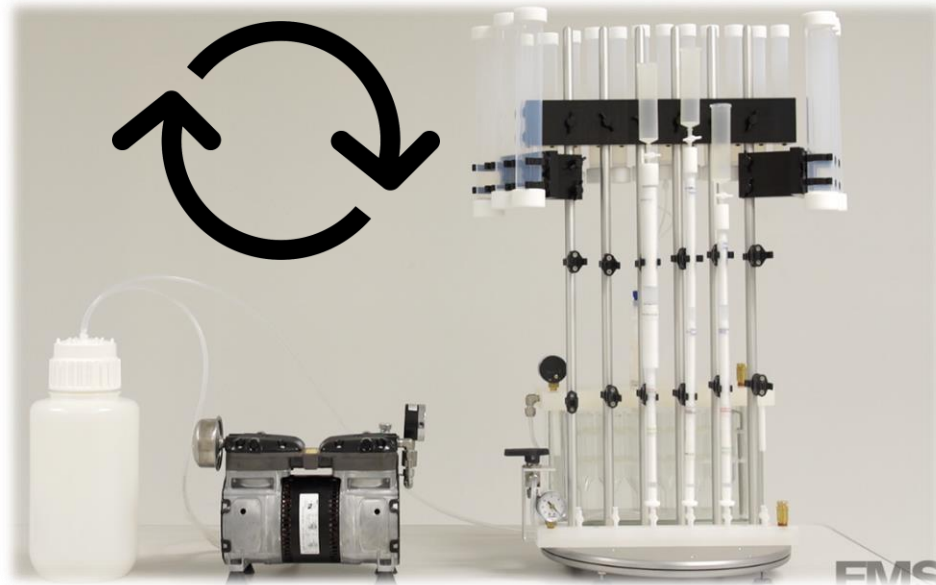
Cycle Time EzPrep
Proccessing 6 Samples

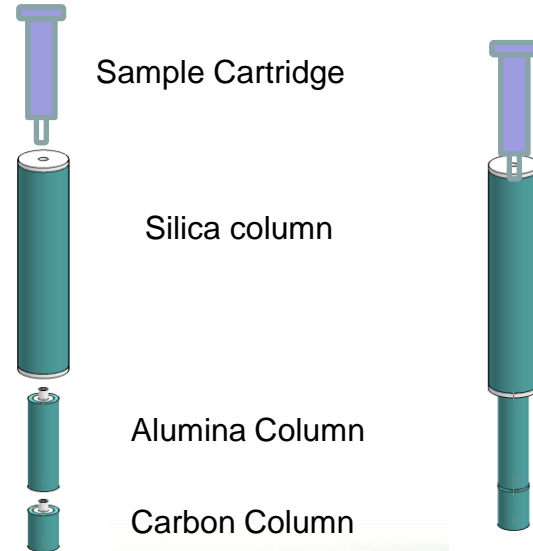|	Automated	Manual
• **Set up time:**		
• Assemble & Install acidic silica-carbon-alumina columns on column rack		
• Place samples cartridges on top of acidic silica columns , Add Solvents to solvent reserve		- 20 min
• **Program 1:**		
elute hexane through all three columns ; apply nitrogen to push hexane onto the columns to waste	- 20 min	
• Disassemble the column set, install carbon and alumina columns on top of manifold		-10 min
• **Program 2:**		
• Dispense Toluene through alumina & Carbon and collect PCBs & Dioxins	-10 min	

Total Cycle Time 60 min

FMS
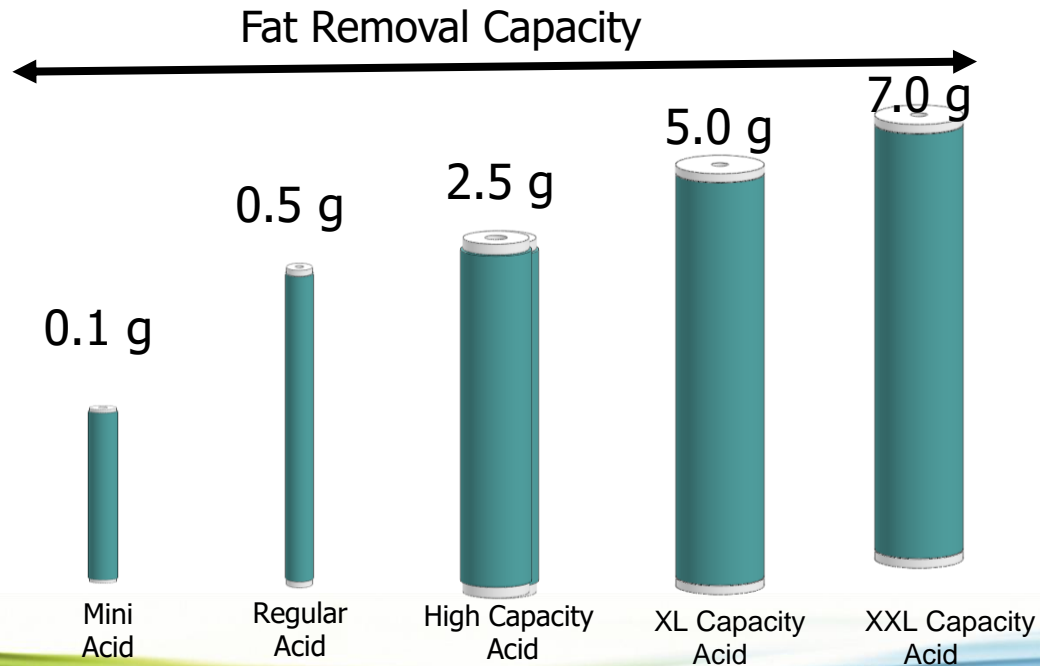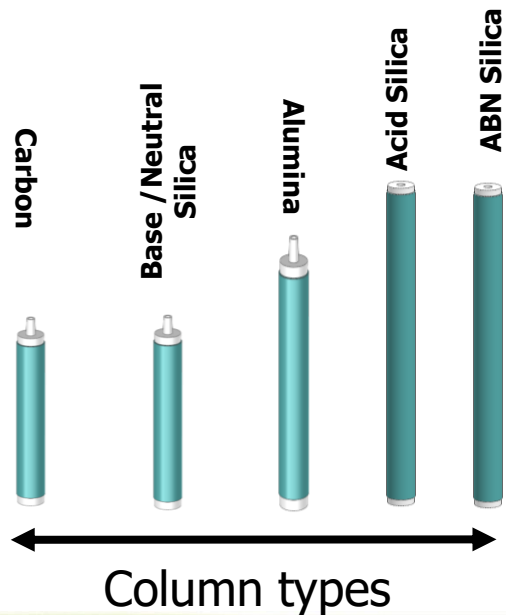Fluid Management Systems

FMS Certified Snap-In columns:

- ➤ **Easy to connect**
- ➤ **NO fittings**
- ➤ **Designed for easier flow**
- ➤ **Different size for different fat capacity from 0.2 up to 7 gm of Fat**

Disassembled   **Assembled**

Sample Cartridge

Silica column

Alumina Column

Carbon Column

Columns/ Fat Removal Capacity

Fat Removal Capacity

Carbon | Base / Neutral Silica | Alumina | Acid Silica | ABN Silica

Column types

0.1 g — Mini Acid

0.5 g — Regular Acid

2.5 g — High Capacity Acid

5.0 g — XL Capacity Acid

7.0 g — XXL Capacity Acid

EzPrep/+

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

Automated EzPrep/+ Sample Clean-up

Benefits:

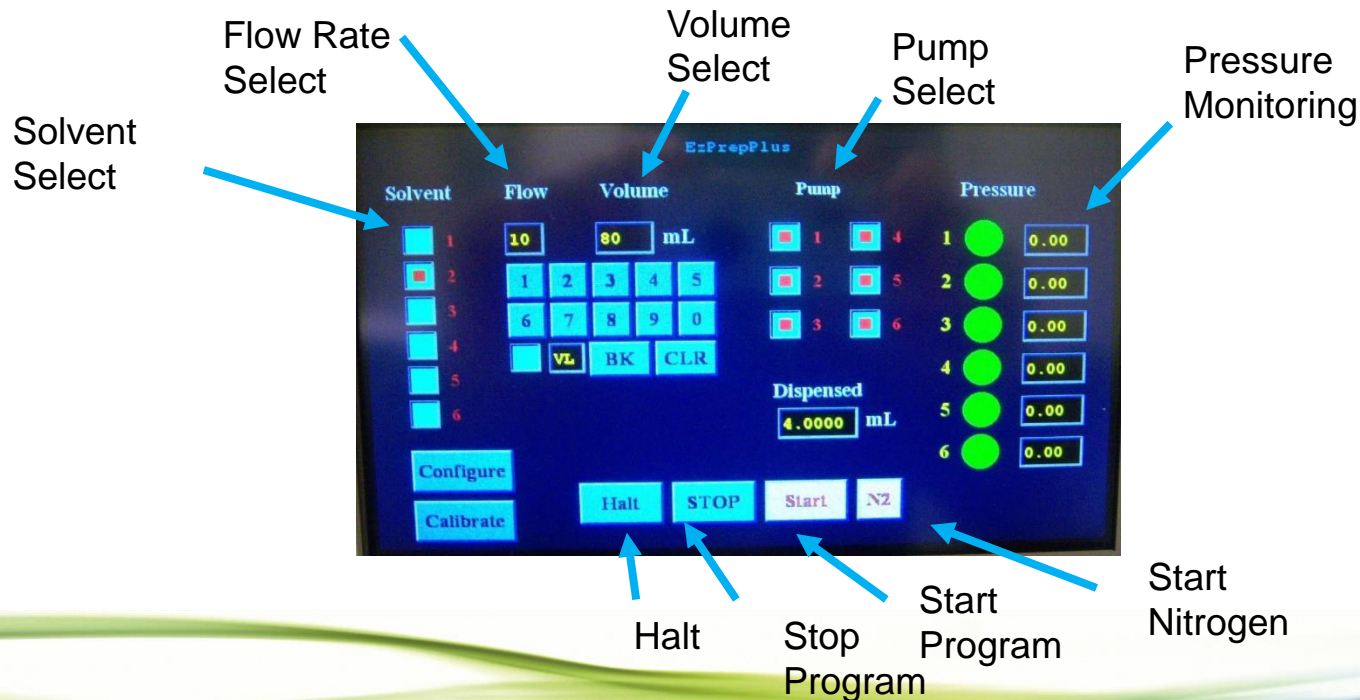|	
➢ Rapid Turn Around Time:	30 to 45 Minutes for 6 Samples
➢ Simple Programming	Just Select Solvent, Set Flow & Volume
➢ High Throughput:	Process up to 48 samples per day
➢ Cleaner Background Interferences:	Closed Loop System
➢ Quality Results:	Certified Pre-packaged Columns
➢ Green Technology:	Low solvent and power use
➢ QA/QC & Accreditation Requirements:	Easy to manage
➢ Reliable	Minimal Electronics & Electro-Mechanical

Attributes EZPrep/+

- ➤ **Closed loop system, eliminates background contaminants & exposure to chemicals**

- ➤ **Optimized for solvent reduction while obtaining highest possible recoveries**

- ➤ **Certified disposable Columns with guarantee 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**
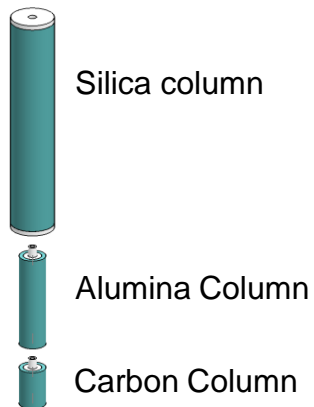
Automated EZprep/+

Control Panel

Sample Cartridge

Silica column

Solvents

Carbon Column

Alumina Column

6 Parallel pumps

EzPrep /+ Control Panel
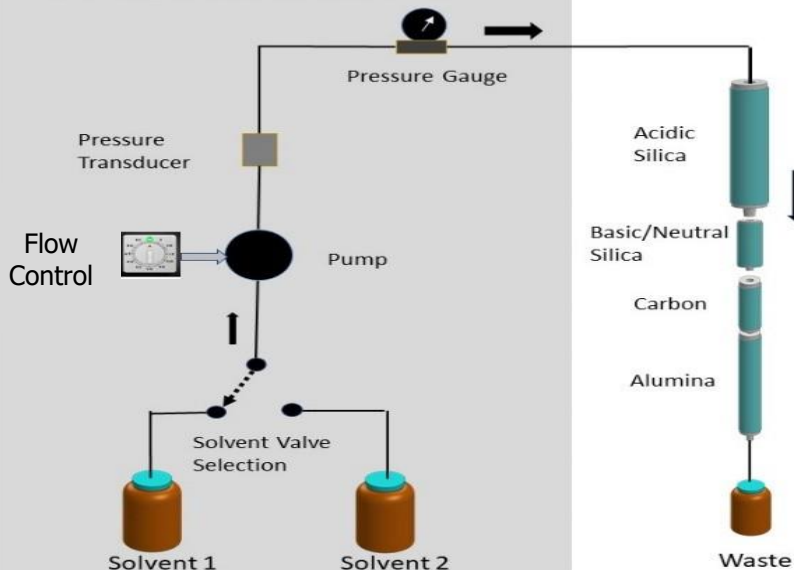
EzPrep – Stage 1

Program1:
- **Load Samples**
- **Elute Dioxins & PCBs**

Flow ml/min	Volume ml	Solvent	Description
10	160	1	**Load sample**
			Elute Dioxins & PCBs

How It Works
Elute Dioxins & PCBs
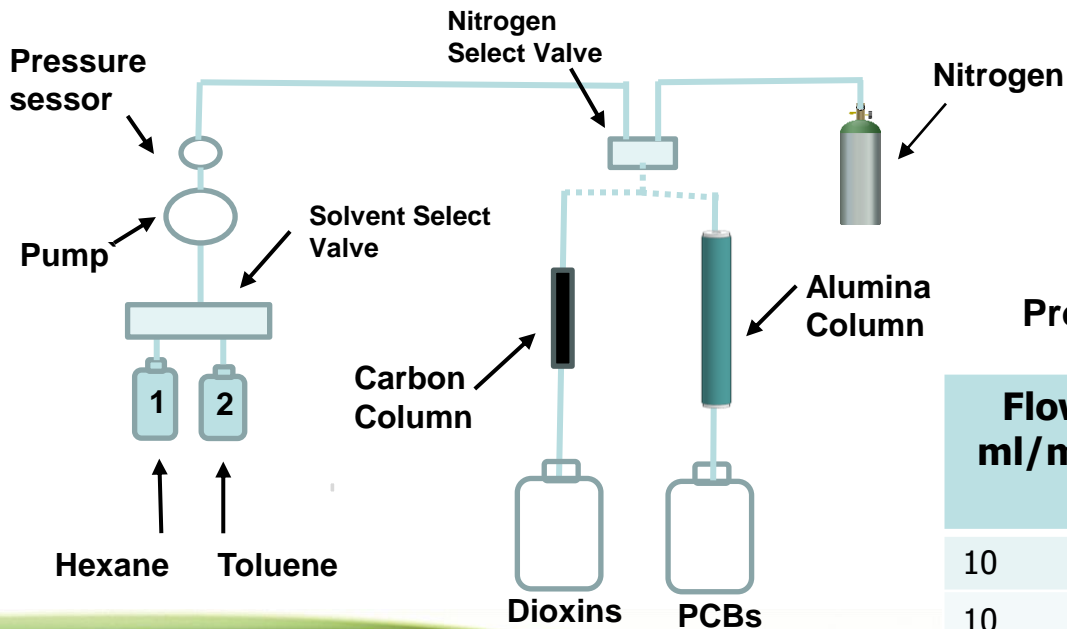
Program2: Dioxins & PCBs, Fractionation

Flow ml/min	Volume ml	Solvent	Description
10	40	2	**Collect Dioxins**
10	40	2	**Collect PCBs**

Cycle Time EzPrep/+

- **Set up time:**
  Automated   Manual
- Assemble & Install acidic silica-carbon-alumina columns on column rack
- Place samples cartridges on top of acidic silica columns   - 10 min

- **Program 1:**
  elute hexane through all three columns ; apply nitrogen to push hexane onto the columns   - 16 min
  to waste
- Disassemble the column set, install carbon and alumina columns on top of manifold   -10 min

- **Program 2:**
- Dispense Toluene through alumina & Carbon and collect PCBs & Dioxins   -10 min

Total Cycle Time 46 min

Combine best features (EZPrep Family)

FMS Fluid Management Systems

Features	EzPrep	EzPrep/+
System run time for 6 samples	45 ~60 min	30 ~ 40 min
Fat Removal Capacity	.1 ~ 5g	.1 ~7g
Programmability	Minimal	Fully programmable
Pumping method	Vacuum	Pressurized
Use of certified pre-pack column	yes	yes
Use of electronics, electromechanical valve	No	Minimal
Labor required time to run 6 samples Cross contamination	30~60 min No Tubing	20 ~ 30 min No Tubing

Comparison of Manual, Automated vs EzPrep Family

| Task	Manual Sample Prep	Automated Sample Prep	EzPrep Semi-Automated	EzPrep/+ Automated
Labor Time	Hours	1 Hour	1 Hour (up to 2.5g fat) 2 Hour (2.5 to 5.0 g fat)	Less than 1 Hour
Accreditation	Slow	Fast	Fast	Fast
Accuracy & Precision	Varies	Excellent	Excellent	Excellent
Matrix	Dependent	Many	Many	Many
Instrument Maintenance	None	Required	Minimal	Minimal
Instrument Down Time	None	Some Times	none	Minimal
Fat Removal Capacity gram	Minimal	0.1 ~ 7.0 Gram	0.1 to 5.0 gram	0.1 to 7.0 g
Human Exposure	High	Minimal	Minimal	Minimal
Cost	5 x	50 x	10 x	25x
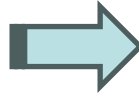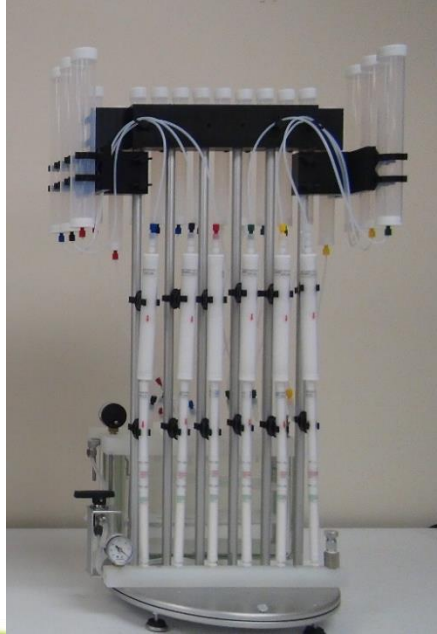
SuperVap Concentration/Evaporation

- System pre-heated to 50 ºC.

- Samples evaporated at stable T under 8 psi nitrogen (sensor).

- 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 tempe
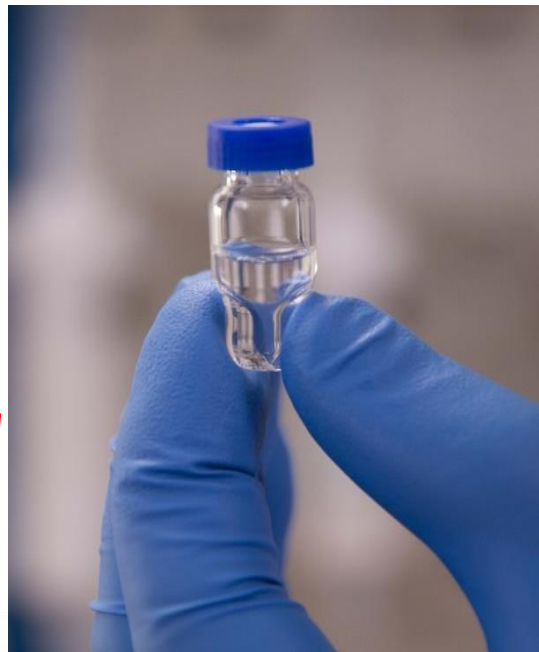
Direct-to-Vial

GC vial

Direct to GC/MS or Triple Quad

Native PCDD/F IDC
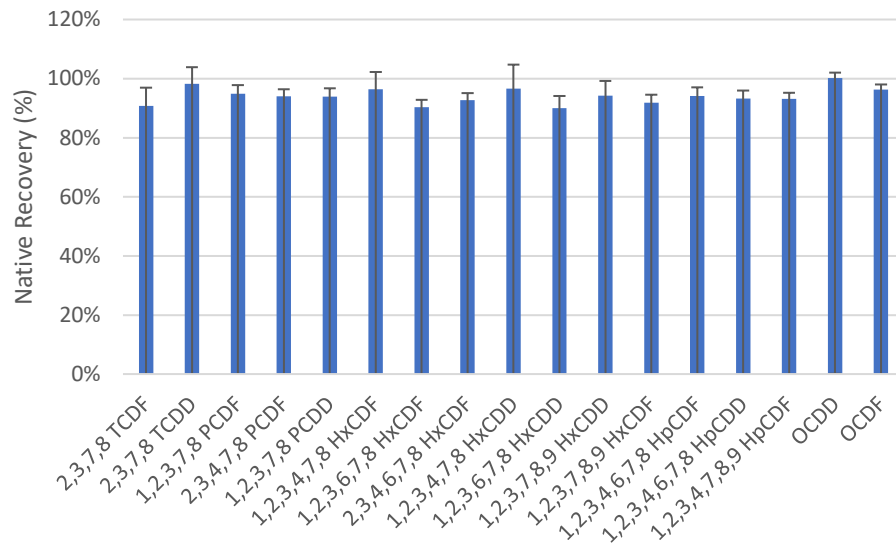
PLE-EZP-conc,
400-4000 pg,
n=6

Native PCB MDL
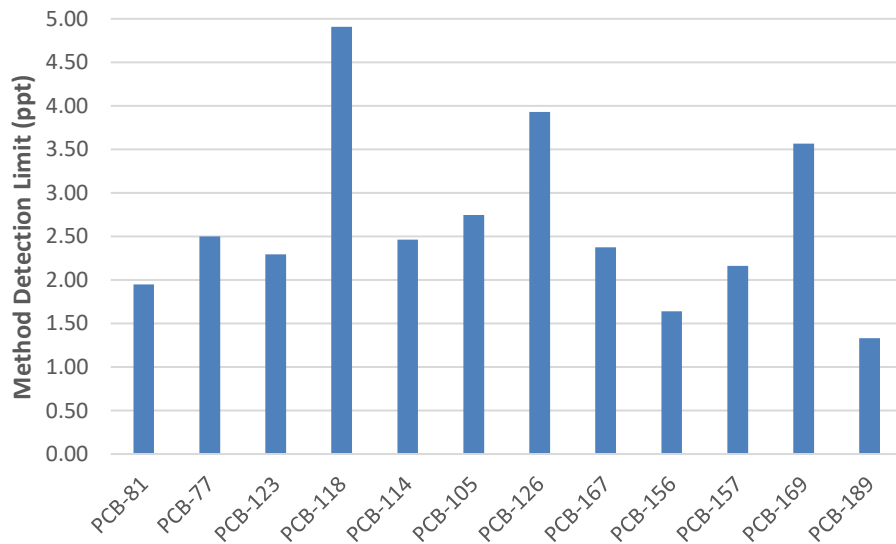
MDL, PLE-EZP-conc, 10 ppt spike, n=7
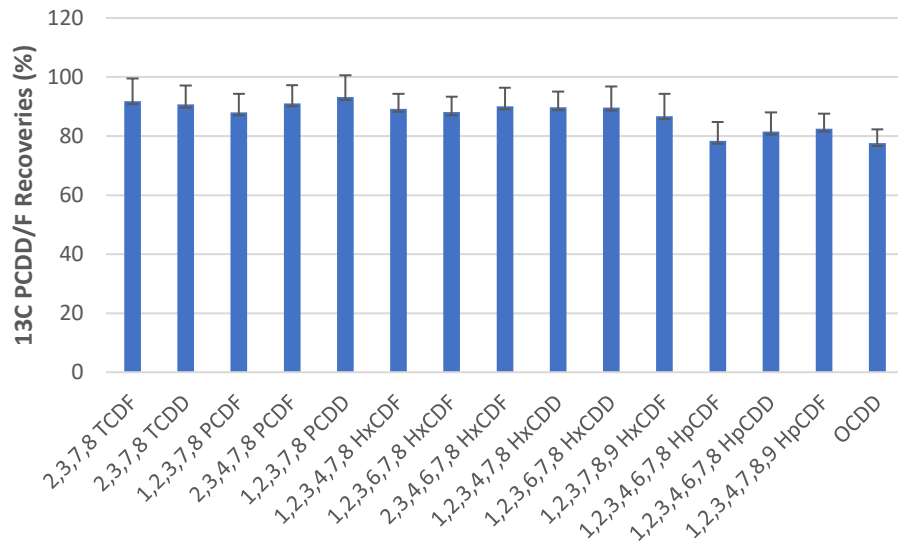
PLE-EZP-conc, Ottawa Sand matrix, n=6

Native PCBs in oil

Natives in pg	Cod Oil		Pumpkin oil		Corn oil	
	Channel-1	Channel-2	Channel-3	Channel-4	Channel-5	Channel-6
PCB-81	0.0	0.0	0.0	0.0	0.0	0.0
PCB-77	0.0	0.0	0.0	0.0	0.0	2.0
PCB-123	787.0	854.0	182.0	196.0	26.0	19.0
PCB-118	5858.0	5451.0	150.0	178.0	17.0	13.0
PCB-114	161.0	102.0	0.0	0.0	0.0	0.0
PCB-105	2027.0	1939.0	66.0	73.0	6.0	4.0
PCB-126	7.0	5.0	8.0	0.0	2.0	5.0
PCB-167	3579.0	3409.0	27.0	33.0	0.0	0.0
PCB-156	1261.0	1199.0	11.0	15.0	15.0	23.0
PCB-157	259.0	244.0	38.0	76.0	24.0	9.0
PCB-169	0.0	0.0	0.0	0.0	0.0	1.0
PCB-189	0.0	0.0	0.0	0.0	0.0	0.0

EZP - conc, 2.5 g oils

Native PCDD/Fs in oils

Natives in pg	Cod Oil		Pumpkin oil		Corn oil	
	Channel-1	Channel-2	Channel-3	Channel-4	Channel-5	Channel-6
T 2,3,7,8 TCDF	3.3	0.1	0.1	0.4	0.2	0.1
T 2,3,7,8 TCDD	0.1	0.1	0.2	0.1	0.0	0.2
T 1,2,3,7,8 PCDF	0.5	1.0	0.1	0.2	0.6	1.6
T 2,3,4,7,8 PCDF	1.4	1.1	0.4	0.4	0.6	1.9
T 1,2,3,7,8 PCDD	0.7	0.1	0.4	0.2	0.7	0.8
T 1,2,3,6,7,8 HxCDF	2.1	0.2	2.2	0.6	0.2	1.8
T 1,2,3,4,7,8 HxCDF	2.0	0.2	2.1	0.6	0.2	1.7
T 2,3,4,6,7,8 HxCDF	2.0	0.7	1.5	0.7	0.2	1.8
T 1,2,3,4,7,8 HxCDD	2.3	1.2	1.0	0.4	1.2	2.6
T 1,2,3,6,7,8 HxCDD	2.2	1.2	0.9	0.4	1.1	2.4
T 1,2,3,7,8,9 HxCDD	2.2	1.2	0.9	0.2	0.9	2.4
T 1,2,3,7,8,9 HxCDF	2.1	1.1	0.6	0.2	0.2	2.2
T 1,2,3,4,7,8,9 HpCDF	1.1	0.5	0.2	0.2	0.7	1.1
T 1,2,3,4,6,7,8 HpCDF	0.9	0.2	0.5	0.2	0.3	1.6
T 1,2,3,4,6,7,8 HpCDD	0.8	0.5	0.4	0.2	0.1	1.0
T OCDF	0.4	2.4	2.0	0.4	1.0	4.2
T OCDD	1.2	0.2	0.3	0.6	0.7	0.1

EZP-conc, 2.5 g oils

^{13}C PCDD/F recoveries in oils

13C recoveries (%)	Cod Oil		Pumpkin oil		Corn oil	
	Channel-1	Channel-2	Channel-3	Channel-4	Channel-5	Channel-6
2,3,7,8 TCDF	95	87	83	91	79	98
2,3,7,8 TCDD	101	94	89	99	84	106
1,2,3,7,8 PCDF	92	84	81	93	75	92
2,3,4,7,8 PCDF	99	89	88	101	81	106
1,2,3,7,8 PCDD	97	87	87	101	80	105
1,2,3,4,7,8 HxCDF	80	72	74	92	74	89
1.2.3.6.7.8 HxCDF	99	91	90	88	86	96
2,3,4,6,7,8 HxCDF	96	85	84	91	80	89
1,2,3,4,7,8 HxCDD	85	76	74	79	70	85
1,2,3,6,7,8 HxCDD	104	95	93	110	87	95
1,2,3,7,8,9 HxCDF	96	85	84	94	82	86
1,2,3,4,6,7,8 HpCDF	82	75	71	79	74	75
1,2,3,4,6,7,8 HpCDD	83	76	75	88	76	95
1,2,3,4,7,8,9 HpCDF	82	73	73	86	76	94
OCDD	74	71	74	77	72	91

EZP-conc, 2.5 g oils

	Fish oil
	1g
BDE-28	66
BDE-47	72
BDE-99	80
BDE-100	81
BDE-153	78
BDE-154	78
BDE-183	81
BDE-209	61

Conclusions

- EzPrep family of products designed to combine the advantages of Manual & Automated Sample prep

- EzPrep family of products designed to eliminate disadvantages of Automated and Manual system

- EzPrep/+ designed for ease of use, and lowering cost by using a minimum number of electronics and Electromechanical valves

- EzPrep family of products uses certified proprietary consumables design to speed up the sample prep workflow

- EzPrep family of products process 6 sample Clean-up per hour & 48 samples per day

- Combining EzPrep family of products with PLE (pressurized Liquid Extraction) allows laboratories to perform up to 48 samples from samples to vial

Conclusions ...

➢ Closed loop system, eliminates background contaminants & exposure to chemicals

➢ Optimized for solvent reduction while obtaining highest possible recoveries

➢ Certified disposable Columns with guarantee Low contaminants background and Excellent Recoveries

➢ Multi pump Solvent Delivery system brings convenient automated solvent selection & dispense with controllable flow & volume

➢ Little washing needed

➢ No cross-contamination

Questions?

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