

Use of Automated Column Chromatography Clean Up with Reduced Solvent Volume in POPs Analysis

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Introduction

- ▶ Stockholm Convention on Persistent Organics Pollutants 2001.
 - ▶ 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.
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Health Effects

- Endocrine disruptors.
- Immune system.
- Nervous system.
- Reproductive functions.
- Carcinogenic.
- Chloracne.
- Main exposure (> 90%) is through dietary intake: meat, dairy, fish

Sample Processing

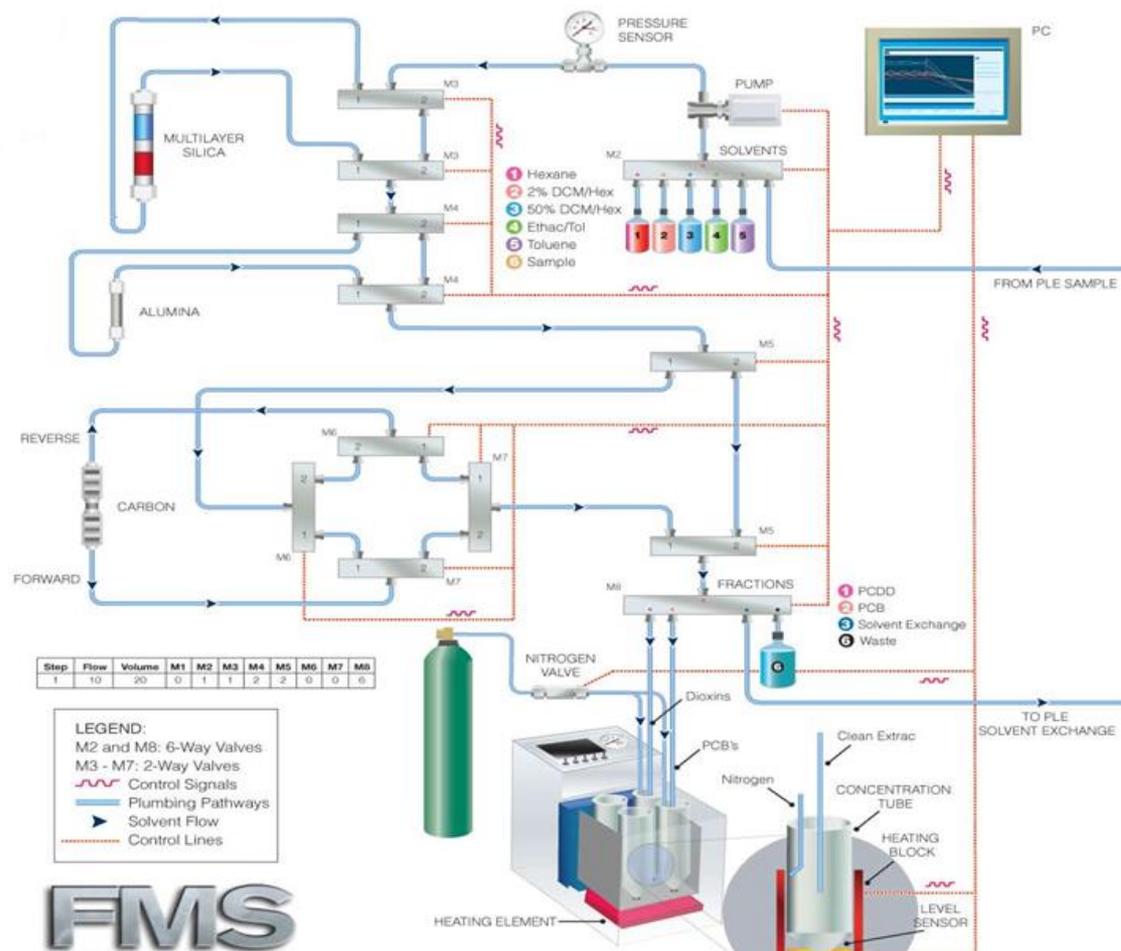
- ▶ Analysis of various matrices for PCDD/Fs and PCBs using extraction and clean up.
- ▶ Soxhlet extraction (typically up to 24-36 h).
- ▶ Preparative multi column chromatography involving various solvents and steps.
- ▶ Can include acid-base-neutral silica, pure acidified silica, alumina, florisil and carbon columns. Use of 22% or 44% H₂SO₄ acid mixed with silica; 33% NaOH mixed with silica.

Automation

- ▶ Advantages of automated sample prep are:
 - ▶ Reduced time: Pressurized Liquid Extraction (PLE) takes 60 min start-to-finish (50/50 DCM/hexane, 20 min at 120 oC, 1500 psi). Compare Soxhlet up to 36 h.
 - ▶ Reduced cost: less labor involved, shorter turnover time per sample.
 - ▶ Reduced volume: less solvent used.

PowerPrep CleanUp System

Power - Prep™



System characteristics

- ▶ Control module that pilots valve drive modules connected to a pump and pressure modules responsible for solvent flow in the valve module.
- ▶ Built in computer that does not need a stand-alone pc.
- ▶ Easy programming and software editing provides custom made sequences of events that drive the required solvent at the right place at the right moment.
- ▶ Low pressure (5-30 psi). Flow rates of up to 10-15 mL/min are used.

Columns

- ▶ Silica - PBDE-free multilayer ABN silica gel column (sizes half, classical, high capacity, XL).
- ▶ Alumina – PBDE-free basic alumina column.
- ▶ Carbon – PBDE-free carbon/celite column.
- ▶ Packed in disposable Teflon tubes; individually sealed in Mylar packaging; production in clean room environment.

Program

- ▶ Condition columns with hexane (step 1-3).
- ▶ Load sample in hexane onto silica (step 4).
- ▶ Elute silica column with hexane, analytes onto alumina (step 5).
- ▶ Flush with 10% DCM/hexane (step 6).
- ▶ Elute alumina with 10% DCM/hexane, collect all PCBs (F1, step 7).
- ▶ Flush system with DCM (step 8).
- ▶ Elute alumina with DCM, PCDD/Fs onto carbon (step 9).
- ▶ Flush with toluene (step 10) and elute carbon with toluene (step 11). Collect all PCDD/Fs (F2).
- ▶ Hexane purge (step 12).

Advantages

- ▶ Original volumes up to 800 mLs.
- ▶ New volumes 250 – 400 mLs depending on silica size (5-40 g).
- ▶ Total processing time for six samples parallel is 30-40 min.
- ▶ Reduced solvent and labor cost.
- ▶ Reproducible sample prep.

6 position evaporator

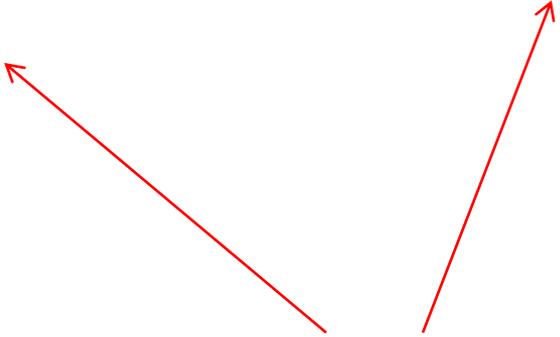
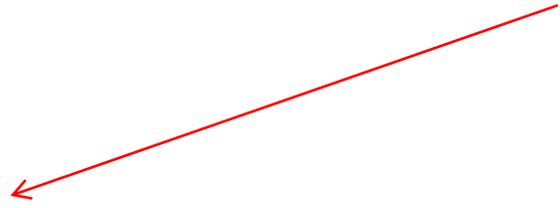


SuperVap Evaporation

- ▶ 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.
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24 position vial evaporator





GC vial



DFS HRGC/HRMS



Data for matrices (1)

	peanut butter	top soil	fish oil
2378-T4CDF	80%	75%	78%
2378-T4CDD	89%	87%	86%
12378-P5CDF	92%	97%	101%
23478-P5CDF	78%	79%	86%
12378-P5CDD	83%	88%	93%
123478-H6CDF	84%	77%	78%
123678-H6CDF	75%	62%	64%
234678-H6CDF	69%	60%	62%
123789-H6CDF	86%	81%	82%
123478-H6CDD	88%	78%	80%
123678-H6CDD	72%	67%	67%
123789-H6CDD			
1234678-H7CDF	78%	71%	71%
1234789-H7CDF	96%	83%	84%
1234678-H7CDD	82%	78%	79%
OCDF			
OCDD	80%	81%	83%

Data for matrices (2)

		peanut butter	top soil	fish oil
33'44'-T4CB	77	72%	70%	77%
344'5-T4CB	81	73%	72%	75%
233'44'-P5CB	105	68%	71%	67%
2344'5-P5CB	114	71%	69%	67%
23'44'5-P5CB	118	67%	69%	68%
2'344'5-P5CB	123	67%	69%	65%
33'44'5-P5CB	126	76%	76%	71%
233'44'5-H6CB	156	65%	63%	60%
233'44'5'-H6CB	157	59%	58%	55%
23'44'55'-H6CB	167	65%	61%	56%
33'44'55'-H6CB	169	69%	67%	65%
233'44'55'-H7CB	170	59%	57%	54%
22'344'55'-H7CB	180	58%	56%	53%
233'44'55'-H7CB	189	64%	62%	58%

Conclusions

- ▶ Excellent recoveries for different matrices for both PCDD/Fs and PCBs.
- ▶ Sample prep for peanut butter and soil included Pressurized Liquid Extraction.
- ▶ Multi column silica, alumina, and carbon clean up delivers clean samples ready for analysis now with reduced solvent use and a 30-40 min minute runtime.
- ▶ PCBs and and PCDD/F in completely separate fractions.
- ▶ Same day sample processing and analysis (HRGC/HRMS): can be easily done in one day.