

Chlorinated Dioxins, Furans and Biphenyls Analysis in Complex Matrices Using Automated Extraction and Reduced Solvent Volume Column Chromatography

Philip Bassignani
Fluid Management Systems
Watertown MA USA



Introduction

- Stockholm Convention on Persistent Organics Pollutants 2001.
- Compounds of interest: polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs), and furans (PCDFs).
- Known toxicity.
- Strict environmental regulations in force in most countries.



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.

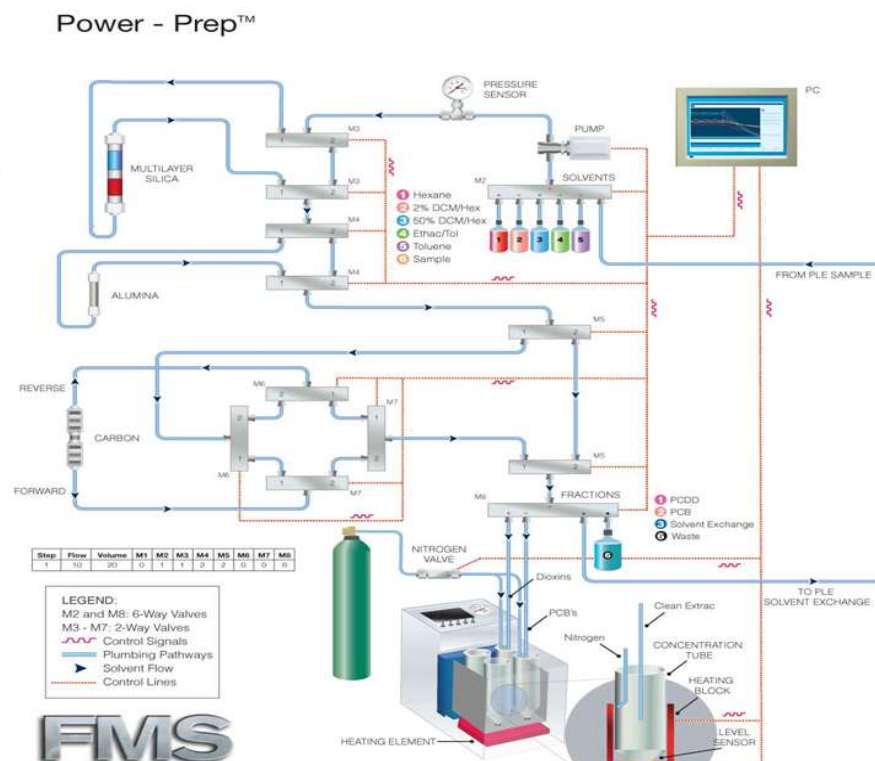


Automation

- 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



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



Program (1)

- 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 system with 10% DCM/hexane (step 6).
- Elute alumina with 10% DCM/hexane, collect all PCBs (F1, step 7).



Program (2)

- 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.



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 (1)

- Excellent recoveries with different matrices for all toxic PCDD/Fs and PCBs.
- Sample Prep for peanut butter and soil includes 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.



Conclusions (2)

- PCBs and PCDD/F in completely separate fractions.
- Same day sample processing and analysis (HRGC/HRMS): can be easily done in one day.

