Analysis of Chlorinated Dioxins, Furans and Biphenyls in Edible Oils

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.

PCDD/Fs

- PCDD/Fs are always unwanted byproducts.
- PCDD/F sources: combustion, incineration, metallurgical industry, pulp and paper bleaching/ production; low natural background (Trace Chemistries of Fire).
- Levels also dropping.
- Still at significant concentrations to pose danger.

PCBs

- PCBs were intentionally produced 1920-1970s.
- Used in capacitators and transformers, also as flame retardants, hydraulic fluids, sealants, and vacuum pump fluids.
- Total production estimated worldwide 1.5 million metric tons. Produced as Aroclor in North-America.
- Levels are now dropping.
- Still at significant concentrations to pose danger.

Health Effects

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

Scope (1)

- PCDDFs and PCBs have lipophilic nature; bio accumulate in adipose tissues and end up in food supplies.
- U.S. FDA and EU have established strict regulations for the monitoring of food products for human consumption, in particular edible oils.
- Manual extractions of oils can be a time consuming procedure often delaying lab turnaround times.

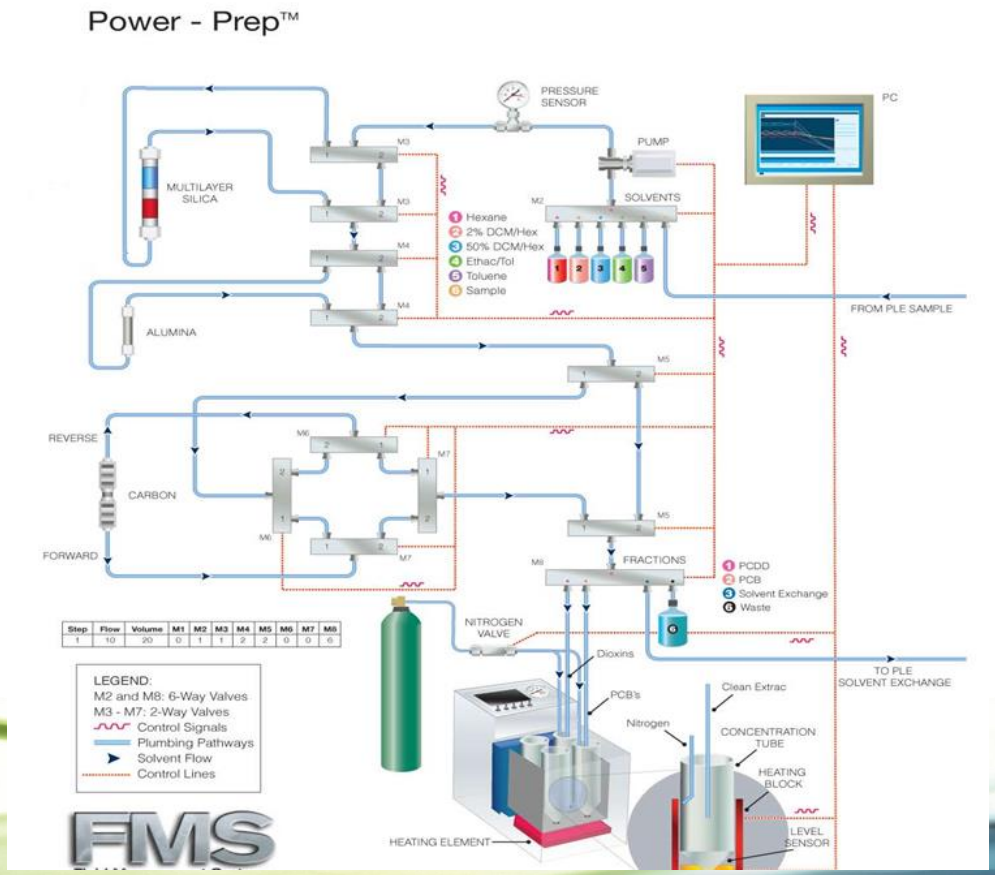
Scope (2)

- By automating the process, food oil samples can be reliably processed with routine 24 hour turnaround times.

Sample Prep

- Various Oil matrices obtained (Lard, Olive Oil, Corn Oil, Cod Oil, Red Palm Oil, Unrefined Pumpkin Oil, Unrefined Vegetable Oil).
- Aliquots of 5 gram samples were spiked with 13C labeled surrogate standards.
- Samples were diluted into n-hexane and drawn up into a gas tight syringe.

PowerPrep Clean Up



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 (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 with 10% DCM/hexane (step 6).
- Elute alumina with 10% DCM/hexane, collect all PCBs (F1, step 7).
- Flush system with DCM (step 8).

Program (2)

- 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).

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6 position evaporator

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.

24 position vial evaporator

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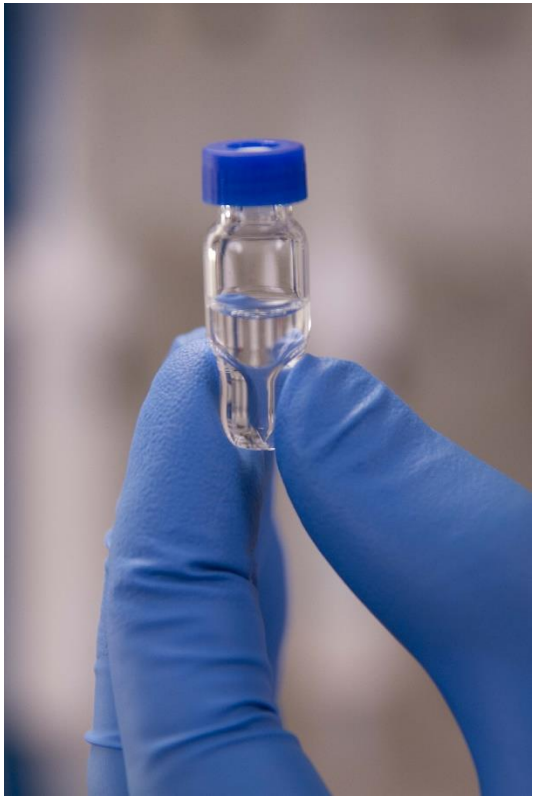
Glass Evaporation tube



GC vial

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DFS HRGC/HRMS

Mean PCDD/F recoveries (6 oils)

Analyte	Mean	Dev	Blk Conc.
2378TCDF	70	8.5	< .1 pg/g
2378TCDD	78	8.6	< .1 pg/g
12378PeCDF	83	13.5	< .5 pg/g
23478PeCDF	81	10.7	< .5 pg/g
12378PeCDD	81	11.6	< .5 pg/g
123478HxCDF	70	7.1	< .5 pg/g
123678HxCDF	62	3.6	< .5 pg/g
234678HxCDF	71	10.0	< .5 pg/g
123789HxCDF	66	6.9	< .5 pg/g
123478HxCDD	81	11.3	< .5 pg/g
123678HxCDD	77	9.4	< .5 pg/g
123789HxCDD	NA	NA	< .5 pg/g
1234678HpCDF	73	5.0	< .5 pg/g
1234789HpCDF	85	9.0	< .5 pg/g
1234678HpCDD	75	7.1	< .5 pg/g
OCDD	70	3.6	< 1 pg/g
OCDF	NA	NA	< 1 pg/g

Mean PCBs recoveries (6 oils)

	Mean	Dev	Blk Conc.
PCB-77	73	14.9	< .5 pg/g
PCB-81	64	11.0	< .5 pg/g
PCB-105	75	15.2	< .5 pg/g
PCB-114	73	11.4	< .5 pg/g
PCB-118	73	8.5	< .5 pg/g
PCB-123	72	8.0	< .5 pg/g
PCB-126	88	19.7	< .5 pg/g
PCB-156	63	7.4	< .5 pg/g
PCB-157	53	8.7	< .5 pg/g
PCB-167	63	6.1	< .5 pg/g
PCB-169	75	10.4	< .5 pg/g
PCB-170	79	9.4	< .5 pg/g
PCB-180	77	14.2	< .5 pg/g
PCB-189	80	9.8	< .5 pg/g

Conclusions (1)

- Analysis of the 6 matrices processed yielded acceptable recoveries for all analytes with standard deviations below 20%.

- Analysis of an n-Hexane blank sample resulted in no detectable target analytes measured within the calibration range of each respective compound.

Conclusions (2)

- With a total processing time of less than 2.5 hours, the FMS PowerPrep® and SuperVap® Concentrator delivers an efficient, totally automated sample prep process for edible oils.