The Analysis of Chlorinated Dioxins and Furans in Pet Food

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.

Health Effects

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

Scope (1)

- Screening for PCDD/Fs in human food supplies is a well established practice.
- Both the EU and US have extensive protocols for the testing of food for human consumption as well as additives to feed for commercial livestock.
- 2007: melamine added to pet foods let to recalls around the world. Caused renal failure in animals.

Scope (2)

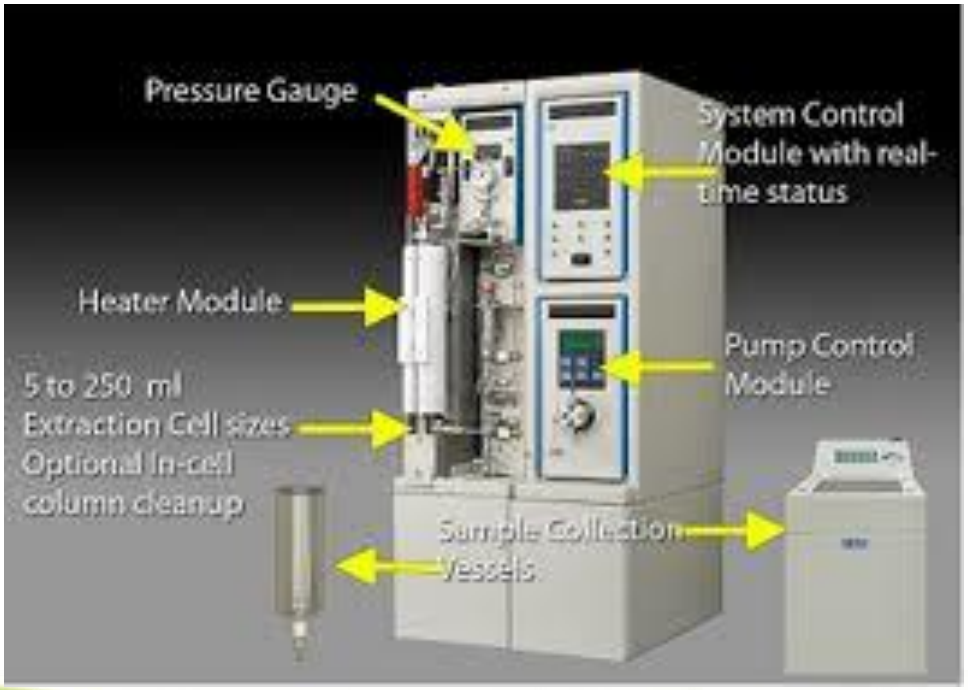
- For Persistent Organic Pollutants, the high lipid content of canned and dried pet foods make them an ideal source of dietary contamination for household pets.

Sample Prep

- Using the FMS Total Prep solution (TRP) for the extraction and extract clean-up of pet food, labs can deliver extracts for same day analysis.

- The following outlines the procedures for processing canned dog food for Chlorinated Dioxin and Difuran analysis via EPA 1613.

Pressurized Liquid Extraction



Extraction (1)

- 3 brands of canned dog food were obtained.
- Aliquots of 10 grams were spiked with 13C labeled surrogate standards.
- Samples were mixed with diatomaceous earth till all moisture was absorbed.

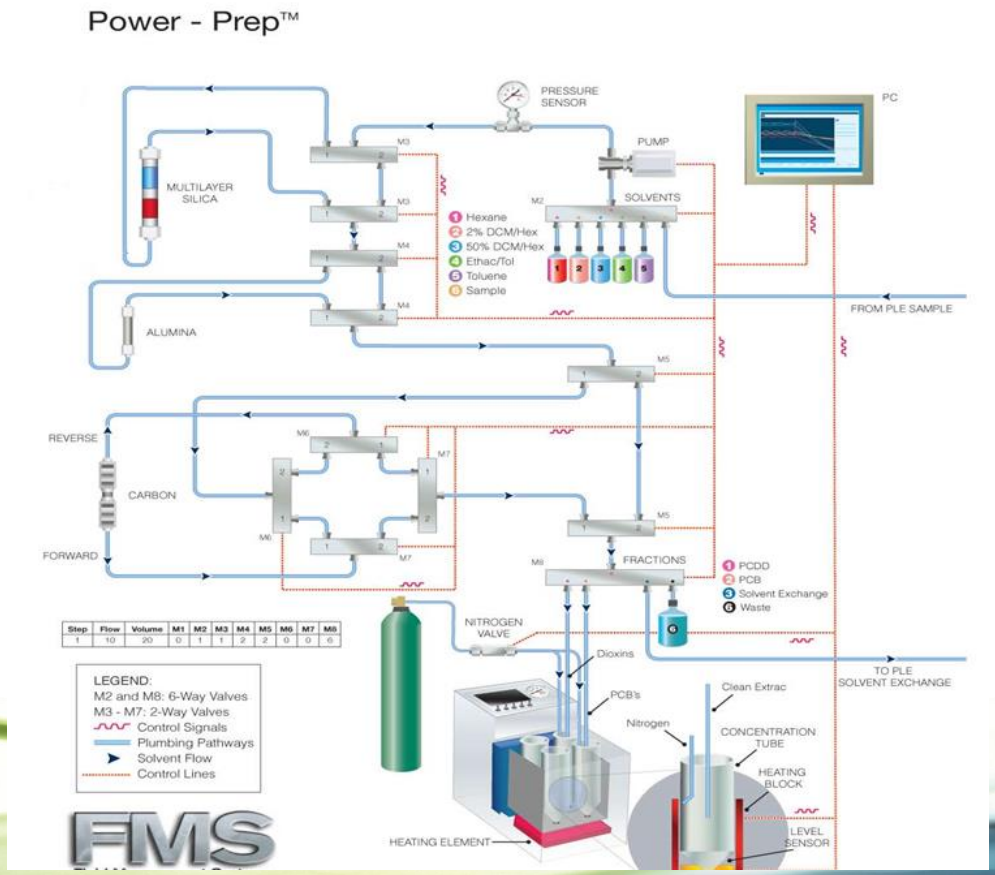
Extraction (2)

- Dried samples are transferred to extraction cells.
- Remaining cell volume topped off with Ottawa Sand.
- Extraction cells loaded onto PLE and filled sequentially with 50% DCM in Hexane.

Extraction (3)

- Extraction cells pressurized to 1500 PSI and heated to 120 oC and held for 20 min.
- Cells cooled to approximately ambient temperature.
- Cells flushed with extraction solvent which was purged from cells.

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

- 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, not done here).

Program

- 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).

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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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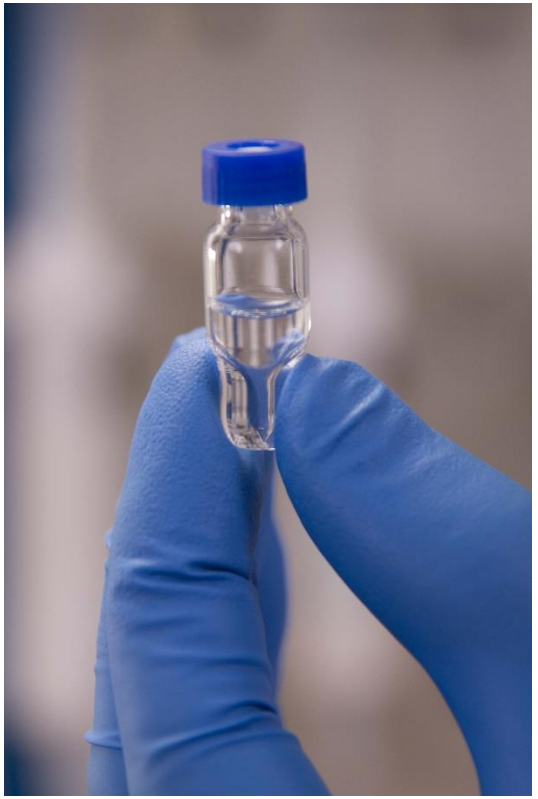
Glass Evaporation tube



GC vial

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DFS HRGC/HRMS

PCDD/F recoveries (3 brands)

	Run #1		Run #2		Run #3		MB	
Analyte	**13C Rec**	**Native**	**13C Rec**	**Native**	**13C Rec**	**Native**	**13C Rec**	**Native**
2378TCDF	82	<.0178	104	0.0456	78	0.0075	90	ND
2378TCDD	84	0.0113	105	0.1394	77	0.0331	92	ND
12378PeCDF	67	<.0291	79	0.037	65	0.0119	74	ND
23478PeCDF	69	0.0162	84	0.0317	70	<.0088	78	ND
12378PeCDD	72	0.0373	85	0.7676	72	<.0174	79	ND
123478HxCDF	84	0.0192	112	<.0216	89	0.0148	96	ND
123678HxCDF	80	0.0148	108	0.0244	83	0.0108	91	ND
234678HxCDF	82	0.0174	105	0.0161	85	0.0116	94	ND
123789HxCDF	90	0.0088	114	0.0262	91	0.0068	99	ND
123478HxCDD	84	0.033	109	0.9383	87	<.0089	93	ND
123678HxCDD	80	0.0246	105	1.3878	85	<.0188	92	ND
123789HxCDD		0.0191		0.9943		0.0119		ND
1234678HpCDF	67	<.0754	85	<.0754	76	0.0701	79	ND
1234789HpCDF	76	ND	97	<.0142	85	0.0114	90	ND
1234678HpCDD	73	0.2057	90	12.2956	81	0.0775	85	ND
OCDD	66	1.2475	75	115.7943	78	0.2291	77	0.2309
OCDF		.0.355		0.0393		<.0556		ND

Conclusions (1)

- Three pet food matrices show 13C recoveries between 65-109%, well within EPA1613 limits.
- Method Blank showed no background levels above the CS 0.1 calibration standard level except OCDD.
- Combining the clean background with good recoveries demonstrates the TRP process' ability to handle wet pet food of various types.

Conclusions (2)

- With a total process time of ~5 hours from start to finish, the TRP process enables sample turnaround for same day analysis.

- This is important to qualify batches for release and prevent product delays.