THE ANALYSIS OF CHLORINATED DIOXINS AND FURANS IN PET FOOD

Bassignani P, Addink R, Germansderfer, P[1*]

[1] Fluid Management Systems, 580 Pleasant Street, Watertown MA, USA

Introduction

Screening for chlorinated dioxins and furans in human 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. With recent contamination issues in pet food like the 2007 melamine incident, there is a growing concern for pet safety. With increasing efforts to screen both finished pet foods and pet food additives, the development of reliable analytical practices is of high priority.

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. Using automated Pressurized Liquid Extraction (PLE) and preparative column chromatography for the extraction and clean-up of pet food, labs can deliver extracts for same day analysis. The following outlines the procedures for processing canned dog food for PCDD/F analysis using the US EPA 1613 method.

Materials and methods

Preparation

Three different brands of canned dog food were obtained for analysis. Aliquots of 10 grams were spiked with ^{13}C labeled isotope dilution standards. The samples were then mixed with diatomaceous earth till all moisture was absorbed. Subsequently the dried samples were transferred to extraction cells. Remaining cell volume was topped of f with Ottawa Sand.

Pressurized Liquid Extraction

The filled extraction cells were loaded onto the PLE system. They were then filled sequentially with a mixture of 50% dichloromethane and 50% hexane. The cells were then pressurized to 1500 psi, heated to 120 ^{o}C and held at that temperature for 20 min. Afterwards they were cooled to ambient temperature and flushed with extraction solvent. This was purged from the cells with nitrogen. The samples collected in glass tubes were then reduced in volume under a nitrogen flow and exchanged to hexane.

Automated Column Chromatography Clean Up

The system uses pre-packaged chromatographic columns. It consists of a control module, valve modules, pump modules, and sample processing modules. The system used was operated via a PC; however, the new generation is stand alone with the computer control built into it with touch screen operation. A total of 3 columns were used: high capacity acid base silica; alumina; and carbon. Solvents used for the sample clean up were hexane, 2% dichloromethane /98% hexane, 50%/50% dichloromethane: hexane, 50%/50% ethyl acetate/benzene, and toluene. The columns were pre-conditioned with the various solvents. Flow rates varied from 5-10 mLs/min. The number of steps involved varies with the analytes; in the case of collecting PCDD/Fs around 25 steps are typically programmed into the system. About half of these are prior to sample loading for purpose of conditioning the columns. The PCDD/Fs were eluted in the last step off the carbon column with toluene. The entire cleanup program ran for about 90 min. New programs with reduced solvent use are forthcoming.[1]

Samples were reduced in volume in a 6 position evaporator: pre-heated for 20 min at 60 ^{o}C, followed by heating under nitrogen at ~ 10 psi. The evaporator has built-in sensors that shut off the nitrogen flow when the sample reaches ~ 0.5 mLs of volume. Further nitrogen blow down in a vial evaporator reduced the final sample volume to 10 uL. Recovery standards were then added.

Samples were analyzed on a high resolution Thermo DFS GC/MS with a Trace Ultra GC containing a 60 m DB-5 like column. Temperature program used was ~ 55 min for PCDD/Fs.

Figure 1. Automated cleanup system, PLE, and evaporator.

Results and Discussion

Data are presented in Table 1. Review of the 3 pet food matrices shows labeled recoveries ranging 65-109%, well within EPA1613 limits. Analysis of the 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 automated process' ability to handle wet pet food of various types. With a total process time of ~5 hours from start to finish, the automated equipment ensures sample turnaround for same day analysis. When factoring in the need to qualify batches for release and product delays, the value of rapid testing becomes critical.

	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

Table1: Analytical results, native compounds in pg/g.

References:

1. Juma, R, Addink, R, Dioxin 2015 contribution.