THE ANALYSIS OF CHLORINATED DIOXINS, DIFURANS AND BIPHENYLS IN EDIBLE OILS

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Introduction

The Dioxin family consists of 210 compounds, of which 17 contain the 2,3,7,8 pattern of chlorination. These 2,3,7,8 containing compounds are of extreme human health concern due to their high level of toxicity. Similarly, 12 of the 209 polychlorinated biphenyls have also been identified as human toxins.

Due to their lipophilic nature, these analytes bio accumulate in adipose tissues and end up in food supplies. For this reason, the U.S. FDA and EU have established strict regulations for the monitoring of food products for human consumption, in particular edible oils. PCDD/F were reported in such oils in the 1990s.[1] Manual extractions of oils can be a time consuming procedure often delaying lab turnaround times. By automating the process, food oil samples can be reliably processed with routine 24 hour turnaround times. The following procedure utilizes an automated sample clean-up system to deliver this process.

Materials and methods

A number of different oil matrices were used: lard, olive oil, corn oil, cod oil, red palm oil, unrefined pumpkin oil, and unrefined vegetable oil. Five grams of each matrix was used as a sample. They were spiked with ^{13}C labeled isotope dilution standards. The samples were then diluted in n-hexane and drawn up into a gas tight syringe. A schematic of the automated column chromatography clean up system is shown in Figure 1.

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 planar PCDD/Fs and co-planary PCBs went through the entire process and 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.[2]

After completion of the chromatography column clean up samples were reduced in volume in a 6 position evaporator. It was pre-heated for 20 min at 60 ^{o}C, followed by heating the samples 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. The collection tubes were then rinsed several times with hexane to make sure that no sample stuck to the glass walls. Direct-to-vial connections ensured that no samples were lost due to transfer. Further nitrogen blow down 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 programs used were ~ 35 min for PCBs and ~ 55 min for PCDD/Fs.

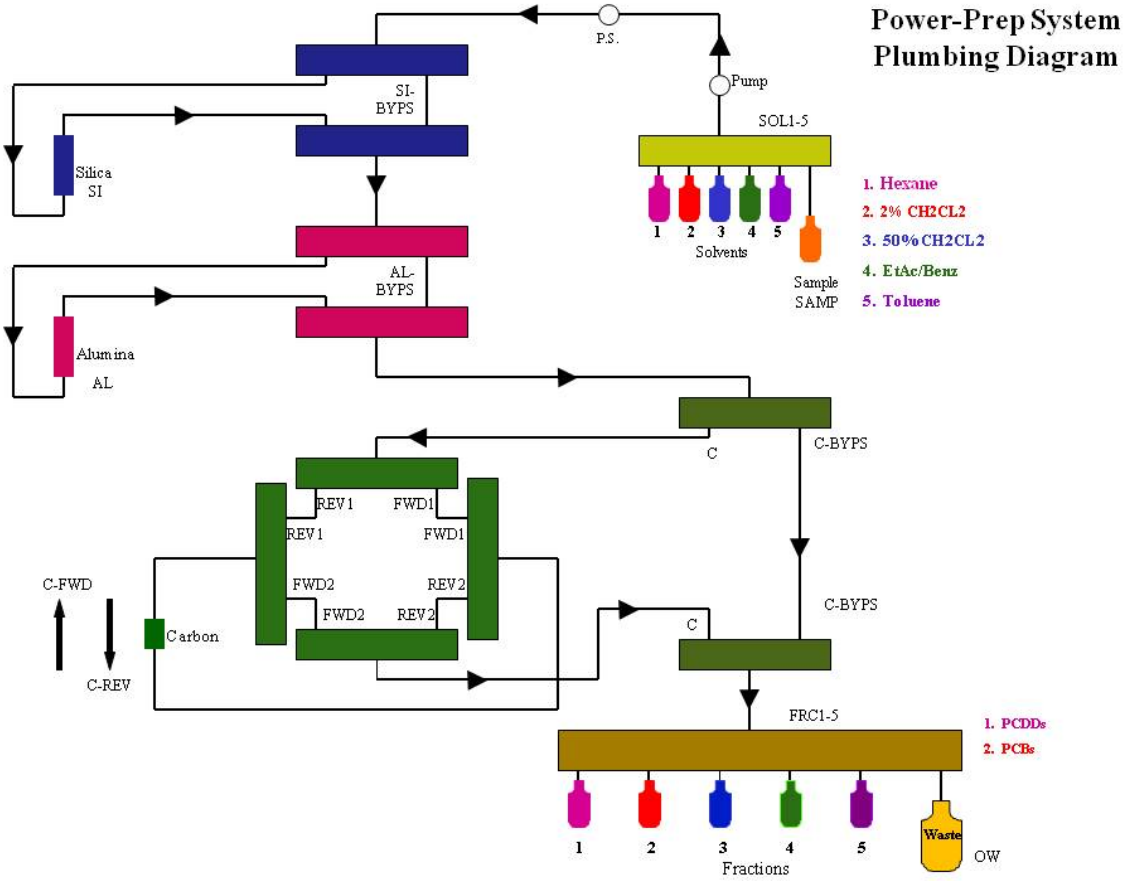

Figure 1. Automated Column Chromatography System Schematic.

Results and Discussion

Table 1 shows the ^{13}C recoveries obtained for the various oils. For each of the six matrices good recoveries were obtained 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. The automated system delivered straightforward clean up of the oils within 2.5 hours of total processing time. This makes same day analysis of the samples possible. The reproducibility of the results as demonstrated by the low standard deviations assures the consistency of the operation of the system.

Automated analysis of edible oils can result in faster turnaround times and improved quality of data which is invaluable for many laboratories. It can reduce labor costs and greatly enhance producitvity.

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	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

Table1: Mean recoveries and deviations for labeled compounds; concentration of blank.

References:

1. Wesp, HF, Rippen, G, Fiedler, H, Lau, C, Hutzinger, O, Sievers, S, Friesel, P, Gras, B, Reich, T, Schacht, U, Vahrenholt, F (1996) *Organohalogen.Cmpds*, 30, 37-42.
2. Juma, R, Addink, R, Dioxin 2015 contribution.