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A HIGH THROUGHPUT, LOW COST AND GREEN APPROACH TO AUTOMATED EXTRACTION, CLEAN UP, AND CONCENTRATION FOR SAME DAY POPS ANALYSIS

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Introduction

Persistent organic pollutants (POPs) are regulated under the Stockholm Convention. Since its entry into force in 2004, individual countries that ratified the convention have taken on obligations to monitor compounds such as polychlorinated dibenzo-p-dioxins, furans (PCDD/Fs), biphenyls (PCBs), and pesticides. Hence there is continued interest in processing of samples containing these compounds. Laboratories around the world are interested in low cost, automated, high throughput equipment to assist them with these tasks.

As part of the automation process, a cleanup system was developed which uses three columns and separates PCDD/Fs completely from PCBs. This was achieved by eluting PCBs directly off the alumina column while bypassing the carbon column. The advantage of this approach is that only two fractions are collected – one with PCBs and one with PCDD/Fs – so that only two analytical runs are necessary.

Materials and methods

Preparation

Between 1 and 20 g sample - animal feed, milk, peanut butter or soil - was mixed with inert material (Hydromatrix)® and spiked with 13C labeled isotope dilution standards. The samples were then transferred to stainless steel extraction cells. Remaining cell volume was topped off with Hydromatrix®.

Pressurized Liquid Extraction

The extraction cells were loaded onto the PLE system. Samples were extracted with a mixture of 50% dichloromethane and 50% hexane. The cells were pressurized to 1500 psi, heated to 120 oC and held at that temperature for 20 min. Afterwards they were cooled to ambient temperature and flushed with extraction solvent. In the final step the cells were purged with nitrogen gas. 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 consists of a control module, valve modules, pump modules, and sample processing modules. A touch screen computer has been built into the system. Programming of the various columns, solvent flows and volumes is done via a plumbing schematic. Chromatographic columns used are pre-packaged and vacuum sealed. Three different columns were used: high capacity acid-base-neutral silica; alumina; and carbon. Flow rates were set at 5-10 mLs/min. Columns were first conditioned with 45 mLs hexane. The samples were then loaded across the system onto the silica columns in hexane, followed by elution of hexane (120 mLs). This transferred the PCDD/Fs and PCBs onto the alumina column. PCBs were then collected by eluting the alumina with 75 mLs 10%:90% v/v dichloromethane in hexane. Subsequently the alumina column was eluted with 50 mLs dichloromethane to bring the PCDD/Fs onto the carbon column. Finally PCDD/Fs were collected from the carbon with 40 mLs of toluene.

Concentration

Samples were reduced in volume in a 6 position evaporator: pre-heated for 20 min at 45-55 oC, followed by heating under nitrogen at ~ 6-8 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.

Figure 1. Automated system for sample cleanup.

Analysis

Samples were analyzed on a high resolution Thermo DFS GC/MS with a Trace 1310 GC containing a 60 m DB-5 like column. Temperature programs used were ~ 35 min for PCBs and ~ 55 min for PCDD/Fs.

Results and Discussion

Table 1. 13C PCDD/Fs recoveries for various matrices.

Table 2. 13C PCBs recoveries for various matrices.

Results and Discussion

Matrices analyzed included environmental (soil) and food applications. Animal feed gave 80-100% 13C PCDD/Fs recoveries (Table 1). Peanut butter gave 60-80% and oils 60-90% (Table 1). For soil 13C labeled PCBs recoveries of 65-90% were achieved (Table 2). Olive oil and red palm canola oil gave 13C PCBs recoveries between 80-100%.

The total amount of solvent used for the cleanup was between 300-350 mLs per sample. The original program which used up to 800 mL of solvent has been drastically cut down resulting in a lower cost per sample. Our work presented here is part of an ongoing effort to reduce these volumes further.1

New developments include a second automated cleanup system with somewhat different plumbing, in which the mono-ortho- and di-ortho PCBs are collected in one fraction and the co-planary or (non-ortho) PCBs in another fraction together with the PCDD/Fs. The choice for one plumbing schematic versus the other may depend on local regulatory requirements. A laboratory may prefer to have all PCBs in one fraction for environmental samples and to have two PCBs fractions for food samples. However both kinds of systems are capable of processing either sample category.

References:

1. Juma, R., Addink, R. (2015) Organohalogen Compounds, 77, 245-248.

Figure 1.

	animal feed	peanut butter	corn oil	olive oil
2378-TCDF 13C12 STD	78%	73%	61%	66%
2378-TCDD 13C12 STD	78%	73%	63%	66%
12378-PeCDF 13C12 STD	78%	78%	66%	69%
23478-PeCDF 13C12 STD	78%	73%	63%	65%
12378-PeCDD 13C12 STD	78%	77%	65%	72%
123478-HxCDF 13C12 STD	97%	74%	90%	78%
123678-HxCDF 13C12 STD	96%	74%	85%	81%
234678-HxCDF 13C12 STD	95%	64%	81%	86%
123789-HxCDF 13C12 STD	98%	80%	88%	84%
123478-HxCDD 13C12 STD	96%	68%	84%	89%
123678-HxCDD 13C12 STD	95%	64%	76%	83%
1234678-HpCDF 13C12 STD	90%	63%	85%	83%
1234789-HpCDF 13C12 STD	94%	66%	90%	87%
1234678-HpCDD 13C12 STD	91%	65%	80%	81%
OCDD 13C12 STD	80%	62%	84%	78%

Table 1.

	soil	milk	olive oil	red palm canola
PCB_77	68%	66%	92%	91%
PCB_81	70%	54%	90%	90%
PCB_105	86%	59%	93%	88%
PCB_114	61%	54%	93%	88%
PCB_118	78%	75%	90%	86%
PCB_123	76%	71%	94%	86%
PCB_126	80%	70%	87%	81%
PCB_156	67%	90%	98%	96%
PCB_157	65%	89%	99%	94%
PCB_167	71%	109%	97%	94%
PCB_169	89%	111%	104%	96%
PCB_170	76%	93%		95%
PCB_180	65%	79%	97%	92%
PCB_189	72%	93%	91%	91%

Table 2.