

## DEVELOPMENT OF AN AUTOMATED CLEANUP SYSTEM FOR THE ISOLATION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS, DIBENZOFURANS, AND POLYCHLORINATED BIPHENYLS IN SEWAGE SLUDGE

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### Introduction

Established techniques<sup>1,2</sup> for the isolation of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/F), and polychlorinated biphenyls (PCBs) from environmental matrices such as soil, sediment, water, and tissue are well known throughout the environmental industry. While these techniques may be used to isolate the target compounds from sewage sludge, the quality control (QC) results do not always meet the same performance standards as with the standard matrices (e.g., soil, water). Sewage sludge or biosolids is typically highly organic and can vary significantly in characteristics depending upon the type of material and treatment process used.

A series of experiments were performed at MRI to evaluate the elution profiles of the 17 2,3,7,8-substituted PCDD/F and the World Health Organization (WHO) list of toxic PCBs using a Fluid Management Systems® (FMS) Power-Prep system. In this paper, we will present the results from the investigation to develop a methodology for the isolation of co-extracted PCDD/F and PCBs from sewage sludge using a FMS® Power-Prep system for extract clean-up.

It is demonstrated that once the correct sequence of columns and solvent systems were selected and the elution profiles were determined, the Power-Prep System provided for stable QC performance with high accuracy and precision.

### Materials and Methods

Four replicate biosolid samples were fortified with a mixture of <sup>13</sup>C<sub>12</sub>-labeled PCDD/F and PCB internal quantitation standards (IQS) and then extracted by Soxhlet/Dean Stark for 21 hours with toluene. Following sample extraction, extracts were fortified with <sup>37</sup>Cl<sub>4</sub>-labeled 2,3,7,8-TCDD and <sup>13</sup>C<sub>12</sub>-PCB-111 as clean-up efficiency standards. Each of the extracts was split into two equal portions. One-half of each extract was processed through Fluid Management Systems® (FMS) Power-Prep system. Prior to loading samples, each extract was filtered through a 0.45 µm filter to prevent etching or plugging of internal valves.

The Power-Prep can be programmed to elute finite volumes at measurable flow-rates under pressures of 5-25 psi. Flow rates can easily be modified via programming and fractions from different stages in the elution can be collected. Extracts are processed sequentially through three columns procured from FMS. The columns included a neutral/acid/base silica gel column, an acid/base alumina column, and an AX-21 carbon column. Individual solvents and mixtures used in the Power-Prep cleanup were all Burdick and Jackson (distilled in glass). The solvents included n-hexane, 2% (v/v) dichloromethane/hexane (2%DCMHX), 50% (v/v) dichloromethane/hexane (50%DCMHX), 50% (v/v) ethyl acetate/toluene (50%ETTOL), and toluene.

For PCDD/F cleanup, extracts are loaded onto the silica column and are eluted directly to the alumina column with hexane. The hexane eluent from the alumina column is directed to waste. Once the analytes are loaded onto the alumina column, the solvent system is changed to 2%DCMHX and the alumina column is eluted to waste. The solvent system is then changed to 50%DCMHX and the alumina column is eluted to the carbon column in the forward direction and to waste. The solvent system is changed to 50%ETTOL and the carbon column is eluted to waste. The solvent system is then changed to toluene and the carbon column is eluted in the reverse direction, collected, concentrated and analyzed for PCDD/F.

For the elution of PCBs, however, the PCDD/F program required modification. Experiments were performed using the biosolids extracts. Five fractions were collected including (1) 2%DCMHX from alumina, (2) 50%DCMHX from alumina, (3) 50%DCMHX from carbon in the forward direction, (4) 50%ETTOL from carbon in the forward direction, and (5) toluene from carbon in the reverse direction. Extract fractions were concentrated by nitrogen evaporation and were fortified with  $^{13}\text{C}_{12}$ -labeled recovery standards in tridecane.

The samples were analyzed by HRGC/HRMS using a Fisons AutoSpec Ultima or VG70-250S high-resolution mass spectrometer interfaced to a Hewlett-Packard 5890 gas chromatograph. A DB-5ms gas chromatography column (60 meter, 0.25 mm ID, 0.25  $\mu\text{m}$  film thickness) was used. Mass spectrometer acquisition was performed at 10,000 resolution in the selected ion monitoring mode (SIM). Standard analysis met USEPA Method 1613 and 1668 CAL-VER limits.

### Results and Discussion

The elution profiles from the fractionation experiments are shown in Table 1. All PCDD/F analytes eluted in the reverse direction from the carbon column and were not found in any other fraction. Coplanar PCBs eluted in both forward and reverse directions off carbon with the majority in the forward direction. The mono-ortho substituted PCBs were the significant challenge as these analytes eluted from both the alumina and carbon in both the waste and collect fractions of the FMS PCDD/F methodology.

Table 1 Elution Profiles

Target Analyte	Elution from Alumina		Carbon –Forward		Carbon-Reverse
	Fraction1	Fraction2	Fraction3	Fraction4	Fraction5
All PCDD/F		C			C
PCB-81		C		P	P
PCB-77		C		P	P
PCB-126		C		P	P
PCB-169		C		P	P
PCB-123	C				
PCB-118	C				
PCB-114	P	P	P	P	
PCB-105	P	P	P	P	
PCB-167	C				
PCB-156	P	P	P	P	
PCB-157	P	P	P	P	
PCB-189	C				

C- Complete elution, P – Partial elution observed.

The 2%DCMHX elution from alumina was found to contain all of PCBs 123, 118, 167, and 189 and also a significant amount of the biosolids matrix. In order to reduce the matrix and isolate these analytes, additional experiments were performed varying solvent flow rates and volumes. Once optimized, the effects of the matrix in the final extract and subsequent analysis were almost unmeasurable.

As mentioned previously, it was observed that the coplanar PCBs elute in both the forward and reverse fractions from carbon. Using the same approach as for the 2%DCMHX fraction, these compounds can be isolated or made to elute with the PCDD/F analytes as needed.

The final methodology was used for the cleanup of approximately 300 biosolid samples. The fractionation was developed to produce a single extract for PCDD/F analytes and a single extract for PCB analytes. The advantage to using the Power-Prep was the reduction in labor necessary to prepare extracts and the reproducibility of the automated elution software. Accuracy and precision results for 15 on-going precision and recovery analyses are presented in Table 2.

Table 2. Accuracy and Precision of PCDD/F and PCB Over 15 Sample Sets

PCDD/F	Spike Average			PCB	Spike Average		
	pg/ $\mu$ L	pg/ $\mu$ L	%RSD		pg/ $\mu$ L	pg/ $\mu$ L	%RSD
2,3,7,8-TCDF	10	9.59	8.4	PCB-81	50	50.4	3.9
2,3,7,8-TCDD	10	7.99	7.0	PCB-77	50	52.3	3.5
1,2,3,7,8-PeCDF	50	58.9	4.5	PCB-126	50	52.5	2.9
2,3,4,7,8-PeCDF	50	50.0	4.3	PCB-169	50	53.6	3.2
1,2,3,7,8-PeCDD	50	57.1	8.0	PCB-123	50	54.9	2.4
1,2,3,4,7,8-HxCDF	50	48.4	4.0	PCB-118	50	64.3	4.5
1,2,3,6,7,8-HxCDF	50	45.4	5.3	PCB-114	50	52.5	3.0
2,3,4,6,7,8-HxCDF	50	48.3	4.2	PCB-105	50	54.5	5.1
1,2,3,7,8,9-HxCDF	50	42.8	4.8	PCB-167	50	56.4	6.2
1,2,3,4,7,8-HxCDD	50	54.7	4.7	PCB-156	50	53.2	6.4
1,2,3,6,7,8-HxCDD	50	45.3	6.0	PCB-157	50	54.1	6.5
1,2,3,7,8,9-HxCDD	50	45.0	8.1	PCB-189	50	53.5	8.3
1,2,3,4,6,7,8-HpCDF	50	44.0	4.4				
1,2,3,4,7,8,9-HpCDF	50	49.7	3.0				
1,2,3,4,6,7,8-HpCDD	50	53.3	5.5				
OCDF	100	90.7	13				
OCDD	100	111	14				

The Power-Prep system presented several advantages over conventional gravity column cleanups. The greatest advantage was the reduction in glassware usage and minimization of the potential for background contamination. Gravity column cleanups for silica, alumina, and carbon also typically require concentration steps between columns and increased opportunity for sample extract and/or analyte loss. With the Power-Prep, the only glassware required is a disposable sample introduction tube, and collection flasks.

Another advantage is the timesaving recognized by the Power-Prep. Up to five samples can be processed through all cleanup columns within 1 1/2 hours. With a cleaning cycle for the valves and flexible tubing, the total time is extended to 2 hours. Following the cleaning cycle, the process can be started again. Therefore, up to 20 samples can be processed through all cleanups in a single 8-hour day.

In summary, once the correct sequence of columns and solvent systems (flows and volumes) were selected and the elution profiles were determined, the Power-Prep System provided for rapid cleanup of a very complex matrix while still maintaining high accuracy and precision.

#### References

1. USEPA Method 1613, "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B." Oct. 1994.
2. USEPA Method 1668, "Toxic Polychlorinated Biphenyls by Isotope Dilution High-Resolution Gas Chromatography / High Resolution Mass Spectrometry, Draft." March 1997.