

# EPA 1613 and 1668C: The Analysis of Polychlorinated Dibenzo-p-dioxins, Furans and Biphenyls in River Sediment with Automated Extraction and Clean Up

## Introduction

Persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs) and biphenyls (PCBs) have been a major environmental concern for a number of decades. Due to their low solubility in water and their resistance to breakdown, they tend to accumulate in river sediment. Analyses of sediment samples using US EPA methods 1613 (PCDD/Fs) and 1668 (PCBs) have been carried out around the world. Study of sediments often involves large amounts of samples, making fast processing (extraction, clean up, analysis) all the more important. This application note describes the automated Pressurized Liquid Extraction (PLE<sup>®</sup>) and automated open column chromatography clean up (PowerPrep<sup>®</sup>) of river sediment. Quick and easy processing results in samples being ready for same-day analysis.

## Instrumentation

- FMS, Inc. PLE<sup>®</sup>
- FMS, Inc. PowerPrep<sup>®</sup>
- FMS, Inc. SuperVap<sup>®</sup> 6 Concentrator
- FMS, Inc. SuperVap<sup>®</sup> Vial Concentrator
- FMS, Inc. 250 mL concentrator tubes (1 mL termination)
- Thermo Trace GC Ultra with high res magnetic sector DFS Thermo mass spec

## Consumables

- FMS, Inc. High Capacity Acidic Silica column with Silver Nitrate bed
- FMS, Inc. Basic Alumina column
- FMS, Inc. Carbon-Celite column
- Fisher Optima<sup>®</sup> Dichloromethane
- Fisher Optima<sup>®</sup> Hexane

- Fisher Optima<sup>®</sup> Toluene
- NIST 1944 New York/New Jersey Waterway Sediment
- Method 1613 and 1668C <sup>13</sup>C<sub>12</sub> spiking and recovery standards

## PLE

- 1 g of sample mixed with 10 g inert Hydromatrix<sup>®</sup> and spiked with surrogates
- Sample placed in extraction cell
- Capped with disposable Teflon end caps
- Heated with 50% Dichloromethane/50% Hexane for 20 min at 120 °C and 1500 psi
- 20 min cool down
- Nitrogen flush to transfer analytes and extract to 250 mL collection tubes

## SuperVap Concentration

- Pre-heat temperature: 55 °C
- Pre-heat time: 15 min
- Heat in Sensor mode: 55 °C
- Nitrogen Pressure: 7-10 psi
- Solvent exchange to hexane

## PowerPrep Clean Up

- Standard program
- Install high capacity silica, alumina and carbon/celite columns
- Solvents used are hexane, dichloromethane, and toluene
- Condition columns with hexane (60 mL)
- Load sample
- Elute silica/alumina with 160 mL hexane
- Elute alumina with 70 mL dichloromethane (collect mono- and di-ortho PCBs)
- Elute carbon in reverse direction with 60 mLs toluene (collect PCDD/Fs)

**SuperVap step** (above)**Vial Evaporator**

- Reduce sample to 10 uL final volume under 1-1.5 psi nitrogen at 25 °C

Table 1 with native sediment values, NIST reference values and <sup>13</sup>C-labeled recoveries.

	native pg/g	NIST1944 pg/g	recoveries %
2378-T4CDF	33.07	39 ± 19	98%
2378-T4CDD	120.19	133 ± 67	95%
12378-P5CDF	38.13	45 ± 22	99%
23478-P5CDF	39.39	45 ± 22	99%
12378-P5CDD	20.13	19 ± 9	105%
123478-H6CDF	179.13	220 ± 110	85%
123678-H6CDF	81.94	90 ± 45	81%
234678-H6CDF	52.06	54 ± 27	80%
123789-H6CDF	13.58		73%
123478-H6CDD	21.44	26 ± 13	86%
123678-H6CDD	52.35	56 ± 28	83%
123789-H6CDD	35.04	53 ± 26	
1234678-H7CDF	972.81	1000 ± 500	82%
1234789-H7CDF	39.20	40 ± 20	97%
1234678-H7CDD	744.78	800 ± 400	87%
OCDF	1164.80	1000 ± 500	
OCDD	5015.97	5800±2900	87%



Table 2 with native sediment values, NIST reference values and <sup>13</sup>C-labeled recoveries.

		native pg/g	NIST1944 pg/g	recoveries %
33'44'-T4CB	77	5714.03		104%
344'5-T4CB	81	307.57		98%
233'44'-P5CB	105	20895.78	24500 ± 12250	109%
2344'5-P5CB	114	1196.34		106%
23'44'5-P5CB	118	56443.83	58000 ± 29000	102%
2'344'5-P5CB	123	4514.92		106%
33'44'5-P5CB	126	206.71		125%
233'44'5-H6CB	156	4936.21	6520 ± 3260	109%
233'44'5'-H6CB	157	941.96		109%
23'44'55'-H6CB	167	2421.59		93%
33'44'55'-H6CB	169	31.58		124%
233'44'55'-H7CB	170	15553.43	22600 ± 11300	100%
22'344'55'-H7CB	180	47244.50	44300 ± 22150	99%
233'44'55'-H7CB	189	532.65		115%

### Conclusions

As can be seen the sediment analysis showed excellent agreement between the values found with our automated extraction and clean up and the acceptable reference values provided for this material. Furthermore, the method gave excellent recoveries. Extraction, clean up and analysis by properly trained personnel can be carried out in one day, resulting in low turnaround times for large (and small) sample batches.



PowerPrep, PLE, and Concentrator

For more information contact FMS:  
 FMS, Inc.  
 580 Pleasant Street  
 Watertown, MA 02472  
 Phone: (617) 393-2396  
 Fax: (617) 393-0194  
 Email: [onlineinfo@fms-inc.com](mailto:onlineinfo@fms-inc.com)  
 Web site: [www.fms-inc.com](http://www.fms-inc.com)