

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) and automated open column chromatography clean up (PowerPrep) of river sediment. Quick and easy processing results in samples being ready for same-day analysis.

Instrumentation

- FMS, Inc. PLE®
- FMS, Inc. PowerPrep®
- FMS, Inc. SuperVap® 6 Concentrator
- FMS, Inc. SuperVap® 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. Jumbo Acidified Silica column with Silver Nitrate bed
- FMS, Inc. Classical Acid-Base-Neutral column
- FMS, Inc. Basic Alumina column
- FMS, Inc. Carbon-Celite column
- Millipore OmniSolv® Benzene
- Fisher Optima® Dichloromethane
- Fisher Optima® Ethylacetate
- Fisher Optima® Hexane

- Fisher Optima® Toluene
- NIST 1944 New York/New Jersey Waterway Sediment
- Cambridge Isotope Labs (CIL) EDF-8999 Method 1613 ¹³C PCDD/F Stock Solution
- CIL EDF-5999 ¹³C PCDD/F Recovery Standard
- CIL EC-4995 ¹³C PCB Internal Isotope Dilution Standard who-12 PCB and 170/180
- CIL EO-5275 ¹³C PCB Recovery Standard

PLE

- 1 g of sample mixed with 10 g inert Hydro-matrix® 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: 45 °C
- Pre-heat time: 15 min
- Heat in Sensor mode: 45 °C
- Nitrogen Pressure: 6-8 psi
- Solvent exchange to hexane

PowerPrep Clean Up

- Standard 25-step program
- Install jumbo silica, classical ABN, alumina and carbon/celite columns
- Mixes used are hexane, 2%/98% dichloromethane/hexane, 50%/50% dichloromethane/hexane, 50%/50% ethylacetate/benzene, and toluene



- Run conditioning steps 1-13 with columns in place
- Load sample (in hexane)
- Elute silica with 150 mLs hexane (waste)
- Elute alumina with 60 mLs 2%/98% DCM/hexane (collect as F1)
- Elute alumina with 120 mLs 50%/50% DCM/hexane (collect as F1)
- Elute carbon with 4 mL 50%/50% ethyl-acetate/benzene (collect as F1)
- Elute carbon with 75 mLs toluene (collect as F2)

SuperVap step (above)

Vial Evaporator

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

Table with native sediment values, NIST reference values and ¹³C-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 with native sediment values, NIST reference values and ¹³C-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

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