

Automated Extraction and Clean Up of Wood Boiler Ash Samples: Dioxins, Furans, and PCBs

Introduction

It has been known since the 1970s that a wide range of combustion processes, fires, and incineration generate polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs) and biphenyls (PCBs) as products of incomplete combustion. Incineration residues such as boiler ash, bottom ash, and fly ash are routinely analyzed for these compounds using US EPA methods 1613 and 1668. Traditionally processing of ashes for chlorinated compounds has involved multi-day Soxhlet extraction and manual sample clean up using column chromatography. As an alternative to obtain faster and more reliable data, these various steps have been automated. This application note describes the automated Pressurized Liquid Extraction (PLE) and automated open column chromatography clean up (PowerPrep) of wood boiler ash.

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
- 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
- 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

- 10 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 wood boiler ash values and ¹³C-labeled recoveries.

	native pg/g	recoveries %
2378-T4CDF	10.50	91%
2378-T4CDD	1.18	91%
12378-P5CDF	6.30	87%
23478-P5CDF	10.47	87%
12378-P5CDD	5.32	90%
123478-H6CDF	5.69	74%
123678-H6CDF	5.35	69%
234678-H6CDF	7.41	69%
123789-H6CDF	3.20	107%
123478-H6CDD	1.94	84%
123678-H6CDD	2.93	79%
123789-H6CDD	3.03	
1234678-H7CDF	13.82	85%
1234789-H7CDF	2.54	105%
1234678-H7CDD	12.34	98%
OCDF	11.45	
OCDD	25.45	93%



Table with native wood boiler ash values and ¹³C-labeled recoveries.

		native pg/g	recoveries %
33'44'-T4CB	77	27.83	72%
344'5-T4CB	81	5.56	67%
233'44'-P5CB	105	33.28	69%
2344'5-P5CB	114	2.68	72%
23'44'5-P5CB	118	56.38	65%
2'344'5-P5CB	123	10.32	67%
33'44'5-P5CB	126	8.34	88%
233'44'5-H6CB	156	13.44	64%
233'44'5'-H6CB	157	4.74	59%
23'44'55'-H6CB	167	7.17	56%
33'44'55'-H6CB	169	1.84	82%
233'44'55'-H7CB	170	20.75	92%
22'344'55'-H7CB	180	62.66	90%
233'44'55'-H7CB	189	2.48	62%

Conclusions

PCDD/Fs and PCBs concentrations found were relatively low (compared to e.g., incinerator fly ash), demonstrating the sensitivity of the sample processing method. Excellent recoveries of the labeled compounds demonstrate the limited loss of analytes during automated extraction and clean up. With extraction times of ~ 60 min and sample clean up taking only a few hours, same-day analysis of (wood boiler) ash samples is now possible.



PowerPrep, PLE, and Concentrator

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