Method Validation of Automated Workflows for Persistent Organic Pollutants (POPs) Analysis in Environmental and Food Matrices

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Introduction

The continued interest in Persistent Organic Pollutants (POPs), such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), and biphenyls (PCBs) has led to a variety of automated systems for the extraction and cleanup of complex sample matrices. This resulted in development of automated Pressurized Liquid Extraction (PLE) (as an alternative to Soxhlet) and automated cleanup (as an alternative to manual preparative open column chromatography).

The PLE technique has been very successful with extraction of a wide variety of, among others, environmental and food samples lasting only about 1 h, with reliable and reproducible accuracy and recoveries.

To meet demands for a low-cost cleanup method that requires little financial investment, we combined the features of the automated systems - accurate, fast, reliable with short turnaround times and low background using FMS pre-packaged columns - with a relatively simple semi-automated approach. An important feature of the semi-automated technique is that a minimum amount of solvent is used, and no dichloromethane is used at all. This is important since many laboratories around the world are phasing out this solvent. This semi-automated method is ideal for those laboratories that want high quality sample processing without much financial investment.

Material and Methods

- FMS, Inc. EZPrep® Dioxin & PCBs sample preparation system
- FMS, Inc PLE® extraction system
- FMS, Inc. SuperVap® 12 position 50 mL Concentrator
- FMS, Inc. SuperVap® Vial Concentrator
- Agilent 7010B TripleQuad GC/MS/MS System with J&W DB-5 GC Column, 60 m, 0.25 mm, 0.25 µm

Consumables

- FMS, Inc PLE endcaps
- FMS, Inc. High-Capacity Acidic Silica column
- FMS, Inc. Carbon column
- FMS, Inc. 6 g Basic Alumina column
- Dichloromethane Pesticide Grade
- Hexane Pesticide Grade
- Toluene Pesticide Grade
- Relevant ^{13}C PCDD/Fs and PCBs isotope dilution and recovery standards

Material and methods

PLE

- 5-10 g sample mixed with Hydromatrix® 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
- Nitrogen flush to transfer analytes and extract to 250 mL collection tubes

SuperVap Concentration

- Pre-heat temperature: 50 °C
- Pre-heat time: 5 min
- Heat in Sensor mode: 50 °C
- Nitrogen Pressure: 8 psi
- Solvent exchange to hexane
- Reduce sample volume to about 5 mL

Sample Clean Up

Procedure

Stage 1:

- Assemble columns in order high-capacity acidic silica-carbon-alumina.
- Syringe vial at top is used for conditioning and sample loading.
- Columns are conditioned with 40 mL of hexane. Hexane is pulled by vacuum pump across all columns into waste.
- Samples are loaded across system in hexane (vacuum, waste)

Stage 2:

- Carbon and alumina columns are eluted in reverse direction with 40 mL toluene for collection under vacuum
- Two fractions are collected: Fraction 1 with PCDD/Fs and co-planary- PCBs and Fraction 2 with mono- and di-ortho PCBs
- Total run time is about 45 min
- Low solvent volume of collected fractions reduces time required for sample concentration

SuperVap step (above)
No solvent exchange

Vial Evaporator

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

Analysis 7010B Agilent TripleQuad GC/MS/MS

Results

natives in pg	spike	IDC-1	IDC-2	IDC-3	IDC-4	Average	RSD(%)	Acceptable window
2,3,7,8 TCDF	400.0	91.8%	97.2%	96.4%	93.4%	94.7%	2.7%	70%-130%
2,3,7,8 TCDD	400.0	93.0%	97.4%	95.4%	94.7%	95.1%	1.9%	70%-130%
1,2,3,7,8 PCDF	2000.0	94.9%	99.9%	95.2%	96.7%	96.7%	2.3%	70%-130%
2,3,4,7,8 PCDF	2000.0	91.9%	96.9%	94.7%	94.4%	94.5%	2.1%	70%-130%
1,2,3,7,8 PCDD	2000.0	96.3%	100.0%	101.5%	98.2%	99.0%	2.3%	70%-130%
1,2,3,4,7,8 HxCDF	2000.0	99.2%	101.9%	99.8%	103.7%	101.2%	2.0%	70%-130%
1,2,3,6,7,8 HxCDF	2000.0	98.8%	101.7%	102.3%	97.0%	100.0%	2.5%	70%-130%
2,3,4,6,7,8 HxCDF	2000.0	99.6%	101.7%	100.7%	102.0%	101.0%	1.1%	70%-130%
1,2,3,4,7,8 HxCDD	2000.0	104.2%	100.4%	99.8%	98.0%	101.1%	3.5%	70%-130%
1,2,3,6,7,8 HxCDD	2000.0	94.5%	107.7%	107.0%	106.1%	103.8%	6.0%	70%-130%
1,2,3,7,8,9 HxCDD	2000.0	105.9%	116.6%	111.6%	107.7%	110.4%	4.3%	70%-130%
1,2,3,7,8,9 HxCDF	2000.0	97.2%	101.8%	99.5%	100.4%	99.7%	2.0%	70%-130%
1,2,3,4,6,7,8 HpCDF	2000.0	94.2%	99.3%	95.6%	93.5%	95.7%	2.7%	70%-130%
1,2,3,4,6,7,8 HpCDD	2000.0	96.8%	99.0%	98.9%	97.9%	98.2%	1.1%	70%-130%
1,2,3,4,7,8,9 HpCDF	2000.0	94.0%	97.3%	97.1%	95.1%	95.9%	1.6%	70%-130%
OCDD	4000.0	97.3%	101.4%	103.3%	101.1%	100.8%	2.5%	70%-130%
OCDF	4000.0	100.7%	104.4%	103.9%	102.0%	102.7%	1.7%	70%-130%

Table 1 - Native PCDD/Fs for Initial Demonstration of Capability - Native spike 400-4000 pg - native amounts reported as percent recovery of spike (extraction, cleanup, and concentration - note that these are not ^{13}C recoveries)

MDL study	native										
	spike	ppt	ppt	ppt	ppt	ppt	ppt	ppt	ppt	ppt	ppt
	ppt	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	MB	STDEV	MDL
PCB_81	10.00	8.28	9.44	8.71	8.91	8.40	8.64	8.78	0.75	0.38	1.19
PCB_77	10.00	8.06	8.04	7.98	8.72	10.66	10.66	10.99	1.35	1.40	4.40
PCB_123	10.00	7.59	8.78	9.16	8.33	9.16	7.30	8.33	0.60	0.73	2.29
PCB_118	10.00	8.88	9.16	9.14	9.40	9.33	11.24	11.92	1.25	1.20	3.76
PCB_114	10.00	7.64	8.85	9.02	8.03	8.74	8.81	8.75	0.10	0.51	1.60
PCB_105	10.00	8.66	8.26	8.79	7.81	8.16	8.06	9.44	2.50	0.55	1.73
PCB_126	10.00	7.83	8.86	8.53	8.29	8.11	8.15	8.14	0.70	0.33	1.05
PCB_167	10.00	8.46	10.10	8.20	8.60	9.54	8.33	8.42	0.95	0.72	2.27
PCB_156	10.00	9.56	7.91	7.32	7.17	6.67	8.41	8.61	0.70	0.99	3.11
PCB_157	10.00	10.08	8.18	10.27	8.35	11.58	9.40	9.61	0.60	1.17	3.67
PCB_169	10.00	8.39	8.71	8.41	8.18	7.31	8.20	7.71	0.85	0.47	1.48
PCB_189	10.00	8.33	9.48	9.39	8.36	9.71	8.64	8.71	0.50	0.57	1.79

Table 2 - Native PCBs Method Detection Limit in pg/g - extraction, cleanup, and concentration -

13C recoveries (%)	Feed-1	Feed-2	Soil-1	Soil-2	MB
2,3,7,8 TCDF	96	83	114	100	93
2,3,7,8 TCDD	103	91	92	89	91
1,2,3,7,8 PCDF	69	80	93	81	88
2,3,4,7,8 PCDF	72	74	91	83	98
1,2,3,7,8 PCDD	76	72	89	74	88
1,2,3,4,7,8 HxCDF	88	84	74	68	90
1,2,3,6,7,8 HxCDF	88	72	82	73	121
2,3,4,6,7,8 HxCDF	83	72	89	78	96
1,2,3,4,7,8 HxCDD	73	71	96	74	125
1,2,3,6,7,8 HxCDD	76	72	93	91	102
1,2,3,7,8,9 HxCDF	96	93	102	103	106
1,2,3,4,6,7,8 HpCDF	79	79	87	70	90
1,2,3,4,6,7,8 HpCDD	79	95	87	93	93
1,2,3,4,7,8,9 HpCDF	75	81	100	108	110
OCDD	76	73	86	84	77

Table 3 - ^{13}C PCDD/Fs - extraction, cleanup, and concentration - 5g feed and 10g soil - MB = method blank

Discussion and Conclusions

Excellent Demonstration of Capability, Method Detection Limit results, and ^{13}C PCDD/F and PCB recoveries are seen with FMS automated extraction, FMS semi-automated cleanup and Agilent 7010B TripleQuad GC/MS/MS analysis. Examples are shown in Tables 1-3. The Pressurized Liquid Extraction (PLE) is much faster than traditional Soxhlet methods and uses less electrical power. The semi-automated FMS EZPrep123 Cleanup System is mostly composed of disposable parts and the risk of cross-contamination is very low. Note that no dichloromethane is used. The system can be set up at low cost and is an inexpensive alternative to the fully automated clean up equipment, and processing times are much shorter than other manual procedures using certified columns. The easy to operate 7010B analytical system has very good sensitivity and is a less expensive alternative to the magnetic sector high resolution instruments. The combination of FMS and Agilent technologies makes same-day POPs results possible.

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