Simple, Quick & Low Cost 6-position Parallel Channel, High Throughput Automated Sample Cleanup for POPs Analysis

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Introduction

Persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs) have been strictly regulated in many countries. This has created a steady flow of samples analyzed by small and large environmental, food and government laboratories worldwide. POPs sample processing is labor-intensive and prone to error. Compliance with regulatory procedures and accreditation requirements can result in a lengthy method validation effort. Strict quality assurance and quality control (QA/QC) requirements apply, and sample matrices can be very complex. In many cases native background interferences can be orders of magnitude higher than analytes. Therefore, in most cases elaborate sample cleanup is needed.

Automation of sample cleanup has focused on reduction of background contamination via use of a closed system and pre-packaged disposable columns (often produced in clean rooms). Automated programs via computer and mechanically driven sample processing channels with solvent pumps can reduce time required of cleanup and can be run largely unattended.

Since fully automated cleanup systems for POPs can be quite expensive, a low-cost automated alternative was developed that requires less financial investment, while having most of the same features (closed system, pre-packaged columns). The system is simple in design and uses stackable columns. It uses a multi-pump to do all the sample prep steps.

Material and Methods

- ■ FMS, Inc. EZPrep Plus Dioxin & PCBs sample preparation system with multi-pump
- ■ 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. High-Capacity Acidic Silica column
- ■ FMS, Inc. Carbon column
- ■ FMS, Inc. 6 g Basic Alumina column
- ■ Fisher Hexane Pesticide Grade
- ■ Fisher Toluene Pesticide Grade
- ■ Relevant ^{13}C PCDD/Fs and PCBs isotope dilution and recovery standards

Pressurized Liquid Extraction

- ■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
- ■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 1 mLs

Sample Clean Up

Procedure

Stage 1:

- ■ Assemble columns in order high-capacity acidic silica-carbon-alumina.
- ■ Sample cartridge on top is used for sample loading and hexane elution.
- ■ Samples are loaded across system and eluted with 160 mL of hexane with multi-pump (waste).
- ■ Remaining solvent is removed with nitrogen flush.

Stage 2:

- ■ Carbon and alumina columns are each individually eluted in reverse direction with 40 mL toluene for collection with multi-pump.
- ■ 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 40 min
- ■ Low solvent volume of collected fractions reduces time required for sample concentration

Analysis

7010 B Agilent TripleQuad GC/MS

Results

natives in pg	spike	IDC-1	IDC-2	IDC-3	IDC-4	Average	RSD (%)	Acceptable window
PCB-81	4000.0	92.3%	93.3%	94.0%	94.1%	93.4%	0.9%	70%-130%
PCB-77	4000.0	97.8%	95.9%	96.3%	98.3%	97.1%	1.2%	70%-130%
PCB-123	4000.0	90.6%	93.4%	95.0%	94.9%	93.5%	2.2%	70%-130%
PCB-118	4000.0	96.3%	107.0%	102.4%	98.8%	101.1%	4.6%	70%-130%
PCB-114	4000.0	88.7%	91.5%	93.1%	94.2%	91.9%	2.6%	70%-130%
PCB-105	4000.0	94.9%	101.0%	99.7%	99.4%	98.8%	2.7%	70%-130%
PCB-126	4000.0	99.7%	101.4%	101.7%	101.4%	101.0%	0.9%	70%-130%
PCB-167	4000.0	90.6%	94.3%	95.7%	96.1%	94.2%	2.7%	70%-130%
PCB-156	4000.0	89.1%	88.2%	78.6%	89.4%	86.3%	6.0%	70%-130%
PCB-157	4000.0	91.5%	90.6%	94.7%	91.9%	92.2%	1.9%	70%-130%
PCB-169	4000.0	91.4%	93.9%	94.1%	94.9%	93.6%	1.6%	70%-130%
PCB-189	4000.0	88.7%	91.0%	92.7%	93.7%	91.5%	2.4%	70%-130%

Table 1 - Native PCBs 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 MDL-1	ppt MDL-2	ppt MDL-3	ppt MDL-4	ppt MDL-5	ppt MDL-6	ppt MDL-7	ppt STDEV	ppt MDL
T 2,3,7,8 TCDF	0.40	0.35	0.30	0.30	0.28	0.32	0.39	0.32	0.04	0.12
T 2,3,7,8 TCDD	0.40	0.39	0.25	0.38	0.30	0.35	0.40	0.31	0.05	0.17
T 1,2,3,7,8 PCDF	2.00	1.84	1.36	1.73	1.42	1.57	2.01	1.63	0.23	0.72
T 2,3,4,7,8 PCDF	2.00	1.85	1.27	1.71	1.36	1.57	1.94	1.66	0.24	0.77
T 1,2,3,7,8 PCDD	2.00	1.82	1.44	1.76	1.29	1.77	1.99	1.57	0.24	0.76
T 1,2,3,4,7,8 HxCDF	2.00	2.00	1.40	1.91	1.46	1.76	2.02	1.96	0.26	0.82
T 1,2,3,6,7,8 HxCDF	2.00	1.93	1.31	1.67	1.35	1.73	1.96	1.62	0.25	0.80
T 2,3,4,6,7,8 HxCDF	2.00	1.89	1.26	1.74	1.38	1.53	2.15	1.78	0.31	0.96
T 1,2,3,4,7,8 HxCDD	2.00	1.85	1.24	1.70	1.27	1.86	1.89	1.62	0.28	0.87
T 1,2,3,6,7,8 HxCDD	2.00	1.84	1.17	1.89	1.40	1.78	2.10	1.77	0.31	0.99
T 1,2,3,7,8,9 HxCDD	2.00	1.86	1.30	1.88	1.48	1.76	2.27	1.88	0.31	0.98
T 1,2,3,7,8,9 HxCDF	2.00	1.91	1.35	1.84	1.30	1.77	1.95	1.82	0.27	0.84
T 1,2,3,4,6,7,8 HpCDF	2.00	1.84	1.61	1.95	1.41	1.76	2.10	1.71	0.22	0.71
T 1,2,3,4,6,7,8 HpCDD	2.00	1.83	1.46	1.85	1.52	2.04	1.89	1.86	0.21	0.66
T 1,2,3,4,7,8,9 HpCDF	2.00	1.96	1.28	1.64	1.43	1.77	2.24	1.62	0.32	1.02
T OCDD	4.00	4.01	2.81	3.98	2.92	4.63	4.59	3.88	0.72	2.27
T OCDF	4.00	4.10	2.50	3.58	2.64	3.51	4.26	3.74	0.68	2.12

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

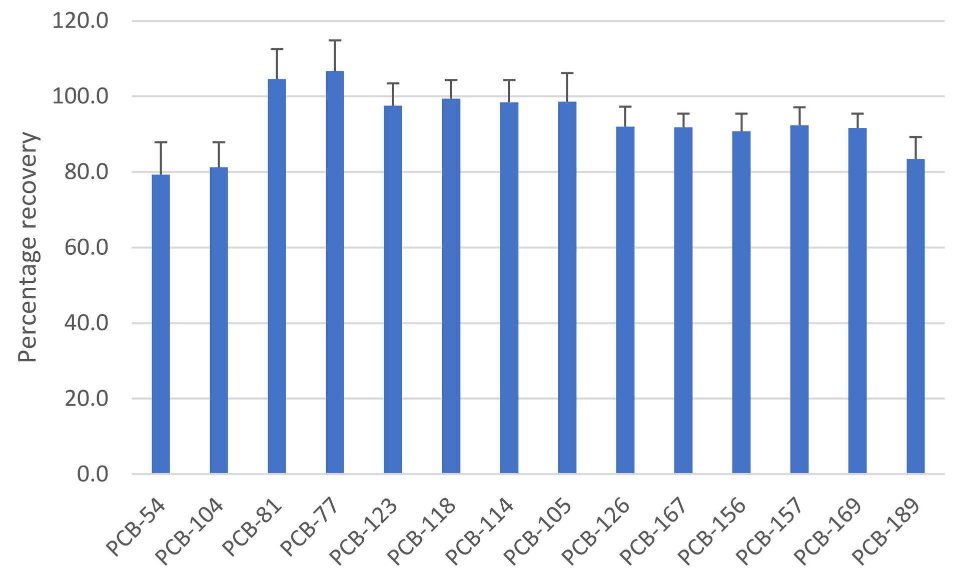

Figure 1 - ^{13}C PCBs recoveries (%) - cleanup, and concentration - 3 g olive oil (n=12).

Discussion and Conclusions

This work shows the feasibility of automation in POPs cleanup. The system can be set up at low cost and is an alternative to other more expensive fully automated clean up equipment. An important feature is also that no dichloromethane is used. Hexane and toluene guarantee an efficient and quick cleanup. Pre-treatment of samples with, e.g., an acid wash, is not necessary when choosing an acidified silica column with sufficient oxidizing capacity.

Combined with the Agilent 7010B TripleQuad GC/MS/MS, the simple, versatile system guarantees same morning or afternoon POPs analysis.

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