EVALUATION OF PARALLEL EVAPORATION FOR PCDD/PCDF AND PCB EXTRACT CONCENTRATION

Karen Tracy[1], Mary E Schrock, Joseph E Tabor, Wesley Baxter, Mark F Misita, Elizabeth Thompson

[1]Battelle

Introduction

Polychlorinated dibenzo-p-dioxin/dibenzofuran (PCDD/PCDF) and polychlorinated biphenyl (PCB) extracts are typically concentrated using conventional techniques such as rotary evaporation (RotoVap), turbo evaporation (TurboVap) and Kuderna-Danish (KD) concentration during extraction and cleanup procedures found in U.S. EPA Method 1668, Revision A[1](1668A) and U.S. EPA Method 1613, Revision B[2] (1613B). These procedures can be time consuming, cause loss of analytes and need to be carefully attended. Parallel evaporators, such as the Büchi Syncore Analyst, combine aspects of the RotoVap, KD and TurboVap in one unit providing a faster concentration of sample extracts. This study evaluates the Syncore Analyst with respect to cross contamination between extracts and recovery of PCDD/PCDF and PCB internal standards.

Materials and Methods

PCB Sample Extract Preparation and Concentration Steps

In order to evaluate the concentration of sample extracts containing PCBs, six simulated "extracts" were prepared. These six extracts were created by adding 130 mL of dichloromethane (DCM) to six individual concentrator tubes. All six tubes were spiked with PCB internal standard (CIL EC-4977) at levels specified in Method 1668A. Three of the tubes were also spiked with native PCB (AccuStandard M-1668A-C-NT-LOC-WD-GCPD) at levels twice those specified in 1668A for an ongoing-precision-and-recovery (OPR) sample. Thereby three method blank (MB) "extracts" and three high concentration PCB (OPR) "extracts" were created. The six simulated extracts were then processed through the following six concentration steps using the Syncore Analyst. These concentration steps represent all of the solvents used in sequence during a typical PCB sample preparation process. The configuration of the six extracts in the Syncore Analyst evaporator (Figure 1) was varied between steps to evaluate cross-contamination.

Step 1:The 130 mL DCM extracts were concentrated (temperature of 35°C) to approximately 0.3 mL using configuration 1.

Step 2:The extracts were brought up to 110 mL with DCM, all extracts except Method. Blank 1 (MB1) were spiked with 50 µL of nonane and re-concentrated (temperature of 35°C) to approximately 0.3 mL using configuration 2. Nonane was not added to MB1 to show effects of a keeper solvent on recoveries.

Step 3:The extracts were brought up to 10 mL with hexane and concentrated (temperature of 50°C) to approximately 0.3 mL using configuration 2.

Step 4:The extracts were brought up to 100 mL with hexane, all extracts except MB1 were spiked with 50 µL of nonane, and all were concentrated (temperature of 50°C) to approximately 0.3 mL using configuration 3.

Step 5:The extracts were brought up to 19 mL with 15 mL hexane, 2 mL 15:4:1 (DCM:methanol:toluene) and 2 mL 1:1 (DCM:cyclohexane). All except MB1 were spiked with 50 µL of nonane and all were concentrated (temperature of 50°C) to approximately 0.3 mL using configuration 4.

Step 6:All extracts were concentrated to 50 µL and spiked with PCB recovery standard (CIL EC-4979) at levels specified in 1668A prior to analysis

Configuration 1 Configuration 2

MB1	MB2	MB3		OPR1	MB2	MB3
OPR1	OPR2	OPR3		MB1	OPR2	OPR3

Configuration 3 Configuration 4

OPR1	OPR2	MB3		OPR1	OPR2	OPR3
MB1	MB2	OPR3		MB1	MB2	MB3

Figure 1. Syncore Analyst “extract” Configurations During Concentration Steps

PCDD/PCDF Sample Extract Preparation and Concentration Steps

Six “extracts” were prepared to simulate the concentration of extracts containing PCDD/PCDF. These six extracts were created in the same manner as the PCB extracts above except they were spiked with PCDD/PCDF internal standard (CIL EDF-8999, per 1613B). Three of the extracts were also spiked with native PCDD/PCDF standard (CIL EDF-7999, per 1613B); thereby creating three MB extracts and three high concentration PCDD/PCDF (OPR) extracts. The six simulated extracts were processed as follows:

Step 1:Same as for PCB.

Steps 2 through 4: Same as for PCB except nonane was not added to any of the extracts.

Step 5:The extracts were brought up to 30 mL with toluene and concentrated (temperature of 60°C) to 0.3 mL using configuration 4.

Step 6:The extracts were concentrated to a final volume of 20 µL and spiked with PCDD/PCDF recovery standard (CIL EDF-5999) per 1613B prior to analysis

Combined PCDD/PCDF/PCB Sample Extract Preparation and Concentration Steps

Six “extracts” were prepared to simulate the concentration of low and high volume extracts to evaluate if low volume extracts would be contaminated by extracts with higher volumes while being concentrated at the same time. These six extracts were created in the same manner as the PCDD/PCDF sample extracts above except all six tubes were spiked with PCDD/PCDF and PCB internal standards and three of the tubes were also spiked with native PCDD/PCDF and PCB standards(three MB and three OPRextracts). The six simulated extracts were processed through the following concentration steps.

Steps 1 through 5: Same as for PCDD/PCDF, except solvent was not added to the MB extracts.

Step 6:The extracts were concentrated to a final volume of 50 µL and spiked with PCDD/PCDF and PCB recovery standards in preparation for analysis.

PCB Sample Extract Analysis

The three method blank extracts (PCB MB1, PCB MB2 and PCB MB3) were analyzed for the 12 World Health Organization (WHO) toxic congeners by HRMS on a VG-Ultima (Micromass) using an SPB-Octyl (30 m x 0.25 mm x 0.25 µm) column (Supelco) following 1668A. The three OPR extracts were archived.

PCDD/PCDF Sample Extract Analysis

The three method blank extracts (DF MB1, DF MB2 and DF MB3) were analyzed by HRMS on a VG-Autospec (Micromass) using a ZB-5 (60 m x 0.32 mm x 0.25 µm) column (Phenomenex) following 1613B. The three OPR extracts were archived.

PCDD/PCDF and PCB Sample Extract Analysis

The three method blank extracts (DFP MB1, DFP MB2 and DFP MB3) and the three OPR extracts (DFP OPR1, DFP OPR2 and DFP OPR3) were analyzed by HRMS using the same columns and methods listed above. The OPR results are not presented here.

Results and Discussion

The method blank results and internal standard percent recoveries for PCBs are shown in Tables 1A and 1B, respectively, and the method blank results and internal standard recovery summaries for PCDD/PCDF are shown in Tables 2A and 2B, respectively. Only analytes which were detected are listed in Tables 1A and 2A.

Table 1A: PCB Method Blank Results (pg/extract)

	PCB MB1	PCB MB2	PCB MB3	DFP MB1	DFP MB2	DFP MB3
PCB-81	--	5.8	--	--	--	--
PCB-77	--	3.8	--	--	--	--
PCB-123	--	4.0	--	--	--	--
PCB-118	10.4	--	--	--	--	--
PCB-114	--	4.0	--	--	--	--
PCB-105	2.8	4.2	3.0	--	--	--
PCB-167	--	1.6	--	--	--	--
PCB-156/157	4.0	2.4	--	--	--	--
PCB-169	9.0	8.6	6.8	4.4	3.2	3.0
PCB-189	10.8	10.0	9.8	6.6	4.0	3.2

-- = not detected.

Table 1B: PCB Internal Standard Recovery (%)

	PCB MB1	PCB MB2	PCB MB3	DFP MB1	DFP MB2	DFP MB3
Lowest Recovery	23	22	19	22	19	20
Highest Recovery	33	32	31	35	32	33
Average Recovery	27	26	25	28	26	27

Table 2A: PCDD/PCDF Method Blank Results (pg/extract)

	DF MB1	DF MB2	DF MB3	DFP MB1	DFP MB2	DFP MB3
1,2,3,7,8-PeCDD	--	--	0.12	--	--	--
OCDD	1.22	--	--	--	--	--
1,2,3,7,8-PeCDF	0.18	--	--	--	--	--
1,2,3,4,7,8-HxCDF	--	--	--	--	0.56	--
1,2,3,6,7,8-HxCDF	--	--	--	--	--	0.27
1,2,3,7,8,9-HxCDF	--	--	--	--	--	0.38
OCDF	0.69	0.59	0.44	2.68	--	--

-- = not detected.

Table 2B: PCDD/PCDF Internal Standard Recovery (%)

	DF MB1	DF MB2	DF MB3	DFP MB1	DFP MB2	DFP MB3
Lowest Recovery	74	83	80	97	88	91
Highest Recovery	108	115	117	121	117	115
Average Recovery	89	94	95	108	104	105

These results show that there is little contamination for either PCB or PCDD/PCDF analytes regardless of the configuration of high and low level concentration samples in the parallel evaporator or the configuration of high and low volume samples. There was little loss of the PCDD/PCDF internal standards during the multiple concentration steps (Table 2B), but substantial loss of the PCB internal standards (Table 1B). The addition of a nonane keeper during PCB concentration steps did not improve PCB internal standard recovery. These data indicate that using parallel evaporation in place of the traditional concentration techniques may be acceptable for PCDD/PCDF sample preparation; however, for PCB analyses it may lead to low internal standard recoveries that potentially do not meet Method 1668A criteria. The Büchi Syncore Analyst parallel evaporation apparatus has undergone modification since this study was conducted. An additional module is available that is intended to improve PCB recovery. This module has not yet been evaluated by our laboratory.

References

1. U.S. EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, (1999), EPA-821-R-00-002 Office of Water.

2. U.S. EPA Method 1613, Revision B: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, (1994), EPA 821-B94-0059. Office of Water, Engineering and Analysis Division.