COMPARISON OF ASE AND SOXHLET TECHNIQUES IN SIMULTANEOUS EXTRACTIONS OF PCDD/PCDF AND PCBS FOR A PAPER SLUDGE MATRIX

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Introduction

Paper sludge is a waste material from preparing paper pulp by chemical or mechanical means from various materials (mostly from wood) and used in making paper and cellulose products. In the United States more and more paper sludge is made from recycled paper products.[1]Extraction using the Soxhlet technique has been the traditional method used in the analysis of this matrix for polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/PCDF) and poly chlorinated biphenyls (PCBs).[2,3,4] The many advantages of using the Accelerated Solvent Extraction (ASE) technique to replace Soxhlet extractions have been well described in many publications. Among these advantages is a decreased extraction time that uses far fewer amounts of solvents.[5,6] In order to maximize this advantage of the ASE method, a single ASE extraction method has been developed for the simultaneous extraction of PCDD/PCDF and PCBs in tissue, soil, sediment and municipal sludge.[6] This method was modified slightly for use in this evaluation.Using this ASE method and a well established Soxhlet extraction method[2] a direct comparison was performed on extracting PCDD/PCDF and PCBs simultaneously from paper sludge made from recycled paper products. This paper describes the methods, results, and conclusions from taking a single homogenized paper sludge sample and extracting six 20-g aliquots, three using the ASE extraction method and three using the Soxhlet extraction method. Along with each triplicate set a method blank, laboratory control spike, and a standard reference material were also extracted to ensure that established quality control criteria were met.

Methods and Materials

ASE Extraction

Three 20-g aliquots of homogenized paper sludge were weighed into jars and spiked with a mixture of $^{13}C_{12}$-labeled PCDD/PCDF and PCB (Cambridge Isotope Laboratories (CIL) EDF-8999 and EC-4977, respectively). After spiking, the samples were dried with at least 3 grams of hidromatrix (Varian 0019-8003). Once dry the samples were packed into individual 33-mL extraction cells containing a Dionex ASE 200 filter, 5 grams of basic alumina (Sigma, type WB-2, Basic) and another Dionex ASE 200 filter. Any remaining space in the extraction cell was filled with hidromatrix and the samples were capped. The samples were extracted using a Dionex ASE 200 at the conditions for ASE extraction listed in Table 1 with dichloromethane (DCM) as the extraction solvent.

Soxhlet Extraction

Three 20-g aliquots of homogenized paper sludge were weighed into jars and were dried with 8 to 10 grams of hidromatrix (Varian 0019-8003). After dying the samples were loaded into a pre-extracted glass fritted thimble containing 2 to 3 grams activated silica (Fisher, type 60A, 100-200 mesh) and spiked with a mixture of $^{13}C_{12}$-labeled PCDD/PCDF and PCB (CIL EDF-8999 and EC-4977, respectively). After spiking, the samples were held in the thimble by pre-extracted glass-wool and loaded into a pre-extracted Soxhlet apparatus. The samples were extracted using the conditions for Soxhlet extraction listed in Table 1 with toluene as the extraction solvent.

Extract Clean Up

After extraction the ASE and Soxhlet extracts were dried with sodium sulfate, the Soxhlet extracts were solvent exchanged into DCM, both sets of extracts were processed through a gel permeation column (GPC), followed by acid / base silica columns and then fractionated during carbon column cleanup. The PCDD/PCDF extract fractions were concentrated to a final volume of 20 µL and spiked with PCDD/PCDF recovery standard (CIL EDF-5999). The

PCB extract fractions were concentrated to a final volume of 200 µL and spiked with PCB recovery standard (CIL EC-4979.)

Table 1. Extraction Conditions for ASE and Soxhlet

ASE Conditions	Soxhlet Conditions
Pressure (psi) at 2000	Siphon (/hr) at 5 or more
Temperature (ºC) at 125	Solvent 100 % Toluene
Static Time (min) at 10	Extraction Time (hrs) at 18
Flush Volume (%) at 60	
Purge Time (sec) at 120	
Number of Static Cycles at 3	
Solvent 100 % DCM	

Sample Analysis

PCDD/PCDF and PCB extracts were analyzed by HRMS on a VG-Autospec (Micromass) using an DB-5 (60 m x 0.32 mm x 0.25 µm) column (J&W Scientific) following general procedures in U.S. EPA Method 1613, Revision Band on a VG-Ultima (Micromass) using an SPB-Octyl (30 m x 0.25 mm x 0.25 µm) column (Supelco) following general procedures in U.S. EPA Method 1668, Revision A, respectively. A DB-225 (30 m x 0.32 mm x 0.25 µm) column (J&W Scientific) was used for second column confirmation of 2,3,7,8-TCDF. All results have been adjusted for the sample percent dry weight (35%).

Results and Discussion

PCDD/PCDF

The results listed in Table 2 demonstrate good precision of each extraction method with the Percent Relative Standard Deviation (RSD) ranging from 2 to 33% for the Soxhlet approach and 0 to 27% for the ASE approach. For both techniques, analyte concentrations generating RSD values greater than 20% were detected below the calibration range. The results listed in Table 3 show good agreement between Soxhlet and ASE extractions of PCDD/PCDF from paper sludge. The Relative Percent Difference (RPD) of the two extraction method average results ranged from 5 to 42%. The PeCDD and PeCDF compounds had the highest RPD most likely because not all concentrations found in each replicate were above the lowest calibration point. All other compounds were within the 25% RPD requirement in SW-846 Method 8290 (Section, 8.3.5.1.1)[2] and ranged from 1 to 22%. The low RPD between the two extraction methods shows that the ASE method as described would be acceptable as a substitution for Soxhlet extraction of PCDD/PCDF from recycled paper sludge.

Table 2: PCDD/PCDF Analysis Results (pg/g dry) and Percent Relative Standard Deviation of Replicates (RSD)

Analyte	Sox1	Sox2	Sox3	RSD (%)	ASE1	ASE2	ASE3	RSD (%)
2378-TCDD	0.64	0.62	0.66	**3**	0.53	0.53	0.48	**6**
12378-PeCDD	0.24	0.19	0.12	**33**	0.12	0.12	0.12	**0**
123478-HxCDD	0.16	0.12	0.14	**14**	0.13	0.16	0.15	**10**
123678-HxCDD	1.87	1.74	1.84	**4**	1.43	1.55	1.41	**5**
123789-HxCDD	0.71	0.82	0.78	**7**	0.61	0.71	0.76	**11**
1234678-HpCDD	44.4	40.3	38.0	**8**	32.4	33.7	32.3	**2**
OCDD	721	669	627	**7**	573	614	589	**3**
2378-TCDF	5.10	5.06	5.29	**2**	4.58	4.51	4.80	**3**
12378-PeCDF	0.32	0.31	0.20	**24**	0.18	0.23	0.20	**12**
23478-PeCDF	0.33	0.33	0.25	**15**	0.17	0.19	0.25	**20**
123478-HxCDF	0.49	0.38	0.39	**14**	0.40	0.48	0.32	**20**
123678-HxCDF	0.13	0.15	0.14	**7**	0.12	0.11	0.11	**5**
123789-HxCDF	--	--	--	**NA**	--	--	--	**NA**
234678-HxCDF	0.14	0.09	0.13	**22**	0.14	0.09	0.09	**27**
1234678-HpCDF	13.5	11.8	11.2	**10**	12.0	13.6	12.4	**6**
1234789-HpCDF	0.49	0.38	0.35	**18**	0.53	0.42	0.38	**18**
OCDF	62.2	54.2	50.9	**10**	53.8	56.7	54.8	**3**

Table 3: Relative Percent Difference (RPD) of PCDD/PCDF Average Results (pg/g dry)

Analyte	Sox Ave	ASE Ave	RPD (%)	Analyte	Sox Ave	ASE Ave	RPD (%)
2378-TCDD	0.64	0.51	**22**	2378-TCDF	5.15	4.63	**11**
12378-PeCDD	0.18	0.12	**42**	12378-PeCDF	0.28	0.20	**31**
123478-HxCDD	0.14	0.15	**5**	23478-PeCDF	0.30	0.20	**39**
123678-HxCDD	1.82	1.46	**22**	123478-HxCDF	0.42	0.40	**5**
123789-HxCDD	0.77	0.69	**10**	123678-HxCDF	0.14	0.11	**21**
1234678-HpCDD	40.9	32.8	**22**	123789-HxCDF	--	--	**NA**
OCDD	672	592	**13**	234678-HxCDF	0.12	0.11	**12**
				1234678-HpCDF	12.1	12.7	**4**
				1234789-HpCDF	0.41	0.44	**9**
				OCDF	55.8	55.1	**1**

PCBs

The PCB extracts were analyzed for all 209 PCBs with the results being summed into total PCB and individual homologs for use in this paper. The results listed in Table 4 demonstrate very good precision of both extraction methods with the RSD ranging from 5 to 15% for the Soxhlet approach and 2 to 9% for the ASE approach. The results listed in Table 5 show a very good correlation between Soxhlet and ASE extractions of PCBs from paper sludge. The RPD of the two extraction method average results ranged from 1 to 19%. The very low RPD between the two extraction methods demonstrate that the ASE extraction method as described would be an acceptable replacement for Soxhlet extraction of PCBs from recycled paper sludge.

Table 4: PCB Analysis Results (ng/g dry) and Percent Relative Standard Deviation of Replicates (RSD)

Analyte	Sox 1	Sox2	Sox3	RSD (%)	ASE1	ASE2	ASE3	RSD (%)
Total MoCB	2.93	2.76	2.57	**7**	2.70	2.64	2.54	**3**
Total DiCB	26.1	21.0	19.6	**15**	22.1	21.2	20.0	**5**
Total TriCB	91.5	87.8	70.8	**13**	76.8	84.4	83.4	**5**
Total TeCB	135	123	116	**7**	103	109	96.5	**6**
Total PeCB	36.1	32.4	32.0	**7**	30.3	31.6	30.3	**2**
Total HxCB	11.6	10.5	11.2	**5**	9.63	10.9	11.4	**9**
Total HpCB	3.47	3.16	2.77	**11**	3.20	3.15	3.24	**2**
Total OcCB	1.30	1.15	1.10	**9**	1.24	1.16	1.20	**3**
Total NoCB	0.30	0.26	0.25	**9**	0.28	0.27	0.28	**2**
Total DeCB	0.07	0.06	0.06	**8**	0.06	0.06	0.06	**3**
Total PCB	308	282	257	**9**	249	265	249	**4**

Table 5: Relative Percent Difference (RPD) of PCB Average Results (ng/g dry)

Analyte	Sox Ave	ASE Ave	RPD	Analyte	Sox Ave	ASE Ave	RPD
Total MoCB	2.75	2.63	**5**	Total HpCB	3.13	3.20	**2**
Total DiCB	22.2	21.1	**5**	Total OcCB	1.18	1.20	**1**
Total TriCB	83.4	81.5	**2**	Total NoCB	0.27	0.28	**2**
Total TeCB	125	103	**19**	Total DeCB	0.06	0.06	**7**
Total PeCB	33.5	30.7	**9**	Total PCB	282	254	**10**
Total HxCB	11.1	10.7	**4**				

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