Extraction of Chlorinated Compounds by Accelerated Solvent Extraction (ASE)

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Abstract
Accelerated solvent extraction (ASE) applies temperature and pressure to accelerate extraction processes and improve the efficiency of solvent extraction. This paper reports the results of a study to compare the results obtained with Soxhlet to those obtained by ASE for various samples containing PCDDs and PCDFs. Contaminated soils and sediments were extracted by ASE and Soxhlet. A review of the data indicates that ASE gives essentially equivalent data to Soxhlet extraction. However, ASE extractions are performed in less time and with less solvent (about 15 mL and less than 15 min for 10-g samples) than by the classical extraction techniques.

1. Introduction

Organic solvents required to extract solid samples can comprise the largest source of waste in the environmental analysis laboratory. Typical solvent volumes can range from 50 mL to over 400 mL per sample analysis procedure when using the solvent intensive methods described under SW-846: Method 3510 (separatory funnel), 3540 (Soxhlet), 3541 (automated Soxhlet) and 3550 (ultrasonic extraction).

A new extraction technique, accelerated solvent extraction (ASE) has recently been introduced[1)]. This technique uses conventional liquid solvents at elevated pressures (1500-2000 psi) and temperatures (50-200°C) to extract solid samples quickly, and with much less solvent than conventional techniques. With ASE, a solid sample is enclosed in a stainless steel vessel which is filled with an extraction solvent and heated to temperature. The sample is allowed to statically extract in this configuration for 5-10 minutes, with the expanding solvent vented to a collection vial. Following this period, compressed nitrogen is used to purge the remaining solvent into the same vial. The entire procedure is completed in 12-17 minutes per sample, and uses approximately 15 mL of solvent for a ten gram sample. ASE takes advantage of the increases in analyte solubilities which occur at temperatures above the boiling points of commonly used solvents. At the higher temperatures used by ASE, the kinetic processes for the desorption of analytes from the matrix are accelerated compared to the conditions when solvents at room temperature are used. Solvent usage is reduced as a result of the higher analyte solubility in the heated

solvent. ASE has been approved by the USEPA as proposed Method 3545 which includes polychlorinated biphenyls (PCBs), organochlorine and organophosphorus pesticides (OCP and OPP), semi-volatiles or BNAs, chlorinated phenoxy herbicides and polycyclic aromatic hydrocarbons (PAH)[1-3].

In this study, data will shown from the extraction of various sediment samples contaminated with PCDDs and PCDFs. The data show that ASE is equivalent to classical extraction methods.

2. Experimental

A sediment sample (EC-2) containing high ppt levels of PCDDs and PCDFs was obtained from the National Water Research Institute (867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario, L7R 4A6). A low-level sediment sample (HS-2) was obtained from the National Research Council Institute for Marine Biosciences (1411 Oxford Street, Halifax, Nova Scotia, B3H 3Z1). Both samples are being investigated as potential standard reference materials and were used as received.

All extractions by ASE were performed at 2000 psi and 150°C with toluene as the solvent. Approximately 15 mL of solvent were used for each sample, and the extraction time was 15 minutes per sample. Stainless steel extraction vessels with internal volumes of 11 mL were used. The extraction method was designed so that the vessel containing the sample was pre-filled with solvent, and then allowed to heat and extract statically for a total elapsed time of 10 minutes. The static valve was controlled so that it opened briefly when the cell pressure exceeded 2200 psi. The solvent that was expelled during this valve opening was routed to the collection vial.

Following the combined heat-up and static extraction period, the static valve was opened, and fresh extraction solvent was introduced for a period of 10-15 seconds (approximately 8 mL), followed by a purge with nitrogen gas at 150 psi. Additional information on the operation of ASE are reported in separate papers[1),2)].

Sample extracts were analyzed by GC/MS/MS (Varian 3400 GC, Finnigan MAT TSQ 70 triple quadrupole mass spectrometer, and an ICIS II data system) or GC/HRMS (Hewlett-Packard 5890 Series II GC, VG Autospec at 10,000 resolution, and an OPUS data system). All samples were chromatographed using a 60m x 0.25 mm i.d. x 0.25 μm film thickness J&W DB-5 fused silica capillary column.

Standard PCDD/PCDF mixtures were prepared from stock solutions obtained from either Cambridge Isotope Laboratories, Inc. or Wellington Laboratories. The internal quantitation standard contained 15 $^{13}C_{12}$ 2,3,7,8-substituted PCDDs and PCDFs (see Table 1 for specific congeners). Following extraction, the samples were spiked with a clean-up standard ($^{37}Cl_4$-2,3,7,8-T_4CDD) in order to differentiate between loses occurring at the extraction and clean-up stages. Prior to injection, the samples were reconstituted with a recovery standard solution containing $^{13}C_{12}$ -1,2,3,4-T_4CDD and $^{13}C_{12}$ -1,2,3,7,8,9-H_6CDD at 100 pg/μL in nonane.

Sample extracts were cleaned-up using a dual stage open column chromatography procedure consisting of modified silica and alumina stationary phases. Samples were further cleaned-up using an automated HPLC carbon-based method to remove diphenylether interferences. Complete details of the analytical procedure are available elsewhere[4].

3. Results and Discussion

A comparison of average results (in ppt) for the Soxhlet and accelerated solvent extraction of the high-level soil sample (EC-2) is presented in Table 1. With a few exceptions, the data compare very favorably. Discrepancies were found to exist mostly with the group total data. For example, despite having found more isomers in the T_4CDF and P_5CDF congener groups via ASE, the total values were appreciably lower than the Soxhlet-based data. These differences may be attributable to sample inhomogeneity. The surrogate recoveries for the two techniques (averaged over the entire data set) were 78% via Soxhlet and 70% using ASE. Loses arises from the clean-up processes were predictably the same (54% average clean-up standard recovery for the Soxhlet data and 63% for the ASE data). The correspondence for the 2,3,7,8-substituted isomers in Table 1 is excellent.

The data for sample HS-2 show similar trends (Table 2). Poorer correspondence is typically observed with the group total data, despite have identified more isomers when using ASE extraction (e.g. P_5CDD). The 2,3,7,8-substituted isomers are once again in excellent agreement. Average surrogate recoveries were 75% using Soxhlet and 73% using ASE. Clean-up standard recoveries were 56% (Soxhlet) and 66% (ASE).

Another evaluation of the ASE technique was attempted using two soil samples containing high levels of co-extractables and oil (Table 3). Aliquots of these samples were taken from a larger container as quantitatively as possible but were not nearly as homogeneous as the rigorously prepared reference materials. Recoveries were outside of control limits (25 to 150%) for T_4CDF and P_5CDF Hamilton Harbour ASE data, which likely accounts for the differences in these data points when compared to the Soxhlet extraction. Similar differences in the group total data were observed for the Parrots Bay samples (e.g. T_4CDF), but no recovery-related problems were observed in this case.

4. Conclusions

The data show that ASE is essentially equivalent to classical extraction procedures such as Soxhlet for the extraction of PCDDs and PCDFs from sediments. As an extraction technique, ASE shows great promise because of its applicability to a wide variety of compound classes.

TABLE 1: Average Values (ppt) from EC-2
Comparison of Soxhlet versus Accelerated Solvent Extraction

	Soxhlet Extraction (n=10)			Accelerated Solvent Extraction (n=2)		
Group Totals	Value	% RSD	Isomers	Value	% RSD	Isomers
Total T_4CDD	430	9.7	8	370	1.9	9
Total P_5CDD	300	3.7	11	280	7.7	11
Total H_6CDD	720	5.8	7	690	2.0	7
Total H_7CDD	1300	7.0	2	1300	0.0	2
Total O_8CDD	4000	6.2	1	4200	0.0	1
Total T_4CDF	620	12	17	380	19	19
Total P_5CDF	820	9.4	14	710	7.0	17
Total H_6CDF	1900	5.7	12	1900	0.0	13
Total H_7CDF	3800	8.2	4	3900	3.6	4
Total O_8CDF	7800	8.3	1	7000	3.1	1
2,3,7,8-substituted isomers	Value	% RSD	% Recovery*	Value	% RSD	% Recovery*
2,3,7,8-T_4CDD	270	9.1	68	270	0.0	72
1,2,3,7,8-P_5CDD	24	12	74	22	3.3	81
1,2,3,4,7,8-H_6CDD	23	8.3	76	24	3.0	80
1,2,3,6,7,8-H_6CDD	83	3.6	78	87	0.8	54
1,2,3,7,8,9-H_6CDD	60	6.2	77	57	7.4	67
1,2,3,4,6,7,8-H_7CDD	720	6.7	81	720	1.0	79
2,3,7,8-T_4CDF**	100	7.3	68	82	2.6	70
1,2,3,7,8-P_5CDF	39	14	74	36	3.9	76
2,3,4,7,8-P_5CDF	62	5.5	79	60	0.0	75
1,2,3,4,7,8-H_6CDF	740	5.3	81	690	0.0	70
1,2,3,6,7,8-H_6CDF	120	6.2	81	120	0.0	50
2,3,4,6,7,8-H_6CDF	45	9.0	82	60	1.2	69
1,2,3,7,8,9-H_6CDF	4.9	31	84	5.3	15	70
1,2,3,4,6,7,8-H_7CDF	2600	6.7	85	2500	0.0	74
1,2,3,4,7,8,9-H_7CDF	160	5.5	83	160	0.0	72

Values are corrected for recovery of ^{13}C- labeled surrogates.
* Refers to recovery of corresponding ^{13}C-labeled surrogate.
** Maximum possible concentration due to potential chromatographic overlap.

TABLE 2: Average Values (ppt) from HS-2
Comparison of Soxhlet versus Accelerated Solvent Extraction

	Soxhlet Extraction (n=4)			Accelerated Solvent Extraction (n=2)		
Group Totals	Value	% RSD	Isomers	Value	% RSD	Isomers
Total T_4CDD	3.9	14	2	2.5	34	5
Total P_5CDD	17	7.8	6	10	10	9
Total H_6CDD	510	5.6	8	570	1.3	7
Total H_7CDD	4700	8.3	2	5100	11	2
Total O_8CDD	6500	4.2	1	7100	0.0	1
Total T_4CDF	39	11	13	24	3.0	14
Total P_5CDF	33	13	8	28	0.0	11
Total H_6CDF	89	3.2	6	87	12	10
Total H_7CDF	293	3.3	4	310	0.0	4
Total O_8CDF	300	3.8	1	280	2.6	1
2,3,7,8-substituted isomers	Value	% RSD	% Recovery*	Value	% RSD	% Recovery*
2,3,7,8-T_4CDD	ND(1)		62	ND(1)		71
1,2,3,7,8-P_5CDD	1.6	4.6	69	ND(1)		75
1,2,3,4,7,8-H_6CDD	4.5	4.8	74	5.2	11	73
1,2,3,6,7,8-H_6CDD	19	4.3	75	21	0.0	50
1,2,3,7,8,9-H_6CDD	24	4.3	74	28	2.6	61
1,2,3,4,6,7,8-H_7CDD	1200	8.1	80	1300	0.0	93
2,3,7,8-T_4CDF**	8.5	11	62	6.6	5.4	65
1,2,3,7,8-P_5CDF	1.9	17	68	2.0	0.0	72
2,3,4,7,8-P_5CDF	3.7	7.9	71	3.7	3.8	59
1,2,3,4,7,8-H_6CDF	17	7.3	79	17	4.3	70
1,2,3,6,7,8-H_6CDF	3.7	5.6	80	4.0	5.4	49
2,3,4,6,7,8-H_6CDF	3.7	18	81	4.4	3.2	61
1,2,3,7,8,9-H_6CDF	ND(1)		83	ND(1)	0.0	75
1,2,3,4,6,7,8-H_7CDF	91	1.6	83	96	3.7	82
1,2,3,4,7,8,9-H_7CDF	5.2	6.7	84	5.3	6.7	83

ND=not detected. Detection limit, in ppt, given in brackets. Values not used for statistical calculations.
Values are corrected for recovery of ^{13}C- labeled surrogates.
* Refers to recovery of corresponding ^{13}C-labeled surrogate.
** Maximum possible concentration due to potential chromatographic overlap.

TABLE 3: Average Values (ppt) from Highly Contaminated Sources Comparison of Soxhlet versus Accelerated Solvent Extraction

	HEAVILY CONTAMINATED SOIL SAMPLES			
	HAMILTON HARBOUR		PARROTS BAY	
	Soxhlet	ASE	Soxhlet	ASE
T_4CDD	50^5	14^2	39^3	48^5
P_5CDD	63^{12}	15^5	87^{10}	66^{10}
H_6CDD	220^7	180^7	230^6	200^7
H_7CDD	850^2	810^2	580^2	530^2
O_8CDD	3100	3100	1900	1600
T_4CDF	370^{17}	130^{11}*	400^{14}	270^{18}
P_5CDF	290^{13}	110^{11}*	180^8	170^{13}
H_6CDF	240^{14}	160^{11}	230^6	230^{10}
H_7CDF	350^4	290^4	400^4	360^4
O_8CDF	270	210	510	370
	2,3,7,8-substituted isomers			
2,3,7,8-T_4CDD	3.7	3.1	19	19
1,2,3,7,8-P_5CDD	5.1	5.4	8.3	6.0
1,2,3,4,7,8-H_6CDD	6.4	7.2	8.6	6.7
1,2,3,6,7,8-H_6CDD	27	26	26	17
1,2,3,7,8,9-H_6CDD	20	28	24	18
1,2,3,4,6,7,8-H_7CDD	460	430	280	250
2,3,7,8-T_4CDF**	61	44*	80	48
1,2,3,7,8-P_5CDF	14	14	ND(20)	9.8
2,3,4,7,8-P_5CDF	26	25*	22	14
1,2,3,4,7,8-H_6CDF	27	37	79	59
1,2,3,6,7,8-H_6CDF	17	16	ND(20)	15
2,3,4,6,7,8-H_6CDF	14	14	21	11
1,2,3,7,8,9-H_6CDF	ND(2)	1.6	4.9	ND(1)
1,2,3,4,6,7,8-H_7CDF	130	130	270	220
1,2,3,4,7,8,9-H_7CDF	14	13	17	12

All concentrations expressed in ppt (parts-per-trillion; picograms (10^{-12} grams) of PCDD/PCDF per gram of sample).
Values are corrected for recovery of isotopically labeled surrogate standards.
* Recoveries outside the range 25% to 150%; results are not to be used for regulatory compliance purposes.
"ND" Not detected. Detection limit in ppt given in brackets ( ).
Superscripts indicate the number of isomers detected.
** Maximum possible concentration due to potential chromatographic overlap.

5. References

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