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Extraction of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans from Environmental Samples Using Accelerated Solvent Extraction (ASE)

Meets the requirements of U.S. EPA Method 3545

INTRODUCTION

Regulatory agencies are concerned with the high toxicity of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); great efforts are expended to monitor their presence in environmental samples. The low concentrations at which these compounds are regulated and the strength of their binding to certain matrices pose special challenges to analytical chemists. The most commonly used extraction procedure is Soxhlet extraction. It is time-consuming (typically 18 to 36 h) and requires large volumes of solvent (250 to 500 mL). An alternative method is warranted.

Accelerated Solvent Extraction (ASE[®]) is equivalent to U.S. EPA Methods 3540, 3541, and 8150 for the extraction of organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs), semivolatiles or base, neutral, acids (BNA), chlorinated herbicides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). ASE complies with U.S. EPA Method 3545 for these compounds. ASE is a technique that uses liquid solvents at elevated temperatures and pressures. These conditions allow extractions to take place in short periods of time with small solvent volumes as compared to conventional techniques such as sonication and Soxhlet extraction. For example, a 10 gram sample can typically be extracted by ASE in less than 15 min with less than 15 mL of solvent as compared to several hours and several hundred milliliters of solvent with Soxhlet. ASE has been applied to the extraction of PCDDs and PCDFs from ground chimney brick, urban dust, fly ash, and sediment samples; the results are reported here.

EQUIPMENT

Dionex ASE 200 Accelerated Solvent Extractor*
Gas chromatograph (GC) equipped with mass spectrometer (MS) (low resolution or high resolution MS-MS)

Low pressure LC system for sample cleanup
Preparative HPLC for sample cleanup

**ASE 150 and 350 can be used for equivalent results.*

SOLVENTS

Toluene, pesticide grade
Acetic acid, reagent grade
Hydrochloric acid, reagent grade
All solvents are available from Fisher Scientific.

SAMPLE INFORMATION

Two sample sets were investigated: one from Germany that included chimney brick, urban dust, and fly ash, and a second from Canada that included four sediment samples. A sediment sample (EC-2) containing high ng/kg levels (ppt) of PCDDs and PCDFs was obtained from the National Water Research Institute (867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario, L7R 4A6, Canada). 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, Canada). Both samples are being investigated as potential standard reference materials and were used as received. Two other sediment samples (Parrots Bay and Hamilton Harbor) were extracted. Both have high levels of coextractable materials.

EXTRACTION CONDITIONS

Table 1 lists the conditions used for the extraction of the chimney brick and urban dust by Soxhlet and ASE.

| Table 1. Extraction Conditions for Chimney Brick and Urban Dust | | |
|--|-----------------|--------------------------------|
| Condition | Soxhlet | ASE* |
| Sample Size | 4–10 g | 4–10 g |
| Solvent | Toluene, 250 mL | Toluene, 15 mL |
| Temperature | <111 °C | 150 °C |
| Pressure | Atmospheric | 1500 psi** |
| Time | 18 h | 5 min heat-up, 5 min static |
| Analytical | GC-MS | GC-MS |

*Duplicate extractions were performed on each sample and are totaled in the results.

**Pressure studies show that 1500 psi is the optimum extraction pressure for all ASE applications.

The procedure for the extraction of fly ash was slightly different than the procedure for the other matrices. Before solvent extraction, the samples were treated with 6 M HCl for 30 min and then rinsed thoroughly with distilled water. The extractions by both Soxhlet and ASE were then performed as listed in Table 1. One additional set of extractions was performed on fresh fly ash samples. Instead of pretreatment with HCl, (5% (v/v) glacial acetic acid was added to the toluene for the ASE extraction. All other conditions were held constant.

The extraction conditions for the sediment samples were changed slightly from those used for the chimney brick and urban dust. Instead of doing two separate extractions on each sample and combining the results, the method was changed to have a double static extraction period. With this method, the complete extraction time was about 17 min, and with the double extractions, the total time was close to 22 min. All other conditions were identical to those listed in Table 1.

QUANTITATION

Sample Cleanup

Cleanup of the chimney brick, urban dust, and fly ash sample extracts was performed by using a chromatographic column packed with multiple layers of silica gel and alumina, in accordance with the German method VDI 3499.

Extracts from the sediment samples 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.¹

Analysis by GC/MS and GC/MS/MS

Extracts of the chimney dust, urban dust, and fly ash samples were analyzed by GC-LRMS. The column used for the chromatography was a 60 m × 0.25 mm i.d. × 0.15 μm film thickness Dioxin column.

Sediment sample extracts were analyzed by GC/MS/MS or GC/HRMS. All extracts were separated using a 60 m × 0.25 mm i.d. × 0.25 mm film thickness fused-silica capillary column.

Standards

An internal standard solution containing 10 reference compounds including ¹³C₁₂-2,3,7,8-T₄CDD was used for the chimney dust, urban dust, and fly ash samples. No cleanup standard was used. Samples were reconstituted with a recovery standard solution (100 μL) containing ¹³C₁₂-1,2,3,4-T₄CDD at 25 ng/mL.

For the sediment samples, 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 ¹³C₁₂-2,3,7,8-substituted PCDDs and PCDFs. The compounds used are those congeners listed in the data tables. Following extraction, the samples were spiked with a cleanup standard (³⁷C₁₄-2,3,7,8-T₄CDD) in order to differentiate between losses occurring at the extraction and cleanup stages. Prior to injection, the samples were reconstituted with a recovery standard solution (10 μL) containing ¹³C₁₂-1,2,3,4-T₄CDD and ¹³C₁₂-1,2,3,7,8,9-H₆CDD at 100 pg/μL in nonane.

RESULTS AND DISCUSSION

Ground Chimney Brick and Urban Dust

Tables 2 and 3 show the results from the ground chimney brick and urban dust as selected congeners and as the total of the isomers. The toxicity equivalent is calculated by adding the weighted factors of each isomer's toxicity.

One is calculated according to a formula from the North Atlantic Treaty Organization (NATO) and the other is from the German health organization BgVV. As can be seen, ASE shows equivalency to the Soxhlet method for recovery of these compounds.

Fly Ash

The results from the extractions of the fly ash are listed in Table 4. The units for this sample are $\mu\text{g}/\text{kg}$ because the sample was so highly contaminated. ASE results are equivalent to those from Soxhlet extractions when the HCl/water pretreatment was used.

Table 5 shows the data from the fly ash extractions when

Table 2. Average Values (ng/kg) from Ground Chimney Brick—Comparison of Soxhlet vs. ASE

| Group Totals | Soxhlet (n=1) | ASE ^a (n=2) |
|--|---------------|------------------------|
| Total T ₄ CDD | 440 | 530 |
| Total P ₅ CDD | 900 | 940 |
| Total H ₆ CDD | 1800 | 2000 |
| Total H ₇ CDD | 2000 | 2100 |
| Total O ₈ CDD | 2900 | 2600 |
| Total T ₄ CDF | 2300 | 2600 |
| Total P ₅ CDF | 4100 | 4300 |
| Total H ₆ CDF | 4700 | 4700 |
| Total H ₇ CDF | 2800 | 2600 |
| Total O ₈ CDF | 2000 | 2000 |
| Congeners | Soxhlet (n=1) | ASE ^a (n=2) |
| 2,3,7,8-T ₄ CDD | 6.0 | 6.0 |
| 1,2,3,7,8-P ₅ CDD | 52 | 57 |
| 1,2,3,4,7,8-H ₆ CDD | 46 | 52 |
| 1,2,3,6,7,8-H ₆ CDD | 120 | 130 |
| 1,2,3,7,8,9-H ₆ CDD | 97 | 1000 |
| 1,2,3,4,6,7,8-H ₇ CDD | 1000 | 820 |
| 2,3,7,8-T ₄ CDF | 160 | 180 |
| 1,2,3,7,8(+1,2,3,4,8)-P ₅ CDF | 430 | 470 |
| 2,3,4,7,8-P ₅ CDF | 390 | 390 |
| 1,2,3,4,7,8(+1,2,3,4,7,9)-H ₆ CDF | 1100 | 1100 |
| 1,2,3,6,7,8-H ₆ CDF | 540 | 570 |
| 2,3,4,6,7,8-H ₆ CDF | 400 | 360 |
| 1,2,3,7,8,9-H ₆ CDF | 42 | 42 |
| 1,2,3,4,6,7,8-H ₇ CDF | 2100 | 2000 |
| 1,2,3,4,7,8,9-H ₇ CDF | 140 | 120 |
| Toxicity equivalent (NATO) | 540 | 540 |
| Toxicity equivalent (BgVV) | 490 | 510 |

Values are corrected for recovery of ¹³C-labeled surrogates.
^aSum of two extractions of each sample.

Table 3. Average Values (ng/kg) from Urban Dust—Comparison of Soxhlet vs. ASE

| Group Totals | Soxhlet (n=1) | ASE ^a (n=2) |
|--|---------------|------------------------|
| Total T ₄ CDD | 182 | 325 |
| Total P ₅ CDD | 175 | 221 |
| Total H ₆ CDD | 86.7 | 81.7 |
| Total H ₇ CDD | 221 | 217 |
| Total O ₈ CDD | 445 | 314 |
| Total T ₄ CDF | 333 | 419 |
| Total P ₅ CDF | 146 | 179 |
| Total H ₆ CDF | 65.9 | 122 |
| Total H ₇ CDF | 13.2 | 29.4 |
| Total O ₈ CDF | n.d. (10) | n.d. (10) |
| Congeners | Soxhlet (n=1) | ASE ^a (n=2) |
| 2,3,7,8-T ₄ CDD | 3.3 | 3.2 |
| 1,2,3,7,8-P ₅ CDD | 11.8 | 13.1 |
| 1,2,3,4,7,8-H ₆ CDD | 9.8 | 8.0 |
| 1,2,3,6,7,8-H ₆ CDD | 11.5 | 9.5 |
| 1,2,3,7,8,9-H ₆ CDD | n.d. (8) | n.d. (8) |
| 1,2,3,4,6,7,8-H ₇ CDD | 113 | 107 |
| 2,3,7,8-T ₄ CDF | 12.5 | 18.6 |
| 1,2,3,7,8(+1,2,3,4,8)-P ₅ CDF | 9.9 | 12.0 |
| 2,3,4,7,8-P ₅ CDF | 13.9 | 18.1 |
| 1,2,3,4,7,8(+1,2,3,4,7,9)-H ₆ CDF | 18.7 | 23.7 |
| 1,2,3,6,7,8-H ₆ CDF | 10.7 | 15.8 |
| 2,3,4,6,7,8-H ₆ CDF | 3.3 | 8.7 |
| 1,2,3,7,8,9-H ₆ CDF | n.d. (2) | n.d. (2) |
| 1,2,3,4,6,7,8-H ₇ CDF | 13.2 | 29.4 |
| 1,2,3,4,7,8,9-H ₇ CDF | n.d. (3) | n.d. (3) |
| Toxicity equivalent (NATO) | 25.0 | 28.7 |
| Toxicity equivalent (BgVV) | 24.2 | 29.2 |

Values are corrected for recovery of ¹³C-labeled surrogates.
 n.d.=not detected. Detection limit, in ppt, given in parentheses.
^aSum of two extractions of each sample.

acetic acid was added to the toluene for the extractions by ASE. The results with the acetic acid are a little lower than with the HCl pretreatment, but the recovery is still close to 96% of that of Soxhlet, making ASE essentially identical to Soxhlet for these compounds.

Table 4. Average Values (µg/kg) from Fly Ash^a Comparison of Soxhlet vs. ASE (HCl Pretreatment)

| Group Totals | Soxhlet (n=1) | ASE ^b (n=2) |
|--|---------------|------------------------|
| Total T ₄ CDD | 12.0 | 12.4 |
| Total P ₅ CDD | 16.6 | 20.5 |
| Total H ₆ CDD | 38.2 | 42.4 |
| Total H ₇ CDD | 15.0 | 19.8 |
| Total O ₈ CDD | 11.4 | 12.8 |
| Total T ₄ CDF | 60.5 | 67.5 |
| Total P ₅ CDF | 83.5 | 87.3 |
| Total H ₆ CDF | 65.2 | 73.5 |
| Total H ₇ CDF | 28.1 | 32.2 |
| Total O ₈ CDF | 13.5 | 15.8 |
| Congeners | Soxhlet (n=1) | ASE ^b (n=2) |
| 2,3,7,8-T ₄ CDD | 0.32 | 0.36 |
| 1,2,3,7,8-P ₅ CDD | 1.6 | 2.1 |
| 1,2,3,4,7,8-H ₆ CDD | 1.2 | 1.4 |
| 1,2,3,6,7,8-H ₆ CDD | 2.4 | 2.7 |
| 1,2,3,7,8,9-H ₆ CDD | 2.4 | 2.3 |
| 1,2,3,4,6,7,8-H ₇ CDD | 8.2 | 9.6 |
| 2,3,7,8-T ₄ CDF | 3.7 | 4.3 |
| 1,2,3,7,8(+1,2,3,4,8)-P ₅ CDF | 4.2 | 4.6 |
| 2,3,4,7,8-P ₅ CDF | 5.6 | 6.6 |
| 1,2,3,4,7,8(+1,2,3,4,7,9)-H ₆ CDF | 7.8 | 8.7 |
| 1,2,3,6,7,8-H ₆ CDF | 7.2 | 8.5 |
| 2,3,4,6,7,8-H ₆ CDF | 6.6 | 7.2 |
| 1,2,3,7,8,9-H ₆ CDF | 0.43 | 0.56 |
| 1,2,3,4,6,7,8-H ₇ CDF | 18.0 | 17.6 |
| 1,2,3,4,7,8,9-H ₇ CDF | 2.3 | 2.4 |
| Toxicity equivalent (NATO) | 7.6 | 8.9 |
| Toxicity equivalent (BgVV) | 7.3 | 14.2 |

Values are corrected for recovery of ¹³C-labeled surrogates.

^aPretreatment with HCl for 30 min followed by water rinse.

^bSum of two extractions of each sample.

High-Level Sediment Samples

A comparison of average results for the Soxhlet and ASE methods for the high-level sediment sample (EC-2) is presented in Table 6. 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 T₄CDF and P₅CDF congener groups with ASE, the total values were lower than the Soxhlet-based data.

Table 5. Average Values (µg/kg) from Fly Ash^a Comparison of Soxhlet^a vs. ASE^b

| Group Totals | Soxhlet (n=1) | ASE ^c (n=2) |
|--|---------------|------------------------|
| Total T ₄ CDD | 12.0 | 10.5 |
| Total P ₅ CDD | 16.6 | 16.2 |
| Total H ₆ CDD | 38.2 | 36.7 |
| Total H ₇ CDD | 15.0 | 16.0 |
| Total O ₈ CDD | 11.4 | 10.6 |
| Total T ₄ CDF | 60.5 | 56.1 |
| Total P ₅ CDF | 83.5 | 77.4 |
| Total H ₆ CDF | 65.2 | 46.1 |
| Total H ₇ CDF | 28.1 | 26.5 |
| Total O ₈ CDF | 13.5 | 13.9 |
| Congeners | Soxhlet (n=1) | ASE ^c (n=2) |
| 2,3,7,8-T ₄ CDD | 0.32 | 0.28 |
| 1,2,3,7,8-P ₅ CDD | 1.6 | 1.7 |
| 1,2,3,4,7,8-H ₆ CDD | 1.2 | 1.2 |
| 1,2,3,6,7,8-H ₆ CDD | 2.4 | 2.4 |
| 1,2,3,7,8,9-H ₆ CDD | 2.4 | 2.2 |
| 1,2,3,4,6,7,8-H ₇ CDD | 8.2 | 8.1 |
| 2,3,7,8-T ₄ CDF | 3.7 | 3.4 |
| 1,2,3,7,8(+1,2,3,4,8)-P ₅ CDF | 4.2 | 3.9 |
| 2,3,4,7,8-P ₅ CDF | 5.6 | 5.8 |
| 1,2,3,4,7,8(+1,2,3,4,7,9)-H ₆ CDF | 7.8 | 5.4 |
| 1,2,3,6,7,8-H ₆ CDF | 7.2 | 5.3 |
| 2,3,4,6,7,8-H ₆ CDF | 6.6 | 4.5 |
| 1,2,3,7,8,9-H ₆ CDF | 0.43 | 0.30 |
| 1,2,3,4,6,7,8-H ₇ CDF | 18.0 | 16.8 |
| 1,2,3,4,7,8,9-H ₇ CDF | 2.3 | 2.0 |
| Toxicity equivalent (NATO) | 7.6 | 7.0 |
| Toxicity equivalent (BgVV) | 7.3 | 6.3 |

Values are corrected for recovery of ¹³C-labeled surrogates.

^aPretreatment with HCl for 30 min followed by water rinse for Soxhlet samples.

^bNo HCl pretreatment, and toluene/acetic acid solvent used for ASE samples.

^cSum of two extractions of each sample.

These differences may be attributable to sample heterogeneity. The surrogate recoveries for the two techniques (averaged over the entire data set) were 78% with Soxhlet and 70% using ASE. Losses arising from the cleanup processes were predictably the same (54% average cleanup standard recovery for the Soxhlet data and 63% for the ASE data). The comparison of the recovery of the specific congeners as shown in Table 6 is very good.

The data for sample HS-2 show similar trends (Table 7). The specific congeners are once again in excellent agreement for the two techniques, but the group results by ASE are lower than those by Soxhlet. Average surrogate recoveries were 75% using Soxhlet and 73% using ASE. Cleanup standard recoveries were 56% (Soxhlet) and 66% (ASE).

Table 6. Average Values (ng/kg) from EC-2—Comparison of Soxhlet vs. ASE

| Group Totals | Soxhlet Extraction (n=10) | | | Accelerated Solvent Extraction (n=2) | | |
|---|---------------------------|-------|-------------------------|--------------------------------------|-------|-------------------------|
| | Value | % RSD | Isomers | Value | % RSD | Isomers |
| Total T ₄ CDD | 430 | 9.7 | 8 | 370 | 1.9 | 9 |
| Total P ₅ CDD | 300 | 3.7 | 11 | 280 | 7.7 | 11 |
| Total H ₆ CDD | 720 | 5.8 | 7 | 690 | 2.0 | 7 |
| Total H ₇ CDD | 1300 | 7.0 | 2 | 1300 | 0.0 | 2 |
| Total O ₈ CDD | 4000 | 6.2 | 1 | 4200 | 0.0 | 1 |
| Total T ₄ CDF | 620 | 12 | 17 | 380 | 19 | 19 |
| Total P ₅ CDF | 820 | 9.4 | 14 | 710 | 7.0 | 17 |
| Total H ₆ CDF | 1900 | 5.7 | 12 | 1900 | 0.0 | 13 |
| Total H ₇ CDF | 3800 | 8.2 | 4 | 3900 | 3.6 | 4 |
| Total O ₈ CDF | 7800 | 8.3 | 1 | 7000 | 3.1 | 1 |
| Congeners | Value | % RSD | % Recovery ^a | Value | % RSD | % Recovery ^a |
| 2,3,7,8-T ₄ CDD | 270 | 9.1 | 68 | 270 | 0.0 | 72 |
| 1,2,3,7,8-P ₅ CDD | 24 | 12 | 74 | 22 | 3.3 | 81 |
| 1,2,3,4,7,8-H ₆ CDD | 23 | 8.3 | 76 | 24 | 3.0 | 80 |
| 1,2,3,6,7,8-H ₆ CDD | 83 | 3.6 | 78 | 87 | 0.8 | 54 |
| 1,2,3,7,8,9-H ₆ CDD | 60 | 6.2 | 77 | 57 | 7.4 | 67 |
| 1,2,3,4,6,7,8-H ₇ CDD | 720 | 6.7 | 81 | 720 | 1.0 | 79 |
| 2,3,7,8-T ₄ CDF ^b | 100 | 7.3 | 68 | 82 | 2.6 | 70 |
| 1,2,3,7,8-P ₅ CDF | 39 | 14 | 74 | 36 | 3.9 | 76 |
| 2,3,4,7,8-P ₅ CDF | 62 | 5.5 | 79 | 60 | 0.0 | 75 |
| 1,2,3,4,7,8-H ₆ CDF | 740 | 5.3 | 81 | 690 | 0.0 | 70 |
| 1,2,3,6,7,8-H ₆ CDF | 120 | 6.2 | 81 | 120 | 0.0 | 50 |
| 2,3,4,6,7,8-H ₆ CDF | 45 | 9.0 | 82 | 60 | 1.2 | 69 |
| 1,2,3,7,8,9-H ₆ CDF | 4.9 | 31 | 84 | 5.3 | 15 | 70 |
| 1,2,3,4,6,7,8-H ₇ CDF | 2600 | 6.7 | 85 | 2500 | 0.0 | 74 |
| 1,2,3,4,7,8,9-H ₇ CDF | 160 | 5.5 | 83 | 160 | 0.0 | 72 |

Values are corrected for recovery of ¹³C-labeled surrogates.

^aRefers to recovery of corresponding ¹³C-labeled surrogate.

^bMaximum possible concentration due to potential chromatographic overlap.

Highly Contaminated Sediment Samples

The ASE technique was also evaluated with two sediment samples containing high levels of coextractables and oil (Table 8). 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 T₄CDF and P₅CDF Hamilton Harbor ASE data,

Table 7. Average Values (ng/kg) from HS-2—Comparison of Soxhlet vs. ASE

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

n.d.=not detected. Detection limit, in ppt, given in parentheses. Values not used for statistical calculations. Values are corrected for recovery of ¹³C-labeled surrogates.

^aRefers to recovery of corresponding ¹³C-labeled surrogate.

^bMaximum possible concentration due to potential chromatographic overlap.

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., T₄CDF), but no recovery-related problems were observed in this case. Generally, the data compare favorably between ASE and Soxhlet for the recovery of PCDDs and PCDFs from these heavily contaminated sediments.

Recommended ASE Conditions for PCDDs and PCDFs

Based on the results of these experiments, the conditions listed in Table 9 are recommended for the extraction of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. The conditions may have to be adjusted slightly to optimize extraction efficiency depending on the sample. Increasing the temperature would be the first parameter to change; increasing the extraction time would be next.

Table 8. Average Values (ng/kg) from Highly Contaminated Sources—Comparison of Soxhlet vs. ASE

| Group Totals | Hamilton Harbor | | Parrots Bay | |
|---|-------------------|--------------------|-------------------|-------------------|
| | Soxhlet | ASE | Soxhlet | ASE |
| Total T ₄ CDD | 50 ⁵ | 14 ² | 39 ³ | 48 ⁵ |
| Total P ₅ CDD | 63 ¹² | 15 ⁵ | 87 ¹⁰ | 66 ¹⁰ |
| Total H ₆ CDD | 220 ⁷ | 180 ⁷ | 230 ⁶ | 200 ⁷ |
| Total H ₇ CDD | 850 ² | 810 ² | 580 ² | 530 ² |
| Total O ₈ CDD | 3100 | 3100 | 1900 | 1600 |
| Total T ₄ CDF | 370 ¹⁷ | 130 ^{11a} | 400 ¹⁴ | 270 ¹⁸ |
| Total P ₅ CDF | 290 ¹³ | 110 ^{11a} | 180 ⁸ | 170 ¹³ |
| Total H ₆ CDF | 240 ¹⁴ | 160 ¹¹ | 230 ⁶ | 230 ¹⁰ |
| Total H ₇ CDF | 350 ⁴ | 290 ⁴ | 400 ⁴ | 360 ⁴ |
| Total O ₈ CDF | 270 | 210 | 510 | 370 |
| Congeners | | | | |
| 2,3,7,8-T ₄ CDD | 3.7 | 3.1 | 19 | 19 |
| 1,2,3,7,8-P ₅ CDD | 5.1 | 5.4 | 8.3 | 6.0 |
| 1,2,3,4,7,8-H ₆ CDD | 6.4 | 7.2 | 8.6 | 6.7 |
| 1,2,3,6,7,8-H ₆ CDD | 27 | 26 | 26 | 17 |
| 1,2,3,7,8,9-H ₆ CDD | 20 | 28 | 24 | 18 |
| 1,2,3,4,6,7,8-H ₇ CDD | 460 | 430 | 280 | 250 |
| 2,3,7,8-T ₄ CDF ^b | 61 | 44 ^a | 80 | 48 |
| 1,2,3,7,8-P ₅ CDF | 14 | 14 | n.d. (20) | 9.8 |
| 2,3,4,7,8-P ₅ CDF | 26 | 25 ^a | 22 | 14 |
| 1,2,3,4,7,8-H ₆ CDF | 27 | 37 | 79 | 59 |
| 1,2,3,6,7,8-H ₆ CDF | 17 | 16 | n.d. (20) | 15 |
| 2,3,4,6,7,8-H ₆ CDF | 14 | 14 | 21 | 11 |
| 1,2,3,7,8,9-H ₆ CDF | n.d. (2) | 1.6 | 4.9 | n.d. (1) |
| 1,2,3,4,6,7,8-H ₇ CDF | 130 | 130 | 270 | 220 |
| 1,2,3,4,7,8,9-H ₇ CDF | 14 | 13 | 17 | 12 |

Values are corrected for recovery of isotopically labeled surrogate standards.

n.d.=not detected. Detection limit, in ppt, given in parentheses.

Superscripts indicate the number of isomers detected.

^aRecoveries outside the range 25% to 150%; results are not to be used for regulatory compliance purposes.

^bMaximum possible concentration due to potential chromatographic overlap.

CONCLUSIONS

The data show that ASE is essentially equivalent to classical extraction procedures such as Soxhlet for the extraction of PCDDs and PCDFs from environmental matrices. As an extraction technique, ASE shows great promise because it can be applied to a wide variety of compound classes. In addition to being equivalent to Soxhlet, ASE can be performed in a fraction of the time (a total of 22 min compared to 18 h) and with much less solvent (15 mL compared to 250 mL).

Table 9. Recommended Conditions for ASE Extraction of PCDDs and PCDFs

| | |
|-------------------------|---|
| Solvent | Toluene or toluene/acetic acid (5%, v/v) if HCl pretreatment currently used |
| Temperature | 175–200 °C |
| Pressure | 13.8 MPa (2000 psi) |
| Static Time | 5–15 min |
| Flush Volume | 60–70% |
| Purge Time | 60–100 s |
| Number of Static Cycles | 2 or 3 |

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