One Step Extraction-Clean Up for PCBs and Automated Column Chromatography for PCDD/Fs in Sediment and Soil

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Introduction

- Compounds of interest: polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs), and furans (PCDFs).
- Known toxicity.
- Strict environmental regulations in force in most countries.
PCBs were intentionally produced 1920-1970s.

- Used in capacitors and transformers, also as flame retardants, hydraulic fluids, sealants, and vacuum pump fluids.

- Total production estimated worldwide 1.5 million metric tons. Produced as Aroclor in North-America.

- Levels are now dropping.

- Still at significant concentrations to pose danger.
PCDD/Fs

- PCDD/Fs are always unwanted byproducts.

- PCDD/F sources: combustion, incineration, metallurgical industry, pulp and paper bleaching/ production; low natural background (Trace Chemistries of Fire).

- Levels also dropping.

- Still at significant concentrations to pose danger.
Health Effects

- Endocrine disruptors.
- Immune system.
- Nervous system.
- Reproductive functions.
- Carcinogenic.
- Chloracne.
- Main exposure (> 90%) is through dietary intake: meat, dairy, fish.
- Non-ortho and mono-ortho congeners (WHO-12) most toxic plus 17 laterally substituted PCDD/Fs.
Properties/Analysis

- Low solubility in water and chemically inert.
- Resist environmental degradation.
- Both PCBs and PCDD/Fs accumulate in soil and river sediment.
- Traditional extraction methods: up to 24-36 h Soxhlet and manual clean up.
- Manual methods are time-consuming; can have poor accuracy and reproducibility.
One Step Extraction + Clean Up

PLE® Fast Extraction & Concentration System

FMS
Fluid Management Systems
Procedure (EPA 8082)

- 10 g sample mixed with Hydromatrix™ to dry, transferred to extraction cells with InCell acid silica end cap.
- Spiked with native and PCBs standards.
- Void volume filled with Ottawa Sand.
- Sample Cells filled with 50% mixture Hexane/Methylene Chloride.
- Cells pressurized to 1500 PSI.
- Heated to 120 °C.
- Temperature held for 20 minutes.
- Extraction cells cooled and flushed with 50% cell volume.
- Additional clean up of sample as extract passes thru acid silica in end cap.
- Extract collected in tubes with direct-to-GC-vial connections.
- PCB-209 added as internal standard.
6 position evaporator
SuperVap Evaporation

- System pre-heated to 45-60 ºC.
- Samples evaporated at stable temperature under 5-6 psi nitrogen.
- 1 mL extract vial transferred directly to connected GC vial.
- Recovery standards added (nonane/dodecane).
- Extract taken 10 uL volume with a gentle stream of nitrogen at ambient temperature.
GC vial
Analysis: Polaris Q
## Results 8082 mix

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spiked ug/kg</th>
<th>Sand Mean Rec ug/kg</th>
<th>Sediment Mean Rec ug/kg</th>
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<tbody>
<tr>
<td>pcb-1</td>
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<td>114</td>
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<tr>
<td>pcb-5</td>
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<tr>
<td>pcb-206</td>
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</tbody>
</table>
Analyzed 1 g of NIST-1944 sediment.
- Spiked with $^{13}$C labeled standards.
- PLE extraction as above (no InCell clean up).
- Volume reduction and solvent exchange to hexane.
- PowerPrep automated clean up.
PowerPrep CleanUp System
Clean Up (1)

- Silica  - High Capacity PCB-free multilayer ABN silica gel column
- Alumina – PCB-free basic alumina column
- Carbon – PCB-free carbon/celite column
Clean Up (2)

- Condition columns 10 mLs or 40 (silica) mLs each.
- Sample loaded onto silica column in hexane.
- Elute silica and alumina with hexane (140 mLs), then 10% DCM/hexane (70 mLs, collect PCBs if present).
- Elute alumina with 50 mLs DCM to get PCDD/F onto carbon.
- Back elute carbon with 35 mLs toluene, collect PCDD/F. Total volume is ~ 375 mLs of solvent.
NIST 1944 sediment analysis (1)
NIST 1944 sediment analysis (2)

% recovery

2378-T4CDF, 2378-T4CDD, 12378-P5CDF, 23478-P5CDF, 12378-P5CDD, 23478-H6CDF, 123678-H6CDF, 234678-H6CDF, 123789-H6CDF, 123478-H6CDD, 123678-H6CDD, 1234678-H7CDF, 1234789-H7CDF, 1234678-H7CDD, OCDD
Conclusions (1)

- Pressurized Liquid Extraction combined with InCell acid silica clean up gives fast and reliable technique for extraction of PCBs in sediments and soils under the 8082 method.
- Up to six position PLE can extract samples in under one hour.
- When analyzing PCDD/Fs under 1613 method, PLE combined with automated multi column silica, alumina, and carbon clean up delivers clean samples ready for analysis.
Conclusions (2)

- Same technique can be used for PCBs (1668) in sediments and soils.
- Same day sample processing and analysis (HRGC/HRMS or other techniques if desired) is now possible.