# Extraction of POPs from Environmental Samples using Accelerated Solvent Extraction (ASE®)

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# Overview

- What is ASE?
- ASE of POPs
  - Soils, Sludges, Waste, and Sediments
  - Biological Samples
- ASE of PBDEs
- Conclusions

# Principles of Extraction

- Physical chemical principles influence solid–liquid extractions
  - Diffusion
  - Viscosity
  - Surface tension
  - Solubility
  - Binding energy of physisorption/chemisorption interactions

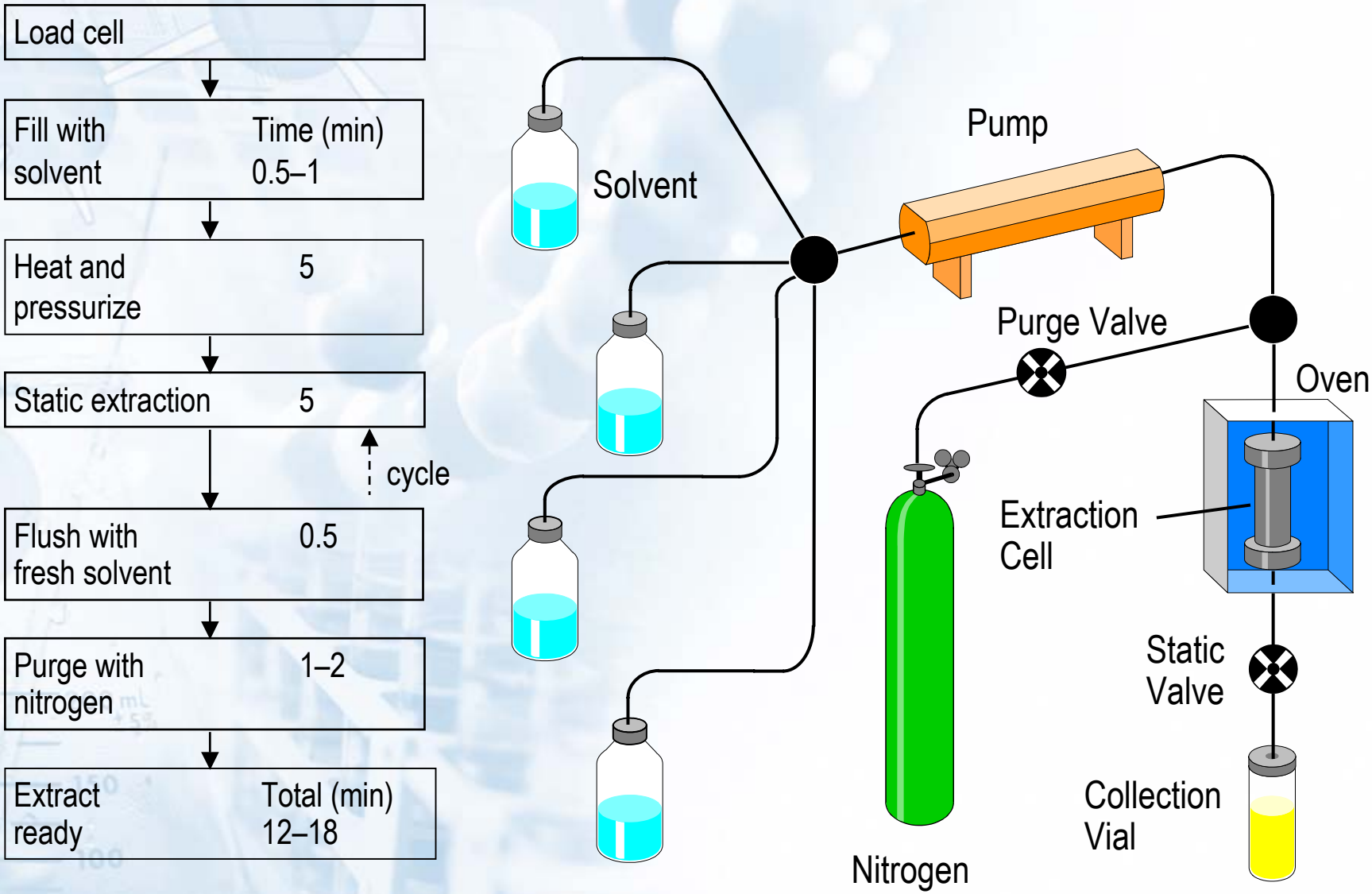
# What is ASE?

- An automated extraction technique that uses liquid solvents and solvent mixtures
- Extracts solid or semisolid samples, and liquids up to 50 mL
- Uses elevated temperatures (40–200 °C) and pressures (1500–2000 psi)
- Use of elevated temperatures and pressures accelerates the extraction process

# What is ASE?

- ASE uses small quantities of solvent and short periods of time
  - 15 mL and 15 min for 10-g samples
- ASE can be used with a range of sample sizes (1–100 g)
- ASE is widely used by government agencies and laboratories worldwide
  - U.S. EPA method 3545A
  - Most of the POPs are included in U.S. EPA method 3545A

# ASE Schematic



# Comparison of Extraction Techniques

| Technique | Sample Size (grams) | Solvent Used (mL) |
|---|---|---|
| ASE | 1–100 | 5–150 |
| Automated Soxhlet | 10 | 50–100 |
| Shake | 30 | 300–500 |
| Microwave | 5–10 | 30 |
| Sonication | 30 | 300–500 |
| Soxhlet | 1–100 | 300–1000 |

# Environmental Matrices Investigated

- Soils
- Sludges
- Sediments
- Plant and animal tissues
- PUF and XAD resins
- Essentially all solid or semisolid matrices analyzed for environmental contaminants

# Extraction Conditions (U.S. EPA Method 3545A)

| Condition | Pesticides | Hexachloro-benzene | PCB | PCDD/F |
|---|---|---|---|---|
| Temperature | 100 °C | 100 °C | 100 °C | 175-200 °C |
| Pressure | 1500 psi | 1500 psi | 1500 psi | 1500 psi |
| Time | 12 min | 12 min | 12 min | 22 min |
| Solvent | Hexane/ acetone | DCM/ acetone | Hexane/ acetone | Toluene |

# Relative Recovery of Pesticides from three soil types*- ASE compared to Automated Soxhlet and Soxhlet

| Pesticide | Average Recovery (% of Auto. Soxhlet or Soxhlet[2]) |
|---|---|
| Heptachlor | 88.0 |
| Aldrin | 94.9 |
| Gamma Chlordane | 99.5 |
| Alpha Chlordane | 102.0 |
| Dieldrin | 101.2 |
| Endrin | 97.2 |
| p,p´-DDT | 74.9 |
| Hexachlorobenzene | 93.7[2] |
| Toxaphene | 94.2[2] |

***Average from extraction of sand, loam and clay soils**

# Recoveries of PCB from Sewage Sludge

| PCB | Average Recovery (%) | RSD (%) |
|---|---|---|
| PCB 28 | 118.1 | 2.5 |
| PCB 52 | 114.0 | 4.7 |
| PCB 101 | 142.9 | 7.4 |
| PCB 153 | 109.5 | 5.8 |
| PCB 138 | 109.6 | 3.9 |
| PCB 180 | 160.4 | 7.5 |

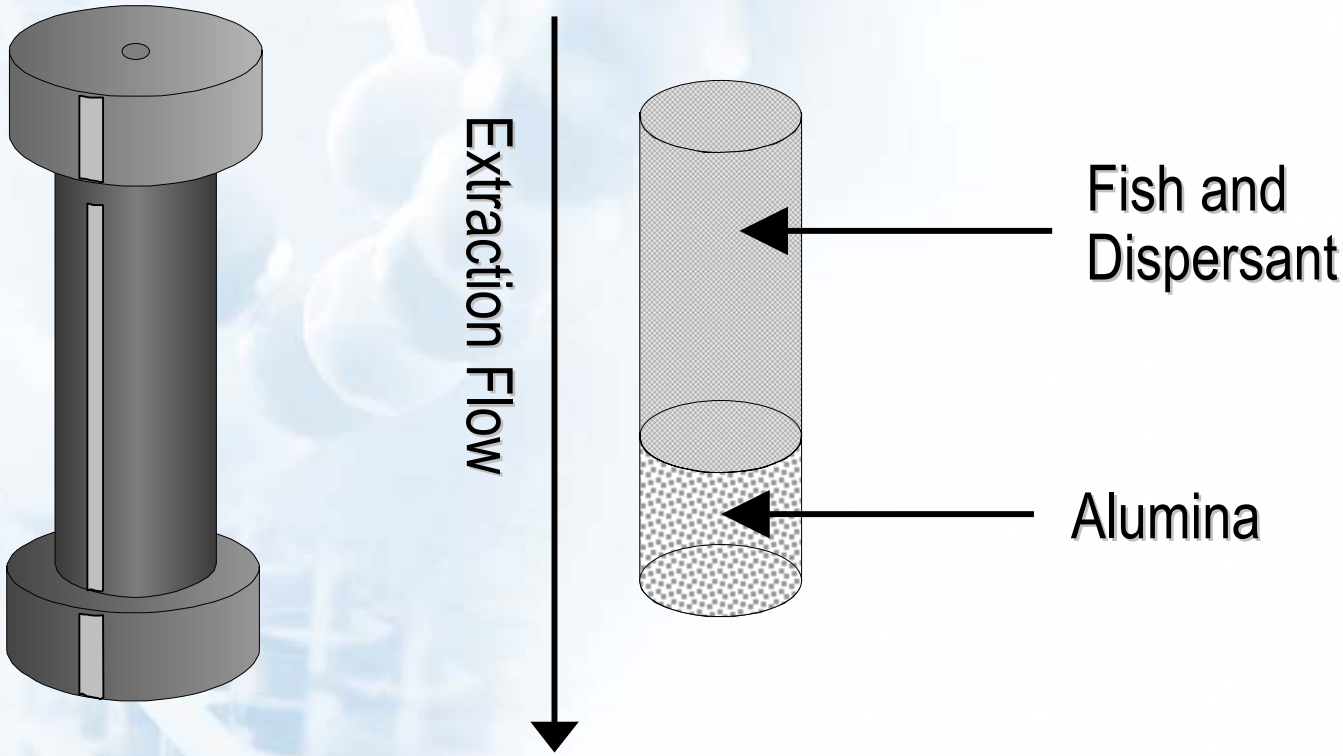
*relativ to Soxhlet

# PCB Recovery in Soil*

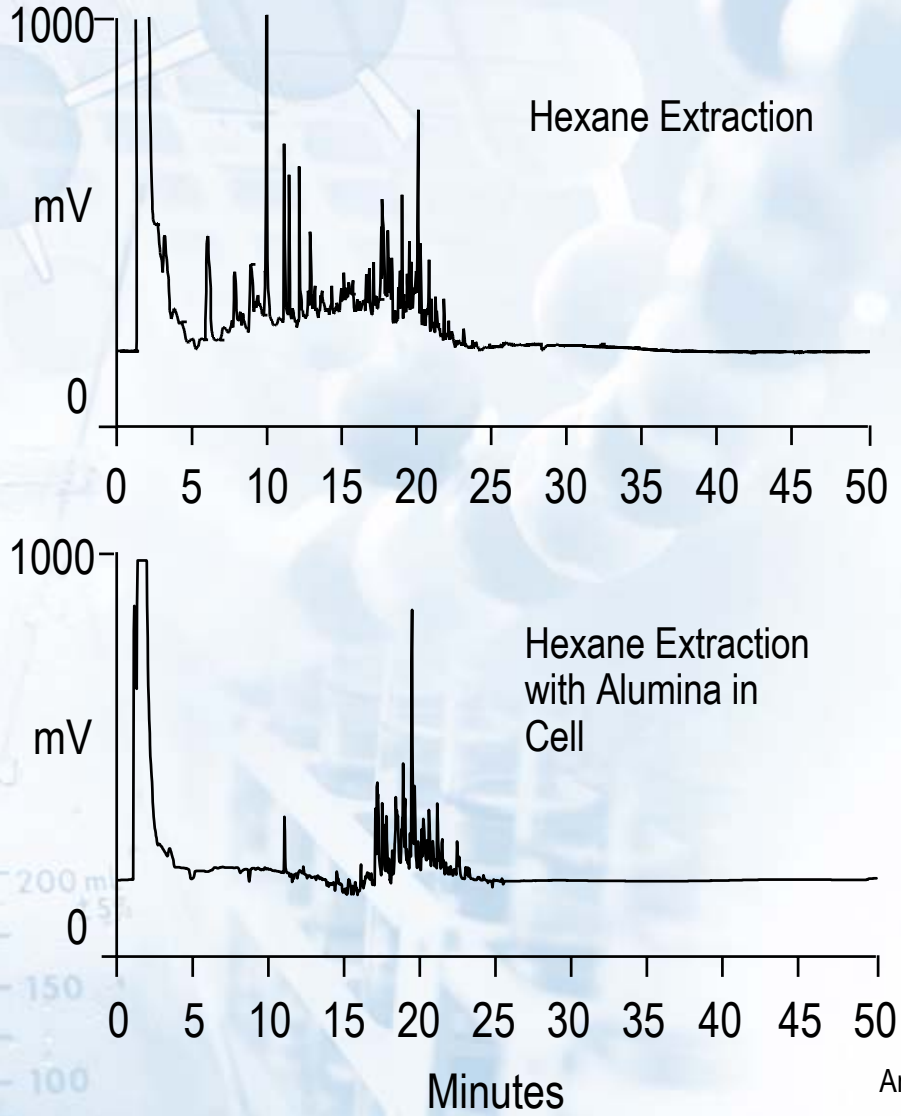
| Sample Run | PCB [µg/kg] |
|---|---|
| 1 | 1290 |
| 2 | 1366 |
| 3 | 1283 |
| 4 | 1369 |
| Average | 1327 (99,0%) |
| RSD | 3.5% |

*1340 µg/kg certified content

# Clean up in ASE Cell



# ASE Extraction of PCBs in Fish Tissue




Columns: 30-m x 0.53-mm i.d. DB-608 (J&W)
30-m x 0.53-mm i.d. DB-1701 (J&W)
Carrier: Helium, 30 cm/s
Injector: Splitless at 220 °C, 5 μL
Detector: Electron capture at 320 °C
Oven: 60 °C to 200 °C at 28 °C/min after
1-min hold, then to 265 °C at 10 °C/min and 20.5-min hold

Analyses performed by Mountain States Analytical, Inc.

American Environmental Laboratory (Dec. 1996, pg 12-13)

# Dioxins and Furans Extraction Conditions (Environmental Samples)

| | ASE | Soxhlet |
|---|---|---|
| **Sample Size** | 4 – 10 grams | 4 – 10 grams |
| **Solvent** | Toluene, 15 mL | Toluene, 250 mL |
| **Temperature** | 150 -180°C | << Boiling point |
| **Pressure** | 10 MPa | Atmospheric |
| **Time** | 2 x 10 min | 18 hours |
| **Analytical** | GC-MS | GC-MS |

Chemosphere, Vol. 34, 985–987

# Comparison of Soxhlet vs. Accelerated Solvent Extraction Total* Polychlorinated Dibenzo-*p*-dioxins

| Sample Matrix | Soxhlet (ng/kg) | ASE (ng/kg) |
|---|---|---|
| Chimney Brick | 8040 | 8170 |
| Urban Dust | 1110 | 1159 |
| Fly Ash | 93200 | 107900 |
| Sediment (EC-2) | 6750 | 6840 |
| Sediment (HS-2) | 11731 | 12783 |
| Hamilton Harbor Sediment | 4283 | 4119 |
| Parrots Bay Sediment | 2836 | 2444 |

* Total of tetra, penta, hexa, hepta and octachlorodibenzo-*p*-dioxins

# Extraction of POPs from Pine Needles and Mosses

- Samples are freeze dried
  - 10 grams mixed with 10 g Florisil/$Al_2O_3$ (2:1) in a 33 mL ASE cell
- ASE conditions
  - Solvent: n-hexane
  - 40 °C and 80 °C 3 x10 min extraction cycles
  - Total time 2 x 35 minutes
- Isotope labeled I.S. added, Concentrated to 2 mL
- Extract cleanup
  - Column packed with Florisil
- Analysis
  - GC/MS

*Wenzel, K.-D., Analytical Chemistry, Vol. 70, No. 22, 1998*

# Extraction of POPs from Pine Needles and Mosses

| | Inner Pine Needle Fraction | | Wax Fraction of Pine Needles | |
|---|---|---|---|---|
| **Compound** | **Sonication** | **ASE** | **Sonication** | **ASE** |
| Sum HCH | 3.23 | 50.8 | 2.31 | 3.48 |
| Sum DDX | 0.47 | 5.99 | 0.89 | 0.73 |
| Sum CB | nd | 0.62 | nd | nd |
| SUM PCB | 0.65 | 77.7 | 0.66 | 1.35 |
| *Sum PAH* | *10.7* | *182* | *15.7* | *24.1* |
| **Sum POP** | **15.05** | **317.11** | **19.56** | **29.66** |

*Wenzel, K.-D., Analytical Chemistry, Vol. 70, No. 22, 1998*

# Matrices Investigated Using ASE for PBDE Determination

- Human breast milk
- Sediments
- Polymers
- Fish tissues

# PBDE from Human Breast Milk

- Samples are freeze dried
  - 3.50 grams mixed with Ottawa sand in a 22 mL ASE cell with filters
- ASE conditions
  - Solvent: hexane, methylene chloride, methanol 5:2:1
  - 80 °C 3–5 min extraction cycles
  - 60% flush and 240-s purge
- Concentration by Turbovap
- Extract cleanup
  - Silica gel and GPC

# Analysis of Human Breast Milk

| Human breast milk sample | PBDE 77 | PBDE 153 | PBDE 209 |
|---|---|---|---|
| Mean recovery as a % of spike | 79.9 | 76.8 | 85.7 |

# PBDE from Sediments

- Samples were dried prior to extraction
- ASE 200 conditions
  - Solvent: Methylene chloride
  - 100 °C  2 x 5 min static cycles
  - 60% flush 60-s purge
- Solvent exchanged to hexane
- Cleanup
  - GPC and silica gel

# Analysis of PDBE from Sediments

- Analysis by GC/ECD
  - 60 m DB-5 column
  - High-temperature program
- Confirmation by GC/MS
  - Full scan electron ionization
  - Quantitation
    - » Summation of three major ions (BDE 47,99,100)

# Summary of PBDE from Sediments

- Fast extractions using ASE: 18 min per sample
- Detection limit of 0.5 µg/kg
- BDE 47 detected in 22% of samples
- Bottom feeding fish (catfish) had a PBDE profile similar to river sediment

# Conclusions

- ASE is faster than conventional liquid extraction procedures.
- ASE uses less solvent than conventional liquid extraction procedures.
- Recoveries are similar or superior
- ASE is an automated extraction technique
- ASE uses the same solvents currently used in conventional procedures; therefore, method development is greatly simplified.