Accelerated Solvent Extraction (ASE®) as a Sample Extraction Technique for Persistent Organic Pollutants in Solid Matrices

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DIONEX

Overview

- Introduction
- What is ASE®?
- ASE and POPs
  - Soils, Sludges, Waste, and Sediments
  - Biological Samples
- Conclusions

Sample Extraction Issues

- Single biggest source of errors is sample handling
- Biggest bottleneck of time for most analysis methods
- Costs of solvent purchase and disposal are increasing
- The data are only as good as the sample preparation
  - High-price chromatography and data systems will not improve the quality of poorly prepared samples
- Dionex has developed ASE® to address these issues

What are POPs?

- POPs are persistent organic pollutants, which are stable in the environment and can be found everywhere in the world.
  - Found in environmental samples such as soils, waste, sludge and sedminents
  - Found in biological samples such as human breast milk, and fish tissue
- Stockholm Convention on POPs:
  - Protect human health and the environment from persistent organic pollutants (POPs)
- Production and use of intentional produced POPs:
  - Elimination of production and use of all POPs; To achieve the this goal, production and use of POPs will be terminated or restricted; in any case, trade will be restricted;
- Unintentionally produced POPs:
  - Minimization of all releases of POPs with the goal of ultimate elimination.

12 Stockholm POPs

Chemical	Pesticide	Industrial Chemical	By-product
Aldrin	+		
Chlordane	+		
DDT	+		
Dieldrin	+		
Endrin	+		
Heptachlor	+		
Mirex	+		
Toxaphene	+		
Hexachlorobenzene	+	+	+
PCB		+	+
PCDD			+
PCDF			+

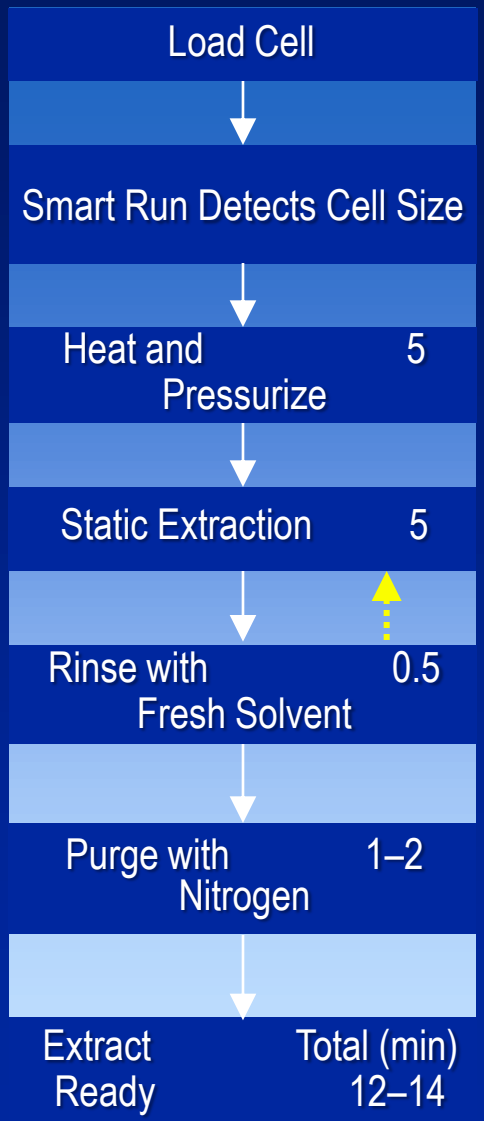
What Is ASE®?

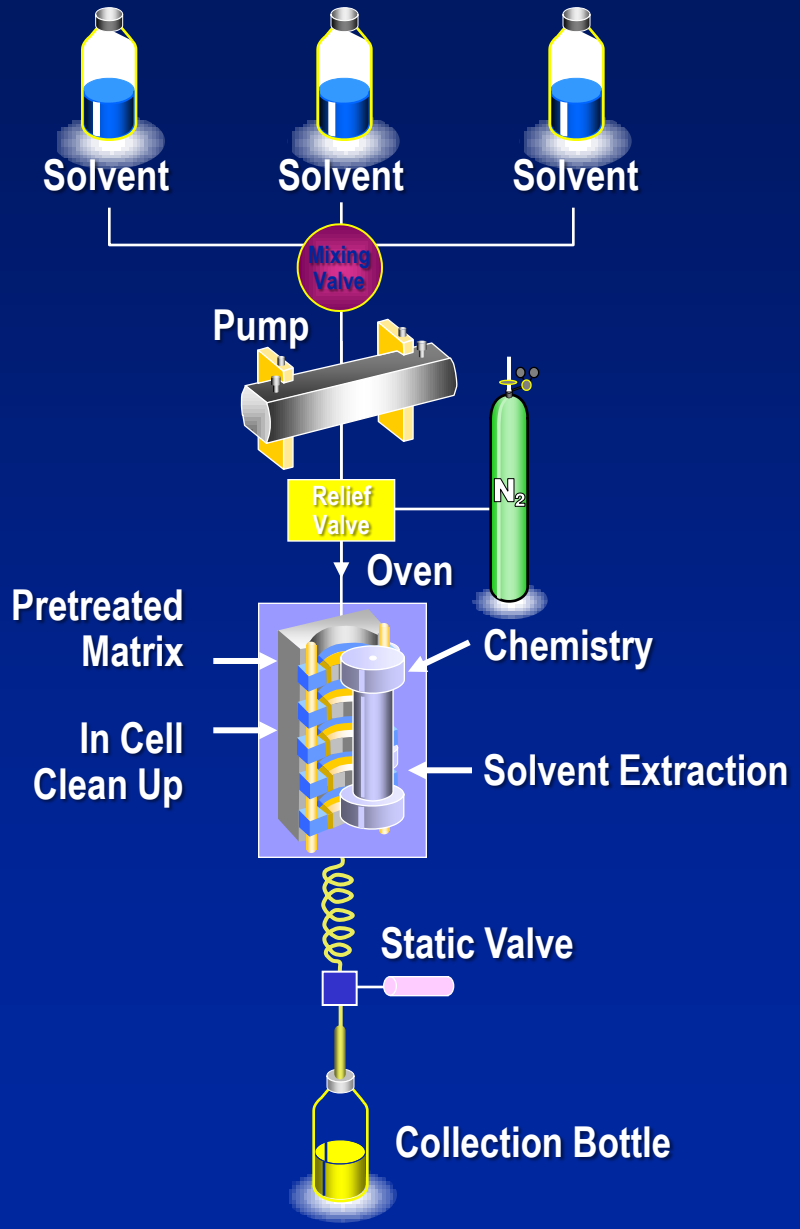
- An automated extraction technique that uses liquid solvents and solvent mixtures
- Extracts solid or semisolid samples
- Uses elevated temperatures (40–200 °C) and pressures (1500–2000 psi)
- Use of elevated temperatures and pressures accelerates the extraction process

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 method 3545A

ASE® Schematic



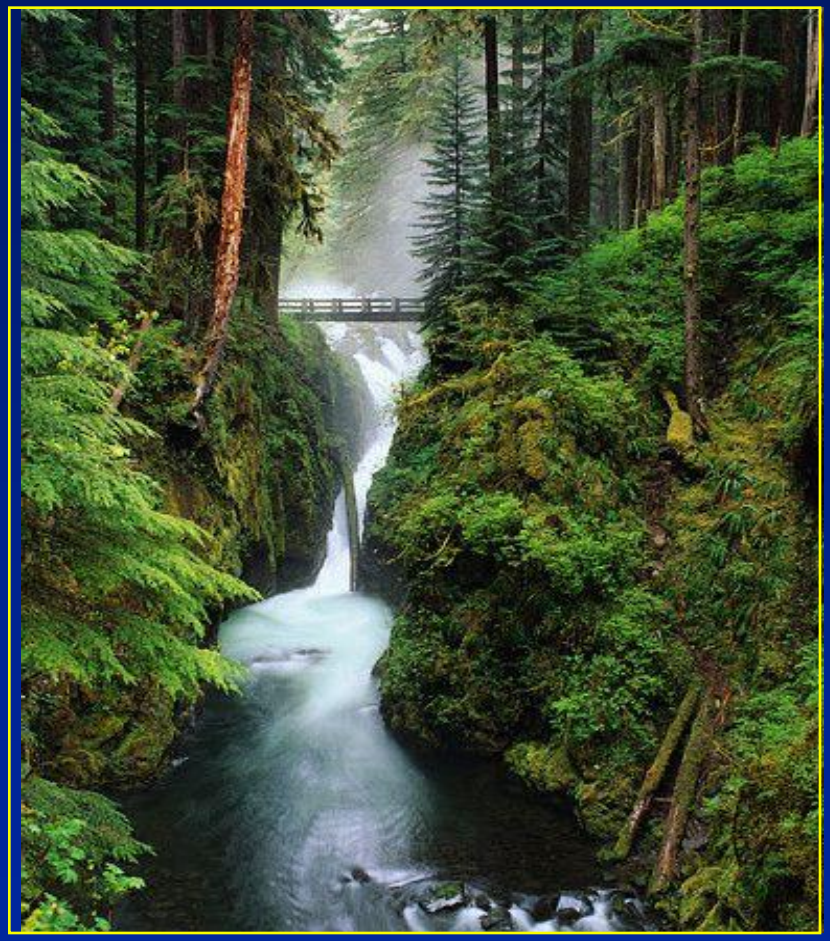


Introducing the New ASE® 150 and 350

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

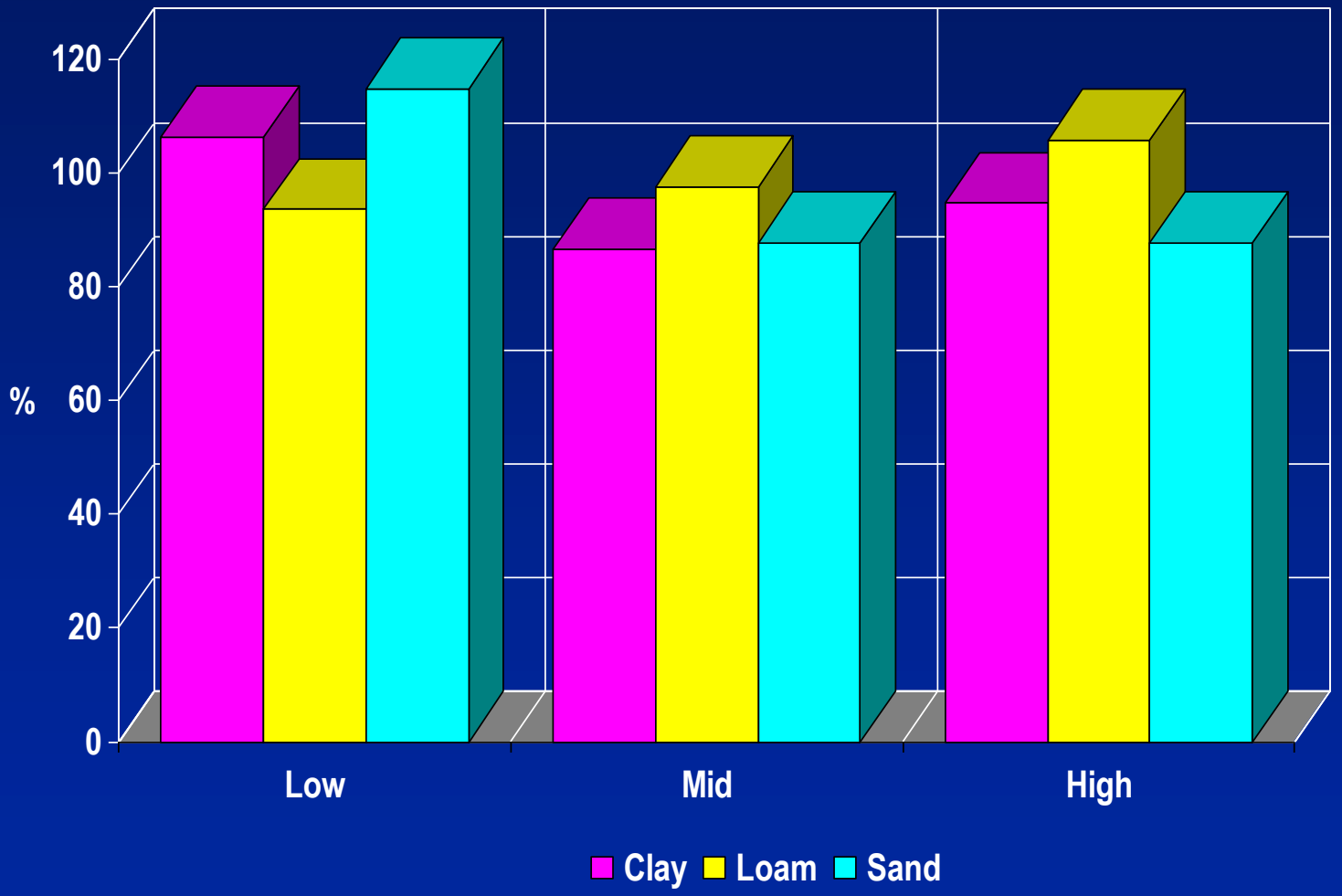


- Soils
- Sludges
- Sediments
- Plant and animal tissues
- PUF and XAD resins
- Essentially all solid or semisolid matrices analyzed for environmental contaminants

Extraction Conditions (U.S. EPA Method 3545)

Condition	Pesticide	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 OCP by ASE



Alpha HCH
Gamma HCH (Lindan)
Beta HCH
Heptachlor
Delta HCH
Aldrin
Heptachlorepoxid
Gamma Chlordan
Alpha Chlordan
Endosulfan I
p,p´-DDE
Dieldrin
Endrin
p,p´-DDD
Endosulfan II
p,p´-DDT
Endrinaldehyd
Endosulfansulfat
Methocychlor
Endrinketon

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

Pesticide	Average Recovery (% of Auto. Soxhlet)
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
Mirex	
Toxaphene	

*Average from extraction of sand, loam and clay soils

Relative Recovery of Hexachlorobenzene from three soil types*- ASE compared to Automated Soxhlet

Analyte	Average Recovery (% of Soxhlet)
Hexachlorobenzene	93.7

*Average from extraction of sand, loam and clay soils

Recoveries of PCB from Sewage Sludge

PCB	Average Recovery (%), n=6	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

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

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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	93,200	107,900
Sediment (EC-2)	6750	6840
Sediment (HS-2)	11,731	12,783
Hamilton Harbor Sediment	4283	4119
Parrots Bay Sediment	2836	2444

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

New/Improved Features of ASE® 150 and 350

- Inert pathway: Dionium
  - Resistant to acids and bases
    - » 0.1N HCl, H_2SO_4, NaOH, KOH
    - » **Cannot** pump strong acids or bases
    - » Can perform acidic alkaline pretreatments or in-cell
  - Inert cells with Dionium™

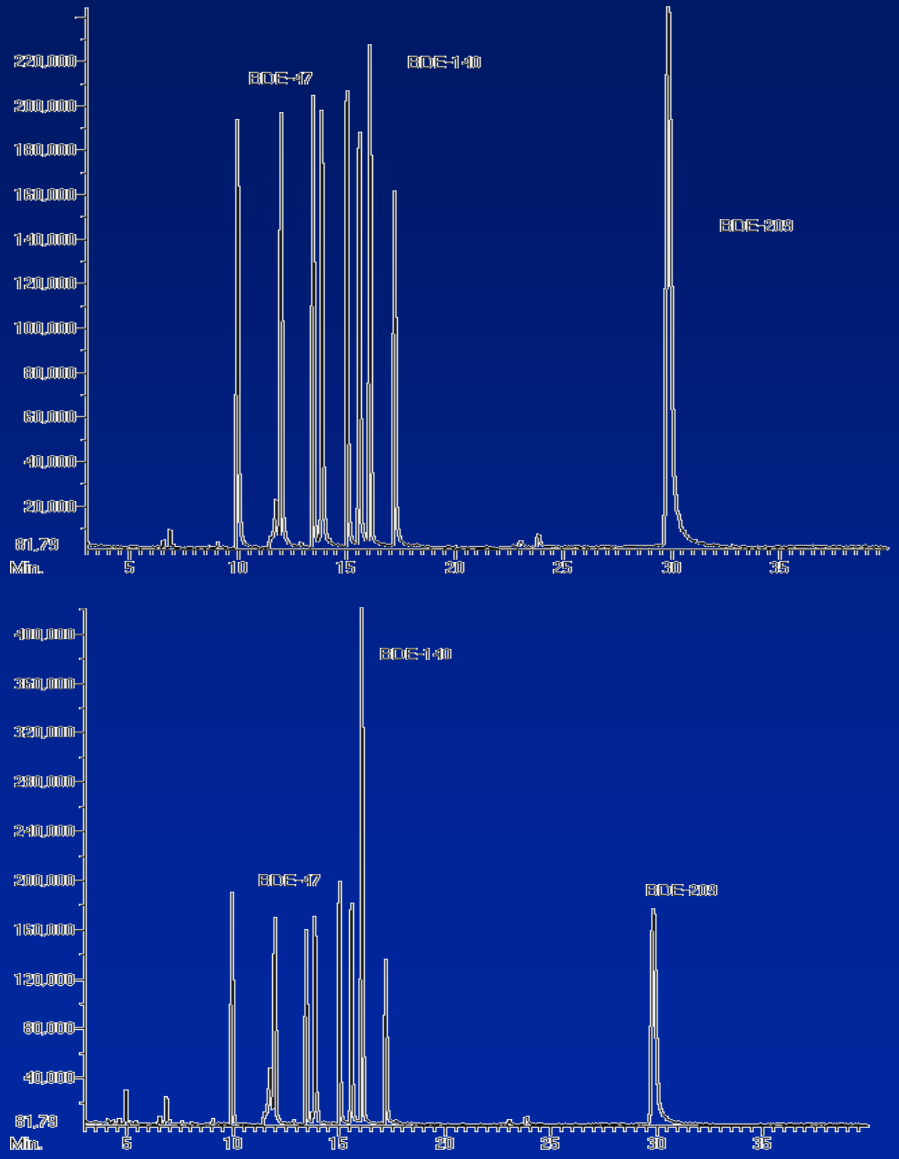
66-mL Dionium Cell Body

8270 Analysis Using 3545 Extraction Procedure with Acid Pretreatment

- 30 g sediment or other solid material
  - Add 4 mL 5% HCL
  - Mix well
- Add acid neutralizing adsorbent to cell
- Add sample to Dionium extraction cell
- Extract with $MeCl_2$/acetone
  - 100 °C or 110 °C
  - 1 × 5 minute static cycle
- Reduce volume to 1 mL
- Analysis by GC/MS

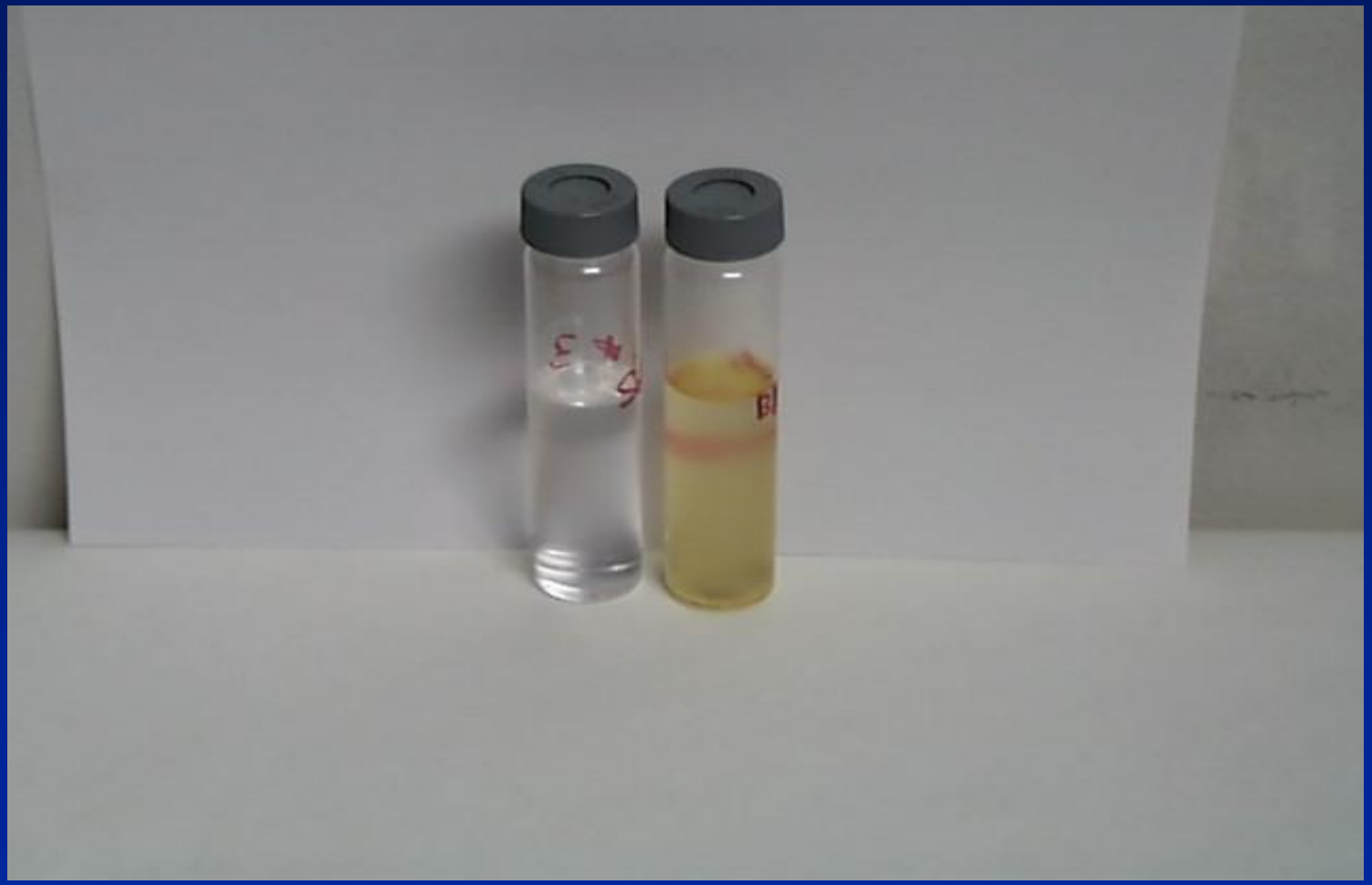
ASE® PBDE Results (Cont.)

- Analyzed by Agilent Tech., (GC) 6890N, with a GCMate II (MS), ionization mode, electron-capture negative ionization (ECNI), monitoring bromines (79 and 81 m/z)
  - DB5-HT column (30m)
  - Top chromatogram is calibration check
  - Second chromatogram is the salmon sample extract within cell clean-up



Data courtesy of Mark LaGuardia of VIMS

Integrated Clean-Up
Salmon Extracts



Extracts With and Without In-Cell Clean-Up of Fish Tissue
Using Alumina, Silica Gel, and Acidic Silica Gel (40% H_2SO_4)

PCDD and PCDFs—Selective Extraction

- 15-g samples of animal feed
- Sulfuric acid/silica gel (40%) in ASE cell
- 120°C, 1500 psi (10.34 MPa)
- 0.5 h total time (16 h for Soxhlet)
- 100 mL as compared to 400 mL

PCDD and PCDFs—Selective Extraction (ng/kg or ppt)

Compound	Soxhlet	ASE
2,3,7,8-TCDD	0.12	0.12
1,2,3,7,8-PCDD	0.13	0.12
1,2,3,4,7,8-HCDD	0.11	0.10
2,3,7,8-TCDF	0.45	0.48
1,2,3,7,8-PCDF	0.14	0.15
1,2,3,4,7,8-HCDF	0.12	0.11
OCDD	2.31	2.54
Total TEQ	0.50	0.48

ASE® Applications Areas

- Environmental
- Pharmaceutical
  - Natural products
  - Formulations
- Foods
  - Contaminants and major components
- Polymers
  - Additives and physical properties
- Consumer products

Conclusions

- ASE is faster than conventional liquid extraction procedures.
- ASE uses less solvent than conventional liquid extraction procedures.
- ASE does not exhibit matrix dependency.
- ASE uses the same solvents currently used in conventional procedures; therefore, method development is greatly simplified.