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Application Note 351

# Rapid Determination of Polybrominated Diphenyl Ethers (PBDEs) in Biosolids and Waste Samples Using Accelerated Solvent Extraction (ASE®)

## INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) were developed in the early 1970s and are used today as flame retardants for various consumer products, including clothing, furniture, and plastics. Many of these consumer products are disposed in municipal landfills where the PBDEs then leach into groundwater and accumulate in certain biosystems. Recent studies indicate that PBDE concentrations in these biosystems are on the rise. In the 1980s, PBDEs were discovered in European waterways, which led the European Union to ban their production and use. Although the toxicity of PBDEs is still under investigation, evidence suggests that PBDEs may compromise endocrine or hepatic functions. Because of this concern, the state of California plans to ban the production and use of PBDEs and other North American states will most likely follow. The European Union also plans to ban PBDEs.

Accelerated Solvent Extraction (ASE), introduced in 1995, was EPA approved under method 3545A and has proven to be a valuable technique for environmental laboratories. ASE uses high temperatures and pressures to increase the kinetics of the extraction process, thus decreasing the extraction time and solvent consumption. Also, because ASE is automated, it allows unattended extraction of up to 24 samples. In this application note, PBDEs were extracted from human breast milk (freeze-dried), sediments, fish tissues, and polymers.

## EQUIPMENT

ASE 200 Accelerated Extractor* with Solvent Controller (P/N 048765)

22-mL Stainless-Steel Extraction Cells (P/N 048764)

11-mL Stainless-Steel Extraction Cells (P/N 048765)

Cellulose Filters (P/N 049458)

Glass Fiber Filters (P/N 047017)

Collection Vials 60 mL (P/N 048784)

Cellulose Thimbles 11 mL (P/N 055708)

Analytical Balance (to read to nearest 0.0001 g or better)

Dispersing agent such as sand (Ottawa Standard, Fisher Scientific, Cat. No. S23-3 20-30 mesh) or ASE Prep DE (P/N 062819)

Cryo-Grinder (6750 Freezer Mill from SPEX CertiPrep)

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

## SOLVENTS

Hexane

Methylene chloride

Methanol

2-propanol

THF*

*(All solvents are pesticide-grade or equivalent and available from Fisher Scientific.)*

## EXTRACTION CONDITIONS

### Human Breast Milk

| | |
|---|---|
| Solvent: | Hexane, methylene chloride, methanol (5:2:1) |
| Temperature: | 80 °C |
| Pressure: | 1500 psi* |
| Static time: | 5 min |
| Static cycles: | 3 |
| Flush: | 60% |
| Purge: | 240 s |

### Sediments and Fish Tissue

| | |
|---|---|
| Solvent: | Methylene chloride (100%) |
| Temperature: | 100 °C |
| Pressure: | 1500 psi* |
| Static time: | 5 min |
| Static cycles: | 2 |
| Flush: | 60% |
| Purge: | 120 s |

### Polymers

| | |
|---|---|
| Solvent: | 2-propanol (100%)* |
| Temperature: | 80 °C |
| Pressure: | 1500 psi* |
| Static time: | 10 min |
| Static cycles: | 2 |
| Flush: | 70% |
| Purge: | 120 s |

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

## SAMPLE PREPARATION

### Human Breast Milk (Freeze-Dried)

Insert a glass-fiber filter into a 22-mL extraction cell. Fill cell with Ottawa sand to 1/2 in. from the top. Weigh out approximately 3.5 g of freeze-dried breast milk into aluminum weigh boat. Add the sand from the extraction cell to the weigh boat containing the breast milk and mix thoroughly. Transfer the sand/milk mixture back to the 22-mL extraction cell and tighten the top endcap.

Note: If using GC/MS this preparation will require ultraclean extracts, which will require ultraclean equipment and reagents.

### Sediments and Fish Tissue (Freeze-Dried)

Insert a cellulose filter into a 22-mL extraction cell. Fill cell with Ottawa sand or ASE Prep DE (1/2 in. from the top). Weigh approximately 5 g of dried sample into aluminum weigh boat. Add the sand or ASE Prep DE from the extraction cell to the weigh boat containing the sample and mix thoroughly. Transfer this mixture back to the 22-mL extraction cell and tighten the top endcap.

### Polymers

Grind polymer pellets to a powder using a cryo-grinder. Place a cellulose thimble into an 11-mL extraction cell. Weigh 0.5 g of polymer powder into the 11-mL cell containing the cellulose thimble. Place endcap on top of extraction cell and tighten.

## EXTRACTION PROCEDURE

Place the cells onto the ASE 200. Label the appropriate number of collection vials and place these into the vial carousel. Set up the above method and begin the extraction. When the extraction is complete, the breast milk, sediments, and fish tissue extracts can then be cleaned using silica gel adsorption followed by gel permeation chromatography (GPC). Any efficient cleaning procedure may be substituted. The polymer extracts do not require further cleanup before analysis.

## RESULTS AND DISCUSSION

Sample preparation is critical to good recoveries. To remove the fat and lipids and prepare the extract for GC-MS analysis, a cleanup process should be used for the milk, sediment, and fish tissue extracts.

Table 1 shows that ASE extracted the PBDE standard spiked onto the freeze-dried breast milk with acceptable recoveries. Table 2 shows that ASE extracted PBDE from ground polymer samples with recoveries comparable to Soxhlet.

With a detection limit of 0.5 µg/kg, the GC/MS analysis found BDE-47 in 22% of the 332 sediment sample extracts. BDE-47 is one of two major constituents of Penta, which is a commercial product used to flame retard polyurethane foam.

With a detection limit of 5 µg/kg, the GC/ECD found BDE 47 in 89% of the 332 fish tissue samples.* Bottom-feeding fish had the same PBDE profile as the sediment samples, implying that fish are being exposed to the PBDE through contact with the sediment.

| Table 1. Analysis of Human Breast Milk | | | |
|---|---|---|---|
| **Spiked Breast Milk Samples** | **PBDE 77** | **PBDE 153** | **PBDE 209** |
| Mean Recovery as a % of Spike | 79.9 | 76.8 | 85.7 |

*Recent work in the Salt Lake City Technical Center has shown even higher recoveries of PBDE using THF.

| Table 2. Analysis of Polymer Samples | | |
|---|---|---|
| **Matrix** | **Compound** | **ASE Recovery (% of Soxhlet)** |
| ABS* | Polybromodiphenylether | 81.3 |
| SB* | Polybromodiphenylether | 76.3 |
| SB | Polybrominated Biphenyl | 76.2 |

*Acrylonitrile butadiene styrene
** Styrene butadiene

## CONCLUSION

For extracting PBDEs from breast milk, ASE proves to be an excellent alternative to the traditional AOAC method using a separatory funnel. ASE was reported easier to use than the separatory funnel, which tended to clog up with milk emulsions. The results for extraction of breast milk by ASE were similar to those achieved by the AOAC method. Furthermore, it was found that ASE could perform well on liquid milk as well as the freeze-dried milk.

For extracting PBDEs from polymers, ASE provided similar results when compared to Soxhlet while reducing the solvent consumption by 40% and cutting the extraction time from 3 h to 25 min.

For extracting fish tissue and sediment samples, ASE is a fast and efficient method. ASE extracted these samples in only 18 min.

## ACKNOWLEDGEMENT

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**Dionex Corporation**
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

**North America**
U.S./Canada (847) 295-7500

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