

One Step Extraction, Cleanup and Concentration for PBDEs in Soil Samples



Introduction

Polybrominated diphenyl ethers are organo-bromine compounds that are used as flame retardants. Like other brominated flame retardants, PBDEs have been used in a wide array of products, including building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles. The hazards of these chemicals have attracted increasing scrutiny, for they have been shown to reduce fertility in humans at household levels and have been linked to liver toxicity, thyroid toxicity, and neurodevelopmental toxicity in laboratory studies on rats. Studies comparing humans who have higher levels of PBDEs present in their umbilical cord blood at birth have been shown to score lower in tests of mental and physical development. Due to these concerns the European Union has banned the use of PBDEs as have several states in the U.S., including California, Washington and Maine.

Instrumentation and Consumables

- FMS, Inc. PowerPrep™ PLE (Pressurized Liquid Extraction) System
- FMS, Inc. PowerPrep™ sample clean-up system
- FMS, Inc. Classical ABN Column
- FMS, Inc. Alumina Column
- FMS, Inc. Carbon/Celite column
- FMS, Inc. SuperVap™ Concentrator system
- Thermo Fisher Scientific Polaris Q GCMS

Method Summary

PowerPrep PLE system

1. Extraction solvent: Hexane/Methylene Chloride (50/50)
2. Extraction temperature: 120 °C
3. Extraction pressure: 1500 PSI
4. Extraction time: 15 minutes

SuperVap Concentrator

1. Pre-heat temp: 55 °C
2. Pre-heat time: 15 minutes
3. Heat in Sensor mode: 65 °C
4. Nitrogen Pressure: 15 PSI

Sample preparation and extraction

10 grams of the sample are weighed out in a 100 mL beaker; the process is repeated for eight replicates.

1. Samples are dried with Varian Hydro Matrix®
2. The dried sample is transferred to a FMS extraction cell
3. The samples are spiked with 1 mL (acetone) of 100 ng/mL labeled 1614 spiking solution
4. The cell volume is filled with Ottawa Sand®, sealed and loaded on the FMS PLE system for extraction
5. The sample is extracted and automatically transferred to the SuperVap Concentrator.

The sample is concentrated to .5 mL final volume.



The FMS TotalPrep™ system for automated extraction, cleanup and concentration.



Sample cleanup

1. The extract spiked with Cambridge Isotope 1614 cleanup internal standard (BDE-139L)
2. The columns are preconditioned with solvent.
3. The sample is loaded onto a FMS Classical ABN silica column using the PowerPrep™ solvent pump.
4. The silica column is eluted with 90 mL of hexane and the elution is automatically transferred onto the alumina column.
5. The alumina column is eluted with 180 mL of hexane/methylene chloride (60 mL 2%, 120 mL 50%), the sample is automatically transferred to the carbon column and collected in SuperVap™ Concentrator and brought to dryness.
6. 2 µL of dodecane is added to the extract that has been evaporated to dryness. Sample reconstituted to 10 µL nonane, spiked with 1 µL Cambridge Isotope 1614 Injection Internal Standard and transferred to GC/MS for analysis.

Results

Table 1: Mean spike recoveries for labeled compounds over eight replicates.

	Amount Spiked	Mean % Recovery
BDE-28L	100 pg	78.3%
BDE-47L	100 pg	95.5%
BDE-100L	100 pg	107.0%
BDE-99L	100 pg	108.0%
BDE-154L	100 pg	112.6%
BDE-153L	100 pg	111.5%
BDE-183L	100 pg	110.1%
BDE-209L	1000 pg	68.4%

Conclusions

Analysis of eight replicates of soil obtained from the banks of the Charles River in Boston, MA U.S.A. indicates consistent, reproducible recoveries of labelled PBDEs when extracted on the FMS PLE system. Recoveries fell well within the EPA 1614 recovery window (25-150%), with standard deviations ranging between 2-5% (14% for BDE-209). Native PBDE concentrations detected in samples were at average concentrations of approximately 15.0 ng/kg for BDE 47 and 22.5 ng/kg BDE-99 (dry weight). Other congeners were non-detect at an R.L. of 2 ng/kg (20ng/kg for BDE-209). Evaluation of the multi column clean-up procedure on the FMS PowerPrep closed system demonstrated efficient sample clean-up allowing low level analysis with excellent reproducibility. Analysis of extracted and cleaned up method blanks verifies FMS columns were free of native PBDEs at instrument detection levels.

Figure 1: Chromatogram of a soil sample and labelled PBDE recoveries.

