Application Note

Solid Phase Extraction of Waste Water Samples by EPA 608

Introduction

Solid Phase Extraction of chlorinated pesticides and polychlorinated biphenyls has long been an accepted sample preparation technique for EPA 500 series drinking water samples. Both C_{18} and DVB cartridges and disks have consistently generated excellent recoveries in drinking water matrices. EPA 600 series methods however, focus on waste water samples that can prove a greater analytical challenge than finished drinking water. The presence of organic materials, surfactants, and other matrix interferences can pose extraction issues for both SPE and traditional LLE (Liquid-Liquid Extraction) techniques. Extract purification is also necessary in most samples, usually involving a Florisil clean-up step.

By using the FMS, Inc. TurboTrace Solid Phase Extraction system together with the PowerPrep sample cleanup and SuperVap concentrator, it is possible to automate the extraction, extract purification and concentration steps of EPA 608.

Instrumentation and Consumables

Instrumentation

- FMS, Inc. TurboTrace SPE (Solid Phase Extraction) System
- FMS, Inc. SuperVap 12 position Concentrator
- FMS, direct-to-vial concentrator tubes
- FMS, Inc Power Prep clean up system
- Agilent 7890 GC with µECD

Consumables

- FMS 1 gram C_{18} cartridges w/pre-filter
- FMS Florisil Columns
- Fisher Pesticide Grade Methanol
- Fisher Pesticide Grade Methylene Chloride
- Fisher HPLC Grade Water
- FMS, Fisher Pesticide Grade Hexanes
- FMS, Fisher Pesticide Grade Acetone
- Fisher Anhydrous Sodium Sulfate

Restek Cat #32005; Toxaphene Solution

Restek Cat#32009; Aroclor 1242 Solution

Restek Cat#32012; Aroclor 1260 Solution

Restek Cat# 32291; Organochlorine Pest AB Mix

Procedure

Synthetic waste waters were created following ASTM D5905-96 guidelines.

1 liter of waste water constitutes:

60 mL light beer

.2 grams bleached flour

1 gram Sea Salts (Sigma #S-9883)

.04 grams Kaolin (Sigma #K-7375)

10 mL of a .12% Triton-X 100 Surfactant (Sigma #X-100)

DI water adjusted to 1 L volume

SuperVap Concentration system

1. Pre-heat temp: 45 ºC
2. Pre-heat time: 20 minutes
3. Heat in Sensor mode: 45 ºC
4. Nitrogen Pressure: 10 PSI
5. End point: 1 mL

TurboTrace SPE System

1. Samples acidified by adding H_2SO_4 drop wise till PH is <2
2. Replicates (3) were spiked with Pesticide, Arochlor and Toxaphene solutions as well as unfortified samples for comparison.

Figure 1. FMS TurboTrace SPE with SuperVap concentrator

FMS
Fluid Management Systems

3. Sample bottles attached to TurboTrace™ SPE system
3. C_{18} cartridges w/pre-filters fitted to sample loop.
4. $NaSO_4$ containing cartridges placed at fraction line termination above collection vials.
5. Cartridges pre-conditioned with 10 mL Methylene Chloride.
6. Cartridges conditioned with 10 mL MeOH
7. Cartridges conditioned with 15 mL H_2O
8. Samples loaded across Cartridges at ~15 mm HG vacuum.
9. Cartridges dried with N_2 for 5 minutes each.
10. Sample bottles rinsed with 25 mL Methylene Chloride.
11. Methylene Chloride rinse loaded across cartridges and collected in fraction vials
12. Cartridges eluted with 10 mL Methylene Chloride.
13. Eluates nitrogen purged through $NaSO_4$ into collection vials.

SuperVap™ Concentrator

1. Preheat temp: 10 minutes at 45 °C
2. Evap mode w/sensor temp: 40 °C
3. Nitrogen pressure: 5 PS
4. When extracts at 1 mL, 5 mL hexane added to vials.
5. Extracts concentrated under N_2 till 1 mL sensor alarm signals.

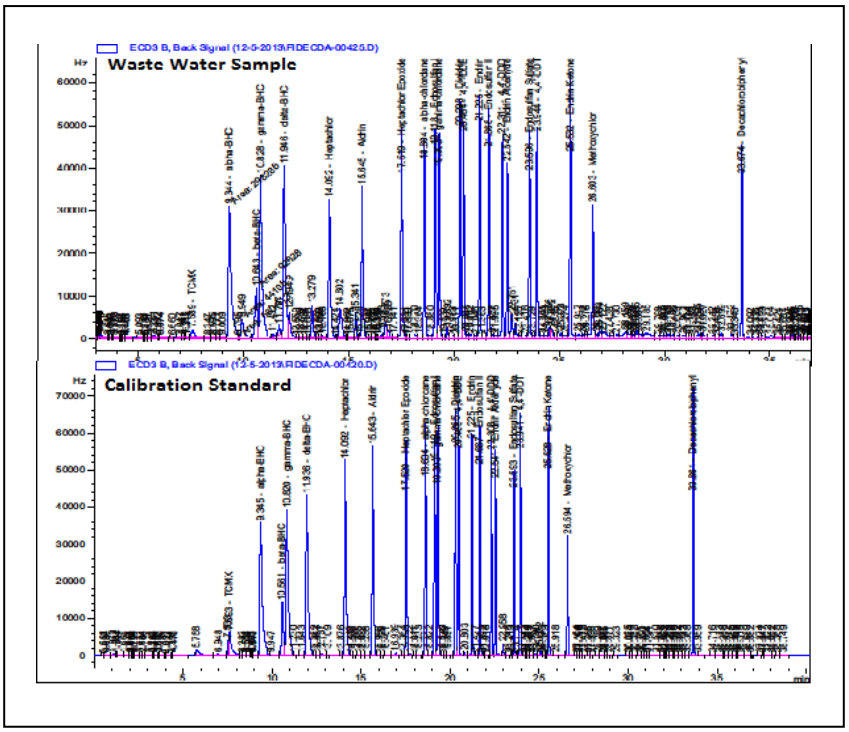
PowerPrep Cleanup

1. Florisil cartridges fitted to Power Prep™ System.
2. Cartridges pre-wet with 10 mL Hexane
3. Sample extracts loaded into Power Prep System.
4. Florisil cartridges eluted with 20 mL Acetone/Hexane (10:90) solution.
5. Elute collected in direct to GC vial tubes and evaporated to 1 mL under same settings as SPE extracts.

Table 1; Results of fortified synthetic waste water samples

Compound	Mean Rec.	Acc. Limit
α-BHC	80.9%	37-134
β-BHC	85.5%	17-147
Lindane	88.6%	32-127
δ-BHC	93.0%	19-140
Heptachlor	65.4%	34-111
Aldrin	62.5%	42.122
Heptachlor Epoxide	81.4%	37-142
α-Chlordane	71.8%	45-119
Endosulfan I	82.7%	45-153
γ-Chlordane	71.8%	45-110
Dieldrin	85.0%	36-146
4,4'-DDE	71.8%	30-145
Endrin	105.6%	30-147
Endosulfan II	90.1%	D-202
Endrin Aldehyde	75.2%	NA
4,4'-DDD	84.8%	31-141
Endosulfan Sulfate	102.4%	26-144
4,4'-DDT	79.3%	25-160
Methoxychlor	112.3%	NA
Endrin Ketone	105.9%	NA
Arochlor 1242	63.2%	39-150
Arochlor 1260	77.7%	8-127
Toxaphene	88.8%	41-126

Figure 2. Overlay of fortified waste water sample with calibration standard.



Conclusions

Analysis of the extracts yielded recoveries for all analytes tested well within EPA 608 acceptance criteria. Using C_{18} cartridges equipped with pre-filtration sufficiently controlled a steady flow through the cartridge preventing clogging. Paired with PowerPrep Florisil clean-up, extracts were purified of non-target interferences preventing matrix interference of target analytes. The closing degradation check on the GC indicated sample extracts did not "dirty" the GC inlet further demonstrating the efficiency of the PowerPrep system.

By using the TurboTrace™ SPE system, emulsions typically formed by LLE procedures were eliminated, often a major cause of analyte loss. Using inline water removal and automated extract cleanup, extraction chemist interaction with the sample was less, thus reducing the risk of human error in the process. By automating EPA 608 with Solid Phase Extraction, waste water samples (typically a challenging matrix) can be extracted more efficiently than by traditional LLE procedures.

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