Application Note

EPA 625, Base, Neutral and Acid Semi-volatiles in Municipal and Industrial Waste Water by SPE

Introduction

Solid Phase extraction has long been used for the analysis of semi-volatile organics in clean matrices. Methods like EPA 525.3 and EPA 8270D outline performance data for a variety of analytes and products. Due to the unique challenges inherent with waste water matrices laboratories have predominately adhered to LLE (Liquid Liquid Extraction) protocols. Recent advances in packing materials and automated extraction systems have now made once unheard of extractions of matrices commonplace for SPE.

Traditionally involving 6 LLE shakes at both pH 2 and 12, plus heavy emulsions and low recoveries, traditional EPA 625 extractions are time consuming and often result in poor results. By incorporating automated SPE with multi-bed sorbents, 625 samples can be extracted with a single pass procedure without emulsions, centrifuging and hours of manual labor. The FMS TurboTrace Semi-Volatile system is a specialized variant of the TurboTrace system. It is designed to handle multiple cartridges, and provides a fully automated solution for the semi-volatile EPA 625 extraction process.

Instrumentation and Consumables Instrumentation

Instrumentation

- FMS, Inc. TurboTrace Semi-Volatile SPE system
- FMS, Inc. SuperVap Concentrator
- FMS, Inc. 200 mL concentrator tubes
- Thermo Trace GC w/DSQ MS

Consumables

- Fisher Pesticide Optima* Methylene Chloride
- Fisher Anhydrous Sodium Sulfate
- Fisher Optima* Methanol
- Fisher HPLC Grade Water
- FMS mixed bed 625 cartridges
- Fisher Concentrated Sulfuric Acid
- Fisher Sodium Hydroxide
- Restek Resprep 2 gram coconut charcoal cartridges (Cat# 26032)
- Restek 8270 matrix spike (Cat# 33073)
- Restek SV Internal Standard Mix (Cat# 31006)
- Restek B/N Surrogate (Cat# 31024)
- Restek Acid Surrogate (Cat# 31025)
- Restek Benzidines mix (Cat# 31834)

Procedure

Prepare 1 liter samples of DI water and ASTM D5905-95 synthetic waste water.

Adjust pH of samples to <2 by adding H_2SO_4 drop wise.

Spike samples with matrix spike, B/N surrogate, and acid surrogate spiking solutions

Load samples onto FMS TurboTrace Semi-Volatile SPE system.

Affix coconut charcoal and mixed bed with pre-filter cartridges to TurboTrace Semi-Volatile SPE system

Figure 1. FMS TurboTrace SPE with SuperVap concentrator

FMS
Fluid Management Systems

SPE

1. Cartridges pre-wet with DCM
1. Cartridges conditioned with MeOH
2. Cartridges conditioned with H_2O
3. Samples passed across both cartridges at ~15 mm HG
4. Mixed bed cartridge partially dried with N_2 at 10 PSI
5. Sample bottles sprayed with DCM
6. DCM bottle spray loaded across mixed cartridge and collected as Fraction #1
7. Cartridges eluted with additional 10 mL DCM
8. Cartridges purged with N_2 passing all DCM to collection vials.
9. Mixed bed Cartridge re-conditioned with MeOH.
10. Both cartridges conditioned with a 1% NaOH solution
11. Cartridges independently dried with N_2 for 1 minute each
12. Mixed bed Cartridge eluted with additional 30 mL DCM and collected as Fraction #2
13. Coconut charcoal eluted with 30 mL DCM and added to Fraction #2
14. Cartridges independently purged of residual solvent via N_2 stream.

Fractions passed through $NaSO_4$ and combined for evaporation.

SuperVap™ Concentrator

1. Preheat temp: 10 minutes at 40 °C
2. Evap mode: 40 °C
3. Nitrogen Pressure: 10 PSI
4. Evaporate extracts 1 mL*

*Evaporator tubes manually rinsed with DCM to ensure no target analytes adhere to evaporator tube walls.

Internal Standard solution added to extract post evaporation for GC/MS analysis.

Table 1; Mean recoveries in synthetic waste water for table #6 analytes from EPA 625

Analyte	Mean Rec	Acc. Limit
Acenaphthene	76.9	47-145
Acenaphthylene	80.6	33-145
Aldrin	84.8	D-166
Anthracene	92.1	27-133
benzo[a]anthracene	96.2	33-143
benzo[b]fluoranthene	95.9	24-159
benzo[k]fluoranthene	109.5	11-162
benzo[a]pyrene	92.5	17-163
benzo[g,h,i]perylene	92.5	D-219
β-BHC	54.0	24-149
δ-BHC	78.5	D-110
bis(2-chloroethyl) ether	80.2	12-158
bis(2-chloroethoxy)methane	79.2	33-184
bis(2-chloroisopropyl) ether	80.5	36-166
bis(2-ethylhexyl)phthalate	108.8	8-158
4-bromophenyl phenyl ether	82.1	53-127
2-Chloronaphthalene	71.7	60-118
4-chlorophenyl phenyl ether	81.8	25-158
Chrysene	99.1	17-168
4,4'-DDE	59.5	D-145
4,4'-DDD	59.9	4-136
4,4'-DDT	64.5	D-203
dibenzo[a,h]anthracene	92.9	D-227
di-n-butyl phthalate	102.2	1-118
1,2-Dichlorobenzene	73.5	32-129
1,3-Dichlorobenzene	69.7	D-172
1,4-Dichlorobenzene	69.7	20-124
3,3-dichlorobenzidine	78.9	D-262
Dieldrin	70.1	29-136
diethyl phthalate	97.0	D-114
dimethyl phthalate	84.2	D-112
2,4-dinitrotoluene	91.9	39-139

Table 2; Mean recoveries in synthetic waste water for additional analytes tested

Analyte	Mean
Pyridine	44.9
NDMA	30.1
Analine	53.8
benzyl_alcohol	73.2
2-methylphenol	63.6
4-methylphenol/3-methylphenol	76.4
4-Chloroanaline	63.4
4-Chloro-3-methylphenol	56.0
2-methlynaphthalene	73.2
1-methlynaphthalene	71.4
hexachlorocyclopentadiene	37.5
2,4,5-Trichlorophenol	59.3
2-Nitroanaline	78.2
1,4-dinitrobenzene	80.5
1,3-dinitrobenzene	83.1
1,2-dinitrobenzene	85.3
3-Nitroanaline	71.1
dibenzofuran	76.4
2,3,5,6-Tetrachlorophenol	51.1
2,3,4,6-Tetrachlorophenol	52.7
4-Nitroanaline	90.3
NDA-NDPA	86.1
Azobenzene	85.4
Carbazole	102.7
butyl benzyl phthalate	79.0
Benzidine	67.1

Conclusions

Analysis of the analytes from table #6 found in EPA 625 shows that the recoveries for the FMS TurboTrace Semi-Volatile system are all well within the acceptance QC limits for actual waste water matrices. Analysis of additional analytes shows the application is also suitable for analytes beyond those with specified QC criteria by the method.

The ability to efficiently load a waste water matrix in a single pass, with no additional manual pH adjustments or manual steps, makes the FMS TurboTrace Semi-Volatile system a more efficient alternative to traditional LLE methods. By adopting the TurboTrace system, laboratories can eliminate time consuming emulsions and error-prone manual steps from their workflow.

For more information contact FMS at:
FMS, Inc.
580 Pleasant Street
Watertown, MA 02472
Phone: (617) 393-2396
Fax: (617) 393-0194
Email: onlineinfo@fms-inc.com
Web site: www.fms-inc.com

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Fluid Management Systems