Determination of Semi-volatile Organic Compounds in Water using Solid-Phase Extraction (SPE) and GC/MS

UCT Part Numbers

EC82701M15
1000 mg 8270 sorbent/15 mL cartridge (≤ 500 mL sample)

EU52112M6
2000 mg activated carbon/6 mL cartridge (≤ 500 mL sample)

EC82702M15
2000 mg 8270 sorbent/15 mL cartridge (> 500 mL sample)

RFV1F15P
15 mL reservoirs with 1 frit, 10-micron porosity

GCLGN4MM-5
GC liner, 4 mm splitless gooseneck

EU52113M6
3000 mg activated carbon/6 mL cartridge (> 500 mL sample)

AD0000AS
Cartridge adaptor

VMFSTFR12
Large volume sample transfer tubes

VMF016GL
16 position glass block manifold

VMF02125
12 position large volume collection rack

ECSS25K
Sodium sulfate, anhydrous, ACS grade, granular, 60 mesh

Summary:

EPA method 8270 allows the use of liquid-liquid extraction (LLE) and solid-phase extraction (SPE) to extract semi-volatile organic compounds (SVOCs) from aqueous samples and TCLP leachates. LLE requires multiple extractions at two different pH values, consumes large amounts of organic solvents. Also, users can face the dreaded emulsions when shaking samples in separatory funnels.

This application note outlines a reliable, efficient, and cost-effective SPE method utilizing two stacked SPE cartridges, UCT's EC8270 and activated carbon cartridges, to extract SVOCs from wastewater and TCLP samples. Prior to SPE, samples are dechlorinated, and the pH is adjusted to pH < 2, The 8270 SPE cartridge retains the majority of the target analytes, including acids, bases, and neutrals with mid to high hydrophobicity, while the carbon cartridge connected downstream will capture a few very polar compounds*, such as 1,4-dioxane, n-nitrosodimethylamine, nnitrosomethylethylamine, methyl-methanesulfonate, ethyl-methanesulfonate, and 1-Nitrosopyrrolidine. High sample throughput is achieved by extracting multiple samples simultaneously using a multi-port SPE glass block manifold.

**** The carbon cartridge is NOT needed when very polar analytes are not required, including analytes on the TCLP list.***

ENVIRO

UCT

SPE Procedure:

1. Sample Pretreatment

a) Dechlorinate the sample with 80 mg/L of sodium thiosulfate if free chlorine is present.
b) Adjust sample pH to < 2 using 6N HCl.
c) Spike with surrogates and target analytes for fortified samples.

Tip 1: *Prepare the spiking solutions in water-miscible solvents that do not cause degradation of the analytes. Check with your reference material provider.*

2. SPE System Setup

a) Connect the carbon cartridge (**EU52112M6** or **EU52113M6** depending on sample volume) to the end of the 8270 cartridge (**EC82701M15** or **EC82702M15** depending on sample volume) using a cartridge adaptor (**AD0000AS**).
b) Insert a loose plug of deactivated glass wool into the 8270 cartridges to prevent the sorbent from clogging because of samples with high particulate content.
c) Attach the connected SPE cartridges to the SPE manifold (**VMF016GL**).

Tip 2: *The carbon cartridge is not needed if very polar analytes, such as 1,4-dioxane, nnitrosodimethylamine, n-nitrosomethylethyl amine, methyl methanesulfonate, ethyl methanesulfonate, and 1-Nitrosopyrrolidine, are not being analyzed.*

3. Cartridge Conditioning

a) Wash the SPE cartridges with 15 mL of dichloromethane (DCM), soak 1 min, and apply full vacuum for 1 min.
b) Condition the SPE cartridges with 10 mL of methanol. Draw most of the way through the column, leaving a thin layer (about 0.5 cm) of the solvent above the frit. Do not allow cartridges to go dry from this step until instructed to do so in the cartridge drying step.
c) Equilibrate the cartridges with 10 mL of reagent water and 10 mL of 0.05N HCl.

4. Sample Loading

a) Attach the large volume sample delivery tubes (**VMFSTFR12**) to the top of the 8270 cartridges, and insert the stainless steel end of each tube into the sample bottles.
b) Adjust vacuum for a fast dropwise sample flow (about 10-15 mL/min), and draw the entire sample through.

5. Washing and Drying

a) Rinse the sample bottle with 10 mL of reagent water, and apply the rinsate to the SPE cartridges. If the sample matrix contains acetic acid (TCLP), rinse the carbon cartridge with 3 - 4 mL ammonium hydroxide (28-30%).
b) Disassemble the transfer tube and the connected SPE cartridges. Dry the 8270 cartridges under full vacuum for 10 min, and the carbon cartridge for 15 min.

Tip 3: Remove all visible water. *Wet sorbent will result in low analyte recovery.*

6. Analyte Elution

a) Insert the collection rack (VMF02125) with 40-60 mL glass vials into the manifold.
b) Elute the SPE 8270 and carbon cartridges separately. Apply elution solvent to the SPE cartridges, draw 1/3 through, soak 1-2 min, and then draw the remaining solvent through the cartridge in a slow dropwise fashion. Leave full vacuum on for 1 min after each elution.

ENVIRO

UCT

EC8270 Cartridge	Carbon Cartridge
10 mL 1:1 acetone:n-hexane into test tube A (bottle rinse with transfer tube)	1 cartridge volume of DCM into test tube C
1 cartridge volume of 2% ammonia in DCM into test tube B (Prepared fresh daily)	

Tip 4: *Bottle rinse is critical for good recovery of PAHs, which tend to adsorb on the glass wall.*

7. Eluate Drying

a) Dry the eluates using a 15-mL reservoir (or a glass funnel stopped with glass wool) holding about 15-20 g of anhydrous Na2SO4, pre-rinse the Na2SO4 with 10mL of DCM.
b) Insert the collection rack with 40-60 mL glass vials into the manifold to collect the dried eluates.
c) Pass the eluates (A, B, and C) through the Na2SO4 bed and collect.
d) Rinse the eluate vials with 2 x 5 mL of DCM, transfer the rinses to the Na2SO4 bed and collect.

Tip 5: *If Na2SO4 appears greenish, rinse with more solvent until it turns white.*

8. Concentration

a) Concentrate the eluates to 0.7-0.9 mL under a gentle stream of N2 at 40 °C.
b) Add internal standards, transfer the extract to a 2-mL auto-sampler vial, and adjust the final volume to 1 mL.
c) The samples are ready for GC/MS analysis.

GC/MS Method:

GC/MS	Agilent 6890N GC coupled to a 5975C MSD
Injection	1 µL splitless injection at 250 °C, split vent of 30 mL/min at 1 min
GC Liner	4 mm splitless gooseneck (GCLGN4MM-5), packed with deactivated glass wool
GC Column	Restek Rxi®-5sil MS 30m x 0.25mm, 0.25µm with 10m integrated guard column
Carrier Gas	Ultra-high purity helium at a constant flow of 1.5 mL/min
Oven Temp. Program	Initial temperature at 40 °C, hold for 3 min; ramp at 15 °C/min to 240 °C; ramp at 6 °C/min to 310 °C, and hold for 2 min
MSD Temp.	Transfer line 280 °C; Source 250 °C; Quadrupole 150 °C
Full Scan Range	35 - 500 amu

ENVIRO

UCT

SPE Setup

Recovery and RSD in Laboratory Fortified Blanks

(500 mL sample fortified with 40 µg/L of 139 analytes and 6 surrogates)

Compound	Ave Recovery %	RSD % (n=4)
1,2,4,5-Tetrachlorobenzene	**99.5**	4.1
1,2,4-Trichlorobenzene	**88.5**	5.7
1,2-Dichlorobenzene	**90.3**	3.9
1,3,5-Trinitrobenzne	**124.4**	2.8
1,3-Dichlorobenzene	**85.8**	2.8
1,4-Dichlorobenzene	**89.1**	1.1
1,4-Naphthalenedione	**95.3**	4.3
1-Chloronaphthalene	**112.2**	2.7
1-Methyl fluorene	**86.9**	0.9
1-Methyl phenanthrene	**89.8**	1.3
1-Methylnaphthalene	**102.1**	2.7
1-Naphthalenamine	**112.3**	4.7
1-Nitrosopiperidine	**88.9**	5.8
1-Nitrosopyrrolidine	**91.8**	7.2

Compound	Ave Recovery %	RSD % (n=4)
2,3,4,6-Tetrachlorophenol	**103.2**	0.9
2,3-Dichloroaniline	**91.4**	0.6
2,4,5-Trichlorophenol	**123.5**	4.7
2,4,6-Trichlorophenol	**106.5**	3.6
2,4-Dichlorophenol	**97.3**	6.5
2,4-Dimethylphenol	**99.0**	6.4
2,4-Dinitrophenol	**122.4**	2.0
2,4-Dinitrotulene	**112.0**	1.7
2,6-Dichlorophenol	**113.3**	0.7
2,6-Dinitrotoluene	**106.3**	2.3
2-Acetylaminofluorene	**109.0**	6.5
2-Chloronaphthalene	**96.9**	2.8
2-Chlorophenol	**99.4**	2.9
2-Isopropyl naphthalene	**73.1**	0.1
2-Methylnaphthalene	**101.2**	4.9
2-Methylphenol	**97.6**	6.7
2-Naphthalenamine	**130.5**	2.7
2-Nitroaniline	**107.5**	3.6
2-Nitrophenol	**98.2**	5.9
2-Picoline	**74.4**	5.0
3&4-Methylphenol	**104.2**	6.6
3,3′-Dichlorobenzidine	**72.3**	11.4
3,6-Dimethyl phenanthrene	**90.6**	0.9
3-Methylcholanthrene	**106.5**	1.4
3-Nitroaniline	**100.4**	4.9
3-Nitrophenol	**99.5**	8.2
4,4′-DDD	**94.4**	0.8
4,4′-DDE	**91.8**	0.4
4,4′-DDT	**94.0**	0.3
4,6-Dinitro-2-methylphenol	**116.8**	4.5
4-Aminobiphenyl	**103.8**	13.5
4-Chloro-3-methylphenol	**111.7**	6.3
4-Chloroaniline	**105.0**	3.9
4-Chlorophenylphenylether	**99.5**	3.0
4-Nitroaniline	**114.9**	4.6
4-Nitrophenol	**97.2**	3.0
5-Nitro-o-toluidine	**94.7**	4.0
7,12-Dimethyl benz[a]anthracene	**99.9**	6.1
Acenaphthene	**100.1**	1.3
Acenaphthylene	**102.6**	0.6
Acetophenone	**101.8**	7.4

ENVIRO

UCT

Compound	Ave Recovery %	RSD % (n=4)
Aldrin	**89.5**	0.8
alpha lindane	**90.1**	0.2
Aniline	**90.0**	3.2
Anthracene	**109.7**	1.1
Azobenzene	**105.5**	5.2
Benz[a]anthracene	**103.3**	6.2
Benzidine	**66.8**	14.0
Benzo[a]pyrene	**99.3**	2.1
Benzo[b]fluoranthene	**99.4**	7.0
Benzo[ghi]perylene	**104.2**	1.1
Benzo[k]fluoranthene	**108.1**	5.4
Benzoic acid	**115.0**	4.7
Benzyl alcohol	**72.9**	12.9
Benzyl butyl phthalate	**111.8**	6.0
beta lindane	**95.2**	1.1
Bis(2-ethylhexyl) phthalate	**113.2**	2.0
Bis[2-chloroethoxy]methane	**91.0**	7.8
Bis[2-chloroethyl]ether	**88.5**	3.0
Bis[2-chloroisopropyl]ether	**87.3**	4.5
Bromophenoxybenzene	**99.6**	4.8
Carbazole	**109.6**	3.3
Chlorobenzilate	**116.3**	9.4
Chrysene	**103.3**	1.2
delta lindane	**95.2**	0.8
Diallate (cis & trans)	**104.7**	4.5
Dibenz[ah]anthracene	**108.8**	2.5
Dibenzofuran	**102.0**	0.6
Dibutyl phthalate	**114.6**	6.2
Dieldrin	**94.5**	0.7
Diethyl phthalate	**110.4**	1.2
Dimethoate	**96.6**	0.7
Dimethyl phthalate	**110.3**	1.3
Di-n-octyl phthalate	**116.6**	5.9
Dinoseb	**121.9**	1.7
Diphenylamine	**109.9**	4.8
Disulfoton	**87.0**	0.6
Endosulfan I	**93.8**	0.7
Endosulfan II	**96.5**	0.5
Endosulfan sulfate	**96.2**	0.7
Endrin	**97.4**	1.0
Endrin aldehyde	**93.4**	0.5

ENVIRO

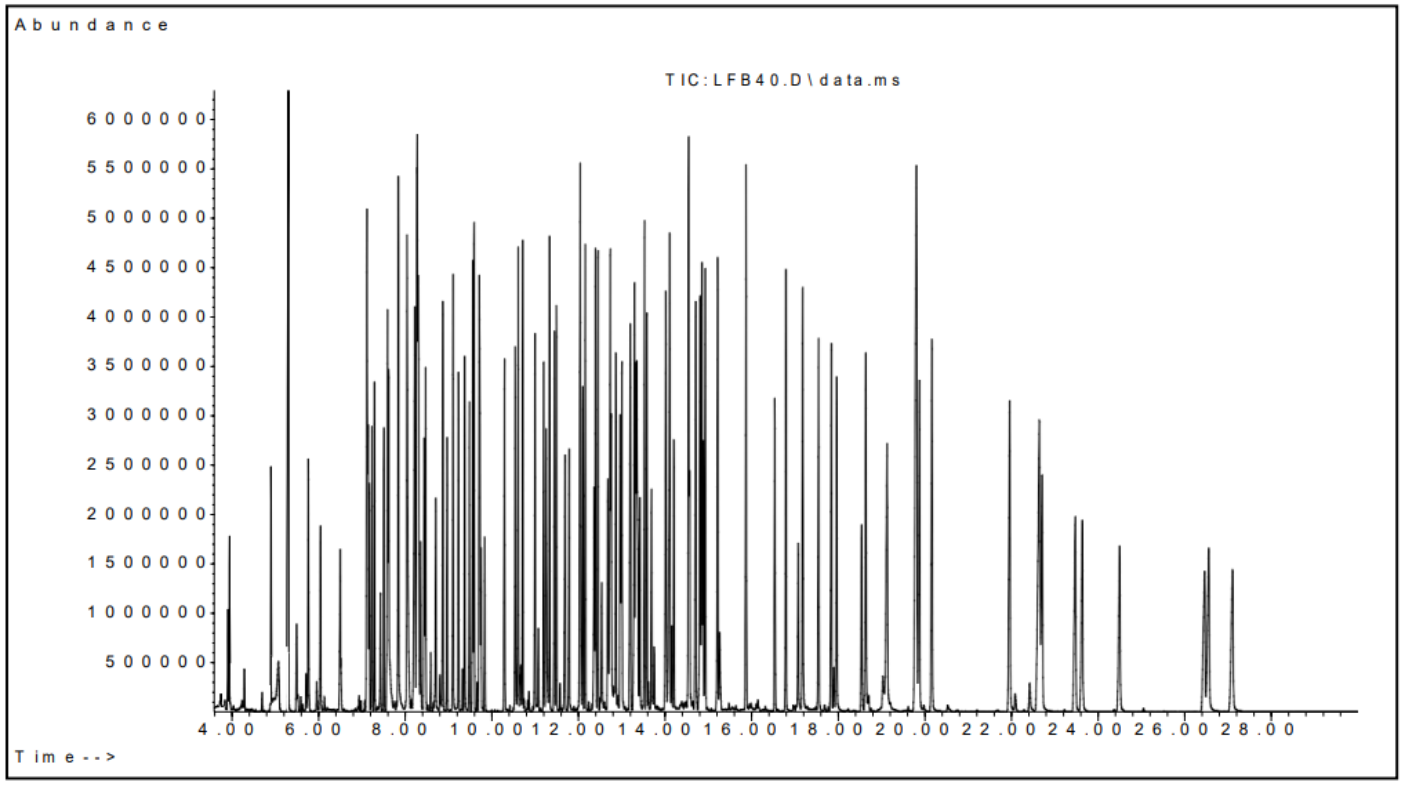
UCT

Compound	Ave Recovery %	RSD % (n=4)
Ethyl methanesulfonate	**92.5**	3.7
Famphur	**109.3**	1.2
Fluoranthene	**105.8**	6.1
Fluorene	**103.7**	2.6
gamma lindane	**93.1**	1.3
Heptachlor	**88.1**	1.0
Heptachlor epoxide	**93.4**	0.9
Hexachlorobenzene	**101.3**	6.1
Hexachlorobutadiene	**85.0**	1.0
Hexachloroethane	**92.6**	6.0
Hexachloropropene	**72.1**	1.1
Hexachorocyclopentadiene	**85.9**	3.1
Indeno[123-cd]pyrene	**103.2**	2.5
Isodrin	**105.1**	7.2
Isophorone	**91.0**	6.8
Isosafrole (cis & trans)	**102.9**	6.1
Methyl methanesulfonate	**70.8**	3.5
Methyl parathion	**96.6**	0.4
Naphthalene	**97.2**	2.3
Nitrobenzene	**94.0**	7.2
N-nitro-di-n-propylamine	**99.3**	6.3
N-nitroso di-n-butylamine	**99.9**	4.7
N-nitrosodiethylamine	**89.4**	3.7
N-nitrosodimethylamine	**68.8**	3.0
N-nitrosomethylethylamine	**87.4**	2.5
o,o,o-Triethylphosphorothioate	**90.8**	0.4
o-Toluidine	**91.4**	9.7
Parathion	**95.8**	0.7
p-Dimethylaminoazobenzene	**91.5**	10.5
Pentachlorobenzene	**90.9**	1.0
Pentachloroethane	**86.0**	3.8
Pentachloronitrobenzene	**104.3**	4.2
Pentachlorophenol	**109.3**	3.3
Phenacetin	**116.4**	3.9
Phenanthrene	**108.0**	0.4
Phenol	**56.2**	4.2
Phorate	**86.7**	0.1
Pronamide	**111.2**	5.2
Pyrene	**109.1**	8.5
Pyridine	**46.1**	8.0
Safrole	**90.7**	4.3
Sulfotep	**92.5**	0.8
Thionazin	**95.1**	0.7
Surrogates		
2-Fluorophenol (S)	**87.2**	0.6
Phenol d6 (S)	**59.1**	0.4
Nitrobenzene d5 (S)	**94.3**	1.0
2-Fluorobiphenyl (S)	**81.5**	0.5
2,4,6-Tribromophenol (S)	**95.4**	0.2

ENVIRO

UCT

Chromatogram of an LFB Fortified at 40 µg/L



5108-04-01

UCT, LLC • 2731 Bartram Road • Bristol, PA 19007 800.385.3153 • 215.781.9255
www.unitedchem.com Email: methods@unitedchem.com