EPA Method 625: Determination of Bases, Neutrals and Acids by Solid Phase Extraction and GC/MS Detection

UCT Part Numbers:
EC82701M15 - 1000 mg 8270 sorbent/15 mL cartridge
or
EC82702M15 - 2000 mg 8270 sorbent/15 mL cartridge
EU52112M6 - 2000 mg activated carbon/6 mL cartridge
or
EU52113M6 - 3000 mg activated carbon/6 mL cartridge
AD0000AS - Cartridge adaptor
VMFSTFR12 - Large volume sample transfer tubes
VMF016GL - 16 position glass block manifold
VMF02125 - 12 position large volume collection rack
RFV1F15P - 15 mL reservoirs with 1 frit, 10 micron porosity
ECSS25K - Sodium sulfate, anhydrous, ACS grade, granular, 60 mesh
GCLGN4MM-5 - GC liner, 4 mm splitless gooseneck, 4mm ID x 6.5mm OD x 78.5mm

EPA method 625 was published many years ago for the analysis of bases, neutrals and acids in municipal and industrial wastewater. The analysis uses liquid-liquid extraction (LLE) and GC/MS detection. This technique requires multiple extractions at 2 different sample pHs and consumes large amounts of organic solvents. EPA method 625.1, an updated version of method 625 has been recently published (by Lemuel Walker, Office of Science and Technology, US EPA) allowing for the use of solid phase extraction (SPE) as an alternative sample preparation technique if the quality control (QC) acceptance criteria are met.

Recently, the Independent Laboratory Institute (ILI) led a working group including regulatory agencies, commercial SPE vendors, analytical testing laboratories and academia. The goal was to validate the performance of SPE and see if it offered comparable extraction results to traditional LLE. Various sample matrices, e.g. reagent water, synthetic wastewater, and TCLP (Toxicity Characteristic Leaching Procedure) buffer samples were investigated. UCT was one of several SPE vendors that participated in this validation study. Clean extracts, low method detection limits and excellent analyte recoveries were obtained using UCT's specially designed SPE sorbents. Results were excellent even for compounds that usually result in low recoveries when using LLE (e.g. 2,4-dinitrophenol and pentachlorophenol).

SPE Procedure:

1. Sample Pretreatment

a) To 200 mL of water sample add 20 mg 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: The spiking solutions should be prepared in water miscible solvents, such as methanol and acetone. If water sample turns milky after spiking, make a more diluted spiking solution or mix with 2-3 mL methanol before spiking the sample. This will help prevent low analyte recovery caused by poor water solubility of some analytes.

2. SPE System Setup

a) Connect the carbon cartridge (**EU52112M6** or **EU52113M6**) to the end of the 8270 cartridge (**EC82701M15** or **EC82702M15**) using a cartridge adaptor (**AD0000AS**).

b) Insert a loose plug of deactivated glass wool into the 8270 cartridge to prevent sorbent clogging caused by 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 several very polar analytes, such as 1,4-dioxane, n-nitrosodimethylamine, n-nitrosomethylethylamine, methyl methanesulfonate, ethyl methanesulfonate, and 1-Nitrosopyrrolidine are not being analyzed.

Tip 3: Use SPE cartridges with higher sorbent amounts (**EU52113M6** and **EC82702M15**) *for samples with > 500 mL volume or highly spiked (> 20 µg for each target analyte).*

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 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 tube (**VMFSTFR12**) to the top of the 8270 cartridge, and insert the stainless steel end of the tube into the sample bottle.

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.

b) Disassemble the transfer tube and the connected SPE cartridges. Dry the 8270 cartridge under full vacuum for 10 min, and the carbon cartridge for 15 min.

Tip 4: Remove as much water as possible, wet sorbents 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.

8270 Cartridge	10 mL 1:1 acetone:n-hexane* (bottle rinse added to 8270 cartridge using transfer tube)
	10 mL DCM
	4 mL ammonium hydroxide (28-30%), drain to waste
	3 x 7 mL DCM
Carbon Cartridge	5 x 3 mL DCM

**: Use 10 mL DCM if Horizon's DryVap is used to dry the SPE eluates, as acetone (water miscible) may cause low recovery for some polar analytes, such as 2,4-dinitrophenol.*

Tip 5: 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 Na_2SO_4, pre-rinse the Na_2SO_4 with 10 mL 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 through the Na_2SO_4 bed.

d) Rinse the eluate vials with 2 x 5 mL of DCM, transfer the rinses to the Na_2SO_4 bed.

Tip 6: If Na_2SO_4 appears greenish, rinse with more solvent until it turns white.

8. Concentration

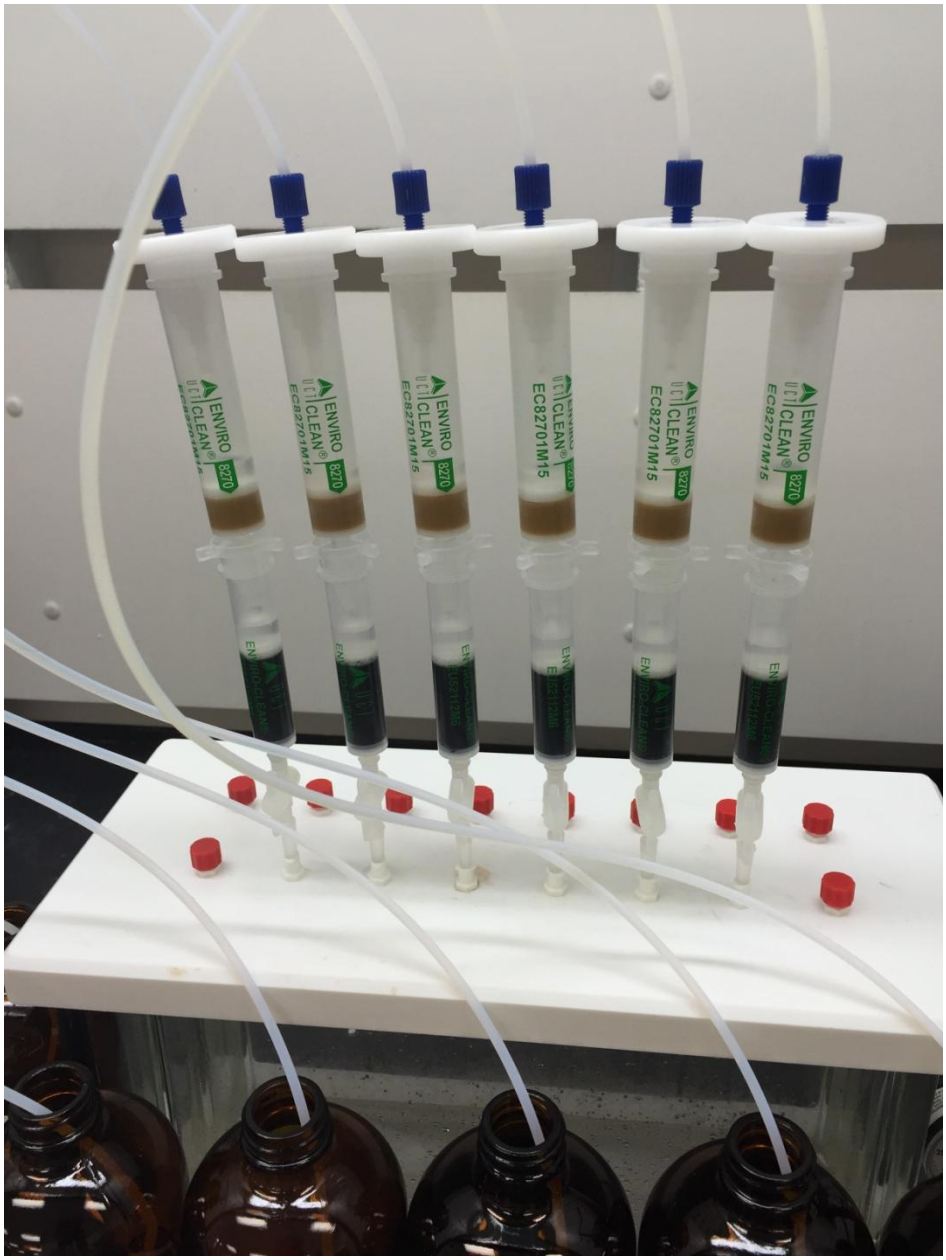
a) Concentrate the eluates to 0.7-0.9 mL under a gentle stream of N_2 at 40 ºC.

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

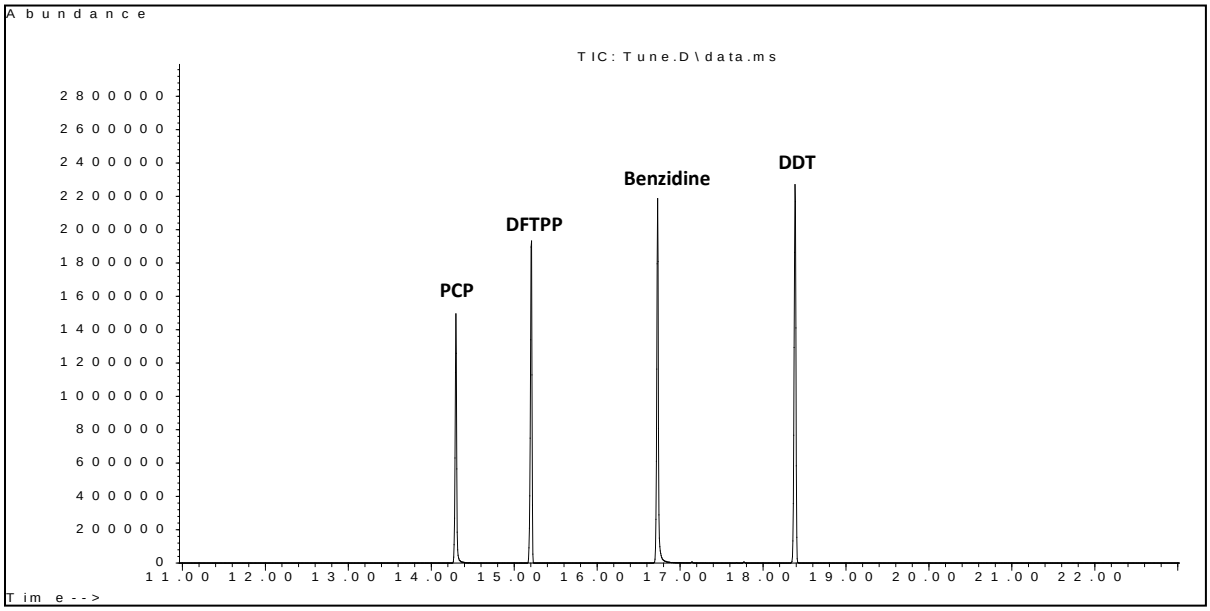
GC/MS	Agilent 6890N GC coupled to a 5975C MSD
Injection	1 µL splitless injection at 250 ºC, split vent of 30 mL/min at 1 min
GC Liner	4 mm splitless gooseneck (GCLGN4MM-5), packed with deactivated glass wool
GC Column	Restek Rxi®-5sil MS 30m x 0.25mm, 0.25µm with 10m integrated guard column
Carrier Gas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



UCT SPE Extraction System

The 8270 cartridge on top captures the majority compounds including bases, neutrals and acids, while the downstream carbon cartridge retains a few very polar compounds, such as 1,4-dioxane, n-nitrosodimethylamine, n-nitrosomethylethylamine, methyl methanesulfonate, ethyl methanesulfonate, and 1-nitrosopyrrolidine.

GC/MS Performance Check using UCT GC Liners (GCLGN4MM-5)



DFTPP tune:

DFTPP tune met the method required criteria.

Tailing factor:

Pentachlorophenol (PCP) = 1.03

Benzidine = 0.88

Tailing factors met the required criteria (< 2).

DDT breakdown:

(DDE + DDD) / (DDE + DDD + DDT) * 100% = 0.4%

DDT breakdown met the required criteria (< 20%).

Target Analyte Recovery from the Spiked DI Water, Synthetic Wastewater (SWW), and TCLP Buffer Samples, including Method Detection Limits (MDL)

Target Analyte	Average Recovery%			MDL
	DI water	SWW	TCLP	(µg/L)
1,4-Dioxane	58	42	50	0.7
Pyridine	59	27	51	0.6
N-nitrosodimethylamine	80	82	83	0.7
2-Picoline	79	82	75	0.7
N-nitrosomethylethylamine	88	92	88	0.9
Methyl methanesulfonate	80	69	68	0.5
N-nitrosodiethylamine	90	99	96	0.7
Ethyl methanesulfonate	93	96	92	1.0
Pentachloroethane	83	73	78	0.7
Aniline	95	86	82	2.1
Phenol	80	102	103	1.1
Bis[2-chloroethyl]ether	89	99	97	0.7
2-Chlorophenol	99	107	101	0.6
1,3-Dichlorobenzene	79	71	76	0.5
1,4-Dichlorobenzene	82	73	78	0.8
Benzyl alcohol	104	93	100	1.8
1,2-Dichlorobenzene	85	78	82	0.9
2-Methylphenol	97	117	103	1.2
Bis[2-chloroisopropyl]ether	89	95	98	0.5
Acetophenone	105	108	107	1.2
1-Nitrosopyrrolidine	95	107	101	1.1
3&4-Methylphenol	106	121	106	3.0
o-Toluidine	94	97	83	1.3
N-nitro-di-n-propylamine	99	111	109	0.9
Hexachloroethane	83	71	76	1.1
Nitrobenzene	96	98	99	1.2
1-Nitrosopiperidine	92	104	103	0.7
Isophorone	95	102	100	1.0
2-Nitrophenol	102	104	100	1.1
2,4-Dimethylphenol	103	107	109	0.8
Bis[2-chloroethoxy]methane	99	108	104	0.8
Benzoic acid	122	116	113	1.1

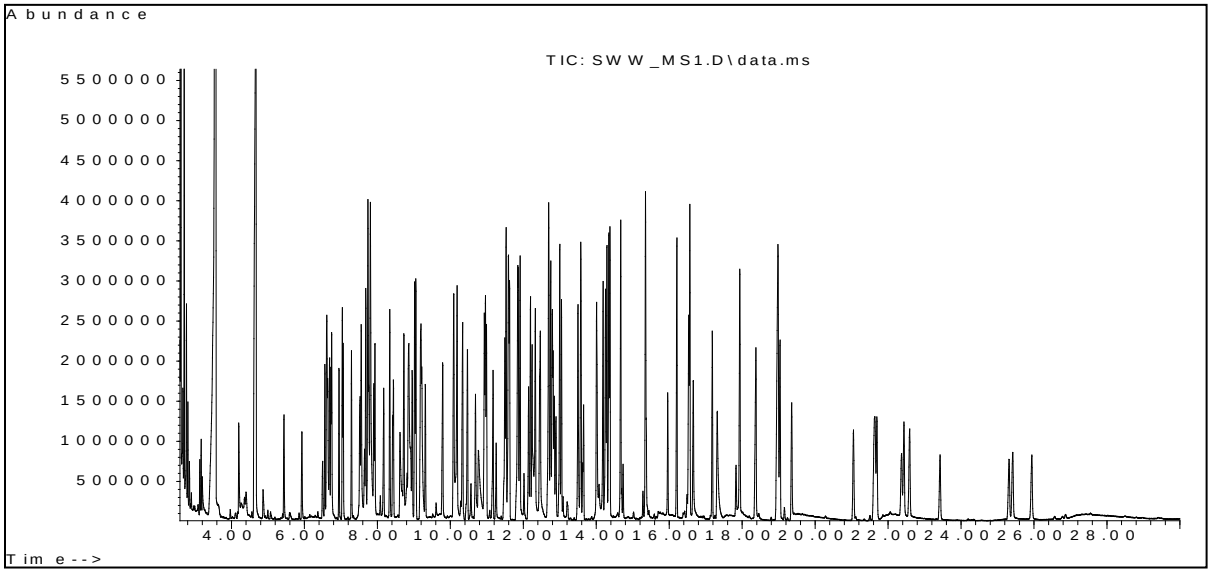
2,4-Dichlorophenol	103	118	106	0.5
1,2,4-Trichlorobenzene	88	82	88	0.7
Naphthalene	94	91	90	0.7
2,6-Dichlorophenol	109	114	105	1.6
4-Chloroaniline	103	108	89	1.0
Hexachloropropene	67	42	76	0.8
Hexachlorobutadiene	71	76	79	1.0
N-nitroso di-n-butylamine	97	107	102	2.3
4-Chloro-3-methylphenol	108	120	106	2.2
Isosafrole (cis & trans)	98	96	94	2.1
2-Methylnaphthalene	96	102	91	2.2
1-Methylnaphthalene	97	95	92	2.2
1,2,4,5-Tetrachlorobenzene	88	86	86	1.7
Hexachorocyclopentadiene	70	31	78	1.1
2,4,6-Trichlorophenol	104	96	100	2.0
2,4,5-Trichlorophenol	108	125	106	2.4
Safrole	91	92	95	1.3
1-Chloronaphthalene	101	93	96	2.1
2-Chloronaphthalene	94	80	85	2.3
2-Nitroaniline	106	116	103	2.4
1,4-Naphthalenedione	93	69	71	1.7
Dimethyl phthalate	106	117	106	2.1
Acenaphthylene	100	101	98	1.9
2,6-Dinitrotoluene	104	118	102	1.9
3-Nitroaniline	100	111	97	0.6
3-Nitrophenol	106	70	98	0.9
Acenaphthene	98	96	94	0.7
2,4-Dinitrophenol	123	91	91	2.4
Dibenzofuran	99	97	94	0.8
4-Nitrophenol	102	106	97	3.3
Pentachlorobenzene	90	81	88	0.4
2,4-Dinitrotulene	108	102	103	1.1
1-Naphthalenamine	111	107	88	2.8
2,3,4,6-Tetrachlorophenol	101	102	98	0.8
2-Naphthalenamine	128	119	107	1.2
Diethyl phthalate	107	116	105	1.4
Fluorene	99	98	96	1.4
4-Chlorophenylphenylether	95	93	92	1.4
5-Nitro-o-toluidine	92	99	95	1.3
4-Nitroaniline	110	107	102	1.6

4,6-Dinitro-2-methylphenol	110	72	95	1.6
Diphenylamine	103	113	101	1.5
Azobenzene	100	97	99	1.5
Diallate (cis & trans)	100	104	102	1.7
1,3,5-Trinitrobenzne	119	80	99	1.4
Bromophenoxybenzene	92	92	90	1.1
Phenacetin	110	116	107	1.4
Hexachlorobenzene	94	65	94	1.1
4-Aminobiphenyl	95	89	82	1.6
Pentachlorophenol	105	99	95	2.6
Pronamide	104	116	104	2.3
Pentachloronitrobenzene	98	79	97	1.4
Phenanthrene	106	104	103	1.0
Dinoseb	119	69	100	1.2
Anthracene	107	104	104	1.4
Carbazole	109	117	107	1.2
Dibutyl phthalate	115	121	111	1.3
Isodrin	108	64	103	1.0
Fluoranthene	107	103	106	1.2
Benzidine	80	27	61	0.9
Pyrene	107	103	106	1.1
p-Dimethylaminoazobenzene	89	94	87	0.6
Chlorobenzilate	116	124	109	0.8
Benzyl butyl phthalate	114	115	109	1.1
2-Acetylaminofluorene	114	123	112	1.3
Benz[a]anthracene	105	79	103	1.4
3,3'-Dichlorobenzidine	72	78	68	1.2
Chrysene	103	78	105	0.6
Bis(2-ethylhexyl) phthalate	115	50	112	1.1
Di-n-octyl phthalate	115	45	112	0.5
Benzo[b]fluoranthene	97	54	103	0.7
Benzo[k]fluoranthene	108	64	109	0.6
7,12-Dimethyl benz[a]anthracene	98	55	101	0.7
Benzo[a]pyrene	101	60	106	0.8
3-Methylcholanthrene	105	48	106	0.7
Indeno[123-cd]pyrene	101	48	104	0.9
Dibenz[ah]anthracene	105	48	104	0.8
Benzo[ghi]perylene	102	47	106	0.9
Overall mean	**98**	**90**	**96**	**1.3**

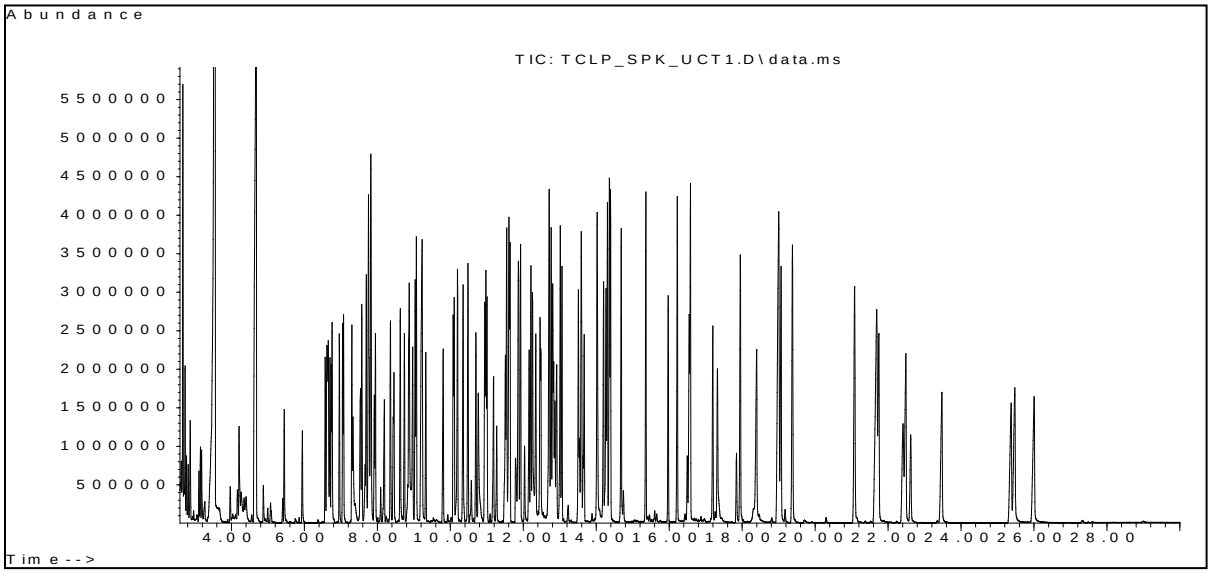
Surrogate Recovery in the Spiked DI Water, Synthetic Wastewater, and TCLP Buffer Samples

Surrogate	Average Recovery%		
	DI water	SWW	TCLP
N-nitrosodimethylamine d6	77	69	81
Phenol d5	80	78	92
Bis(2-chloroethyl) ether d8	89	82	94
2-Chlorophenol d4	95	86	92
4-Methylphenol d8	99	98	98
Nitrobenzene d5	91	81	91
2-Nitrophenol d4	100	87	93
2,4-Dichlorophenol d3	98	95	96
4-Chloroaniline d4	94	85	79
Dimethylphthalate d6	99	95	94
Acenaphthylene d8	93	81	86
4-Nitrophenol d4	111	88	86
Fluorene d10	92	85	89
4,6-Dintro-2-methylphenol d2	119	69	96
Anthracene d10	92	84	90
Pyrene d10	95	86	93
Benzo(a)pyrene d12	95	50	98
Overall mean	**95**	**82**	**91**

GC/MS Chromatograms



200 mL Synthetic Wastewater Spiked with 100 µg/L of Target Analytes



200 mL TCLP Sample Spiked with 100 µg/L of Target Analytes

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