COMPLETE DETERMINATION OF ACIDS, BASES, AND NEUTRALS IN WATER USING SOLID PHASE EXTRACTION FOR EPA METHOD 8270

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1. INTRODUCTION

A reliable, efficient, and cost-effective solid phase extraction (SPE) method has been developed for EPA Method 8270 utilizing two stacked SPE cartridges, UCT 8270 and activated carbon cartridges. This extraction method offers several advantages over the traditional liquid-liquid extraction. Liquid-liquid extraction requires multiple extractions at two different pH values and consumes large amounts of organic solvents (360-1000 mL). This newly developed SPE method needs only one extraction and consumes much less organic solvents (70 mL). High throughout can be achieved by extracting multiple samples simultaneously using a multi-port SPE manifold.

A wide range of 137 target analytes and 6 surrogates have been analyzed using this method. The UCT 8270 cartridge retains many of the target analytes including acids, bases, and neutrals; meanwhile the carbon cartridge, connected downstream from the 8270 cartridge, captures several very polar compounds, such as n-nitrosodimethylamine, n-nitrosomethylethylamine, methyl methanesulfonate, ethyl methanesulfonate, and 1-Nitrosopyrrolidine. The carbon cartridge is NOT needed if none of these very polar analytes is being analyzed.

2. EXPERIMENTAL

2.1 Apparatus, reagents and standards

SPE manifold:
16-port or 24-port vacuum manifold (UCT part#: **VMF016GL** or **VMF024GL**), or 6-station universal manifold (UCT part#: **ECUCTVAC6**).

SPE cartridges and adaptors:
1. UCT8270 cartridge: 1000 mg 8270 sorbent in 15 mL cartridge (UCT part#: **EC82701M15**);
2. Carbon cartridge: 2000 mg activated carbon in 6 mL cartridge (UCT part#: **EU52112M6**).
3. Cartridge adaptor: Connects cartridge of any size onto a 1, 3, 6, 10 or 15 mL cartridge (UCT part#: **AD0000AS**).

Other apparatus needed:
pH meter, large sample delivery tubes, 15 mL empty fritted polypropylene reservoirs (UCT part#: **RFV1F15P**), TurboVap, glass vials and other commonly used labware.

Reagents:
HPLC grade Methanol (MeOH)
Pesticide grade Acetone
Pesticide grade Dichloromethane (DCM)
Pesticide grade Ethyl acetate (EtOAc)
ACS grade Ammonium hydroxide (28-30%)
6N Hydrochloric acid (HCl)
Reagent grade Sodium thiosulfate

All reagents were purchased from J.T. Baker, Spectrum, or Sigma-Aldrich. ACS grade anhydrous sodium sulfate (Na_2SO_4) was from UCT (Part#: **ECSS25K**).

Standards:
137 target analytes, 6 surrogates, 6 internal standards (IS), and GC/MS tune mixture were purchased from Restek, Cerilliant, or Sigma-Aldrich.

2.2 SPE procedure

1. Sample pretreatment

a) Transfer 500 mL of water sample to a 1-L amber glass bottle; add 40-50 mg of sodium thiosulfate if free chlorine present.
b) Adjust sample pH to less than 2 using 6N HCl.
c) Spike with surrogates, and target analytes for fortified samples.

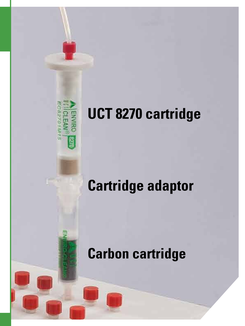

Figure 1
UCT SPE System for EPA Method 8270

2. SPE system setup

a) Connect the carbon cartridge (**EU52112M6**) to the end of the 8270 cartridge (**EC82701M15**) using cartridge adaptor (**AD0000AS**).
b) Insert a loose plug of deactivated glass wool into the 8270 cartridge. This will minimize sorbent clogging caused by samples with a high particulate content.
c) Attach the connected SPE cartridges to the SPE manifold.

3. Cartridge conditioning

a) Wash the cartridges with 10 mL of dichloromethane (DCM), allow them to soak for 1 min, and then apply full vacuum for 1 min.
b) Condition with 10 mL of methanol. Do not let cartridges go dry from this step on until instructed to do so in the cartridge drying step.
c) Equilibrate with 10 mL of reagent water and 10 mL of 0.05N HCl.

4. Sample extraction

a) Attach the large sample delivery tube to the 8270 cartridge, and insert the stainless steel end of the tube into the sample bottle.
b) Turn on the vacuum to the manifold and adjust it for a fast, dropwise sample flow (about 10 mL/min). Draw the entire sample through the cartridges.

5. Washing and drying

a) Rinse the sample bottle with 10 mL of reagent water, and apply the rinsate to the cartridges.
b) Disassemble the tube and separate the connected SPE cartridges. Dry the 8270 cartridge under full vacuum for 10 min and the carbon cartridge for 15 min.

Note: Remove as much water as possible, wet sorbent results in low analyte recovery.

6. Analyte elution

a) Insert glass containers into the manifold to collect eluents.
b) **The 8270 and Activated Carbon Cartridges are eluted separately.**
Apply the elution solvents described below to the respective SPE cartridges; draw 1/3 through, allow the solvent to soak for 1 min., and draw the remaining through in a slow dropwise fashion.
   1) **8270 cartridge elution:** Add about 2 cm of anhydrous Na_2SO_4 to the 8270 cartridge. Elute with: 2 * 2.5 mL of acetone; followed by 5 mL of DCM; then 1 mL of ammonium hydroxide (28-30%); and lastly 2 * 5 mL of DCM.
   2) **Activated Carbon Cartridge elution:** Elute with: 3 * 5 mL of DCM.

7. Eluate drying

a) Dry the eluate using a blank cartridge (**RFV1F15P**) (or a glass funnel stopped with glass wool) holding about 20 g of anhydrous Na_2SO_4, pre-rinse the Na_2SO_4 with 5 mL of DCM.
b) Insert a 50-mL glass vial into the manifold to collect the dried eluate.
c) Pass the eluate from both the 8270 cartridge and the activated carbon cartridge through the Na_2SO_4 bed.
d) Rinse the sample bottle with 5 mL of DCM, transfer the bottle rinse to the eluate vial, cap and shake before passing the rinsate through the Na_2SO_4.
e) Repeat Step d) with 5 mL of EtOAc.

Note: Bottle rinse is critical for good recovery of PAHs, which can be adsorbed onto the glass wall. If the Na_2SO_4 appears greenish, rinse with additional solvent until it turns white.

8. Concentration

a) Concentrate the dried eluate to about 1 mL under a gentle stream of N_2 at 40 °C.
b) Transfer the concentrated extract to a 2-mL autosampler vial, adjust the final volume to 1 mL with EtOAc.
c) Add IS and mix well. The samples are ready for GC/MS analysis.

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2.3 GC/MS parameters

GC/MS: An Agilent 6890N GC coupled with a 5975C MSD and a 7683 autosampler
Liner: 4 mm splitless gooseneck liner packed with deactivated glass wool (UCT part#: **GCLGN4MMGW**)
Injector: 1 µL splitless injection at 250 °C, with a split vent of 30 mL/min at 1 min
GC capillary column: Restek Rxi®-5sil MS, 30m*0.25mm*0.25µm, with 10 m integrated guard column
Temperature program: Initial oven temperature of 40 °C, hold for 3 min; ramp at 5 °C/min to 240 °C; ramp at 6 °C/min to a final temperature of 310 °C, hold for 2 min.
Carrier gas: Ultra high purity Helium at a constant flow of 1.5 mL/min.
MSD condition: Aux temperature: 280 °C; MS Source: 230 °C; MS Quad: 150 °C
Tune: dftppp.u
Full scan: 35-500 amu

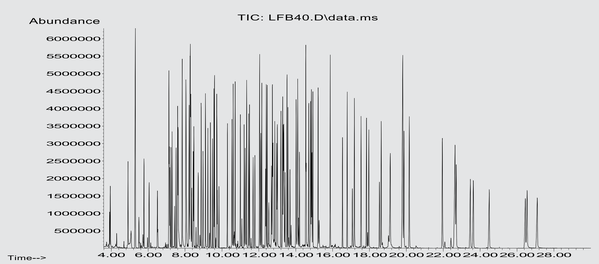
3. RESULTS

Samples were analyzed in compliance with the quality control requirements in EPA Method 8270, including DFTPP tune, DDT breakdown, initial calibration criteria, and continuous calibration check. Laboratory fortified blank (LFB) samples were spiked with 40 µg/L of target analytes and surrogates, and were extracted in 4 replicates. Excellent recoveries and relative standard deviations (RSD) were obtained using UCT's newly developed method for EPA method 8270.

Lake water sampled from Mercer Lake (West Windsor, NJ, USA) was extracted as well as matrix spike (MS) and matrix spike duplicate (MSD) samples. Acceptable recoveries were obtained for the majority of target analytes. The few exceptions were 1,4-naphthalenedione, 3,3'-dimethyl benzidine, benzidine and kepone. These recoveries may have been affected by the matrix effect, as high amounts of cyclic octaatomic sulfur (S8) and other interferences were found in the lake water tested.

Method detection limits (MDL) were determined by extracting 7 replicates of LFB samples spiked at trace levels and calculated according to 40 CFR Part 136. MDLs ranged between 0.26 and 3.08 µg/L for 500 mL water samples.

Figure 2: Chromatogram of a Laboratory Fortified Blank at 40 µg/L



W W W . U N I T E D C H E M . C O M

Compound	Fortified reagent blank		Lake water		MDL (ug/L) (n=7)
	Recovery%	RSD% (n=4)	MS (%)	MSD (%)	
1,2,4,5-Tetrachlorobenzene	64	8.4	57	58	2.5
1,2,4-Trichlorobenzene	82	3.7	63	68	2.3
1,2-Dichlorobenzene	87	1.1	64	71	2.0
1,3,5-Trinitrobenzene	91	3.7	95	93	1.1
1,3-Dichlorobenzene	75	2.0	56	62	2.1
1,4-Dichlorobenzene	79	1.8	59	65	2.0
1,4-Naphthalenedione	83	0.4	1	1	1.5
1-Methyl fluorene	74	8.1	79	77	0.8
1-Methyl phenanthrene	79	7.5	77	73	0.8
1-Naphthalenamine	106	3.1	95	94	0.4
1-Nitroso pyrrolidine	115	0.1	86	93	0.4
1-Nitrosopiperidine	117	1.4	82	87	0.3
2,3,4,6-Tetrachlorophenol	105	2.4	86	88	0.5
2,3-Dichloroaniline	89	1.0	88	83	0.8
2,4,5-Trichlorophenol	110	1.8	95	98	0.6
2,4,6-Trichlorophenol	105	1.2	88	93	1.4
2,4-Dichlorophenol	117	0.4	92	97	0.6
2,4-Dimethylphenol	118	0.8	93	98	0.6
2,4-Dinitrophenol	97	6.6	89	103	0.9
2,4-Dinitrotoluene	112	0.8	95	91	0.5
2,6-Dichlorophenol	110	2.1	93	98	0.5
2,6-Dinitrotoluene	110	0.2	98	101	0.4
2-Acetylaminno fluorene	116	1.3	104	99	0.7
2-Chloro naphthalene	90	3.2	69	68	0.5
2-Chlorophenol	114	1.8	85	93	0.4
2-Isopropyl naphthalene	51	0.9	55	57	0.6
2-Methyl naphthalene	95	1.4	75	79	0.4
2-Methylphenol	117	0.4	89	95	0.8
2-Naphthalenamine	114	3.4	119	119	1.4
2-Nitroaniline	112	0.2	96	99	0.6
2-Nitrophenol	112	1.2	83	91	0.5
2-Picoline	92	1.0	46	48	2.3
3,3'-Dichlorobenzidine	93	3.7	78	78	1.8
3,3'-Dimethyl benzidine	74	7.6	14	17	1.3
3,6-Dimethyl phenanthrene	79	7.3	85	80	0.9
3/4-Methylphenol	116	0.6	98	103	0.5
3-Methylcholanthrene	85	2.4	74	70	0.6
3-Nitroaniline	101	2.0	94	94	0.5
4,4'-DDD	81	7.0	90	86	0.8
4,4'-DDE	77	6.6	83	78	0.9
4,4'-DDT	84	6.4	63	56	0.7
4,6-Dinitro-2-methylphenol	98	3.3	96	100	0.7
4-Aminobiphenyl	95	5.2	86	84	0.6
4-Chloro-3-methylphenol	115	1.1	98	101	0.4
4-Chloroaniline	105	0.9	86	90	2.0
4-Chlorophenylphenylether	77	0.9	77	78	0.6
4-Nitroaniline	102	0.2	100	99	0.7
4-Nitrophenol	98	1.1	91	94	0.8
5-Nitro-o-toluidine	111	0.2	96	93	0.6
7,12-Dimethyl benz[a]anthracene	84	0.5	81	75	0.5
Acenaphthene	95	0.3	81	83	0.5
Acenaphthylene	97	0.2	83	87	0.6
Acetophenone	119	0.1	83	90	0.5
Aldrin	69	15	42	34	1.0
alpha lindane	102	2.2	91	90	0.7
Aniline	107	0.2	74	81	3.6
Anthracene	92	1.4	87	85	0.5
Azobenzene	97	1.9	87	90	0.5
Benz[a]anthracene	92	0.4	92	86	0.5
Benzidine	78	4.5	5	7	1.2
Benzo[a]pyrene	94	0.3	91	86	0.5
Benzo[b]fluoranthene	91	0.3	83	78	0.6
Benzo[ghi]perylene	89	3.0	77	72	0.6
Benzo[k]fluoranthene	97	1.4	100	92	0.6
Benzoic acid	109	2.1	66	70	0.4
Benzyl Alcohol	114	1.0	63	66	0.7
Benzyl butyl phthalate	102	0.4	94	92	0.8
beta lindane	106	0.5	97	93	0.8
Bis(2-ethylhexyl) phthalate	107	1.2	97	87	2.1
Bis(2-chloroethoxy)methane	117	0.1	86	92	0.5
Bis(2-chloroethyl)ether	114	0.7	77	86	0.3
Bis(2-chloroisopropyl)ether	118	1.3	84	93	0.4

Compound	Fortified reagent blank		Lake water		MDL (ug/L) (n=7)
	Recovery%	RSD% (n=4)	MS (%)	MSD (%)	
Bromophenoxy benzene	78	2.8	80	81	0.4
Carbazole	115	0.4	99	97	0.7
Chlorobenzilate	111	0.3	99	96	0.7
Chrysene	96	0.4	91	86	0.5
delta lindane	110	3.2	94	89	0.7
Diallate (cis & trans)	106	2.0	92	93	0.6
Dibenz[ah]anthracene	85	1.3	77	72	0.6
Dibenzofuran	92	1.2	83	85	0.5
Dibutyl phthalate	117	2.2	95	94	0.8
Dieldrin	83	5.4	90	85	1.0
Diethyl phthalate	116	0.8	98	100	0.6
Dimethoate	111	4.1	100	97	0.9
Dimethyl phthalate	113	0.5	96	99	0.6
Di-n-octyl phthalate	103	0.1	95	90	1.0
Diphenylamine	108	0.4	95	96	0.6
Disulfoton	90	5.1	85	70	1.0
Endosulfan I	86	6.3	89	83	0.8
Endosulfan II	90	6.2	90	85	1.0
Endosulfan sulfate	94	3.0	90	84	0.6
Endrin	87	4.7	94	91	0.9
Endrin aldehyde	64	18	55	42	0.9
Ethyl methanesulfonate	113	1.4	80	86	0.3
Famphur	129	0.2	92	90	0.8
Fluoranthene	94	0.3	90	86	0.6
Fluorene	92	0.8	84	85	0.6
gamma lindane	106	2.9	94	90	0.7
Heptachlor	69	13	71	60	1.1
Heptachlor epoxide	89	5.5	81	76	0.8
Hexachlorobenzene	78	1.0	81	79	1.1
Hexachlorobutadiene	37	24	33	35	3.7
Hexachlorocyclopentadiene	40	29	43	48	2.9
Hexachloroethane	52	8.8	38	38	3.1
Hexachloropropene	45	36	20	18	3.0
Indeno[123-cd]pyrene	86	3.1	76	71	0.5
Isodrin	86	0.6	26	27	0.6
Isophorone	115	0.5	82	90	0.4
Isosafrole (cis & trans)	106	0.3	83	90	0.5
Kepone	97	5.0	3	5	1.8
Methyl methanesulfonate	80	2.7	65	72	0.3
Methyl parathion	114	2.0	99	96	0.9
Naphthalene	103	1.0	80	87	0.4
Nitrobenzene	116	0.9	83	91	0.4
N-nitroso-di-n-propyl amine	112	4.7	95	103	0.8
N-nitroso-di-n-butyl amine	112	1.0	89	95	0.5
N-nitrosodiethylamine	112	1.5	75	83	0.3
N-nitrosodimethylamine	82	1.9	60	68	0.3
N-nitrosomethylethylamine	108	1.6	72	78	0.5
o,o,o-Triethylphosphorothioate	104	4.1	82	80	1.0
o-Toluidine	115	0.5	82	87	0.7
Parathion	105	2.7	91	88	0.8
p-Dimethylamino azobenzene	117	0.3	82	78	0.7
Pentachlorobenzene	57	2.0	68	68	3.0
Pentachloroethane	86	0.3	63	70	1.9
Pentachloronitrobenzene	88	2.0	91	87	0.6
Pentachlorophenol	94	1.6	94	95	0.7
Phenacetin	121	0.2	111	108	0.8
Phenanthrene	94	1.2	86	85	0.6
Phenol	97	1.8	37	39	0.3
Phorate	96	3.4	86	75	1.0
Pronamide	113	0.6	104	101	0.6
Pyrene	94	0.8	90	86	0.6
Pyridine	71	0.9	27	30	2.0
Safrole	99	0.2	89	102	0.6
Sulfotep	105	4.1	90	88	0.9
Thionazin	113	1.2	96	94	0.9
Surrogates					
2-Fluorophenol (S)	98	0.1	80	86	
Phenol d6 (S)	94	0.3	44	47	MDL not determined for surrogates
Nitrobenzene d5 (S)	99	1.0	110	120	
2-Fluorobiphenyl (S)	89	0.3	102	110	
2,4,6-Tribromophenol (S)	96	1.3	126	126	
p-Terphenyl d14 (S)	92	1.8	151	98	
Overall mean	**96**	**2.8**	**81**	**81**	**0.9**

4. CONCLUSIONS

This poster presents a new and efficient SPE method for EPA method 8270 water analysis, compared to LLE or SPE that requires at least two extractions (acidic and basic), this newly developed method offers the following advantages:

- Cost-effective
- Reduced usage of organic solvents
- Simple and fast: only one sample pass is needed
  - 5-6 hrs for a batch of 24 samples
- No emulsion or white precipitate generated
- Shorter solvent evaporation time
- Shorter sample turnaround time
- High sample throughput
- Excellent recovery and reproducibility
- Cleaner extracts and chromatograms

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