A Novel Empore 8270 Disk to Extract 125 Sei-volatile Organic Compounds from Water Samples per EPA 8270E Method

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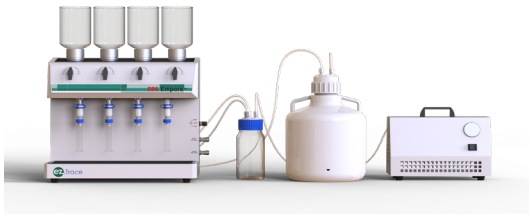
Application Note
Environmental

Abstract
The application note developed a new EPA 8270E method by using CDS Empore 8270 disk to maximizes the advantages of the membrane solid-phase extraction technology, which include easy to stack and apply, easy reverse elution, and relatively shorter drying time, etc. The method quantitatively extract a wide range of compounds with most compounds having recovery rates higher than 75%, and the RSDs less than 15%. This method provides a very versatile option for wastewater detection.

Introduction
Semi-volatile organic compounds (SVOCs) have a variety of chemical properties that have been
found to cause harmful effects to both humans and the environment. Accurate measurements are
challenging to obtain for the environmental industry because SVOCs readily adsorb onto a variety of surfaces and are found in common household items, such as cleaning agents, personal care products, electrical components, pesticides, water, and food. The known effects to health include allergenic symptoms, reproductive and endocrine issues, depending on the chemical nature of the compound in conjunction with the degree of exposure.

Laboratories around the world measure these compounds in water, soil, and leachates from waste sites. US EPA Method 8270E can be used to determine the concentration of SVOCs extracted from liquid, solid and leachate samples in effort to limit exposure and the spread of these persistent organic pollutants. While most laboratories test for fewer than the full list of 243 compounds included in the method, typical laboratories will often measure a large suite of more than 100 compounds. The extracted compound classes by this method include polynuclear aromatic hydrocarbons (PAH), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols.



This application note will demonstrate the results of evaluations for compliance with US EPA Method 8270E to determine a list of 125 semi-volatile organic compounds that are neutral, acidic, and basic. Solid phase extraction is described as a suitable sample preparation alternative in Method 8270 and companion method US EPA 3535 outlines the general use of SPE. CDS Analytical Empore 8270 Disk has been demonstrated to successfully extract 125 SVOC compounds from water per EPA Method 8270 standards.

Experiment Setup
Materials
The following standard chemicals were bought from Restek: 8270 MegaMix (31850), 8270 Benzidines mix (31834), Revised B/N surrogate mix (31888), Acid surrogate mix (4/89 SOW) (31063), Methapyrilene standard (32460), Benzoic acid (31879), Appendix IX mix #2 (31806), Appendix IX mix #1 (32459), and Revised SV internal standard mix (31886).

In the preparation of the primary dilution standards (PDS), according to the recommendation in EPA Method 8270, leave the nitrosamines in a separate vial and avoid mixing amines with aldehydes. Ammonia methanol solution (499145) was bought from Sigma-Aldrich.

Solid-phase Extraction media: in a single extraction, one Empore 8270 disk (SKU #: 98-0604-0246-0, CDS Analytical) and two Empore Carbon disks (SKU #: 98-0604-0235-5, CDS Analytical) were used.

Solid-phase Extraction Equipment: CDS Empore EZ-Trace (SKU #: 98-0604-0801-7, CDS Analytical)

GC Conditions
GC/MS: Shimadzu GCMS-QP2010
GC conditions:
Injection: splitless at 250 °C
Sampling Time: 1.00 min
Linear Velocity: 44.0 cm/sec
Oven Temperature Program

Rate (°C/min)	Temperature (°C)	Hold Time (min)
-	40.0	3.00
15.00	240.00	0.00
6.00	310.0	2.00

MS conditions:
Ion Source: 250 °C
Interface: 280 °C
Solvent Cut Time: 3.34 min
Acquisition: Scan
Event Time: 0.30 sec
Scan Speed: 1666
Start m/z: 35
End m/z: 500

Solid-phase Extraction Method
Take a bottle of 250-mL water sample. Add 0.4 mL concentrated hydrochloric acid into the water sample and shake thoroughly, letting the pH value of the water sample lower than 2.0. Add 20 mg of thiosulfate and shake thoroughly. Spike 8270 standards PDS to the water sample at 20 ug/L, shake thoroughly and set aside.

Preparation of SPE media:
Place an Empore 47 mm 8270-disk on the top of two layers of Empore 47 mm activated carbon disks, forming a composite disk, with the 8270-disk on the top and the two activated-carbon disks at the bottom. Put the disk into the EZ-Trace equipped with a vacuum pump.

Solid-phase extraction process
Conditioning:
Load the disk with 5 mL DCM and apply a vacuum to pass 1/3 of DCM volume through the disk to a waste bottle. Stop the vacuum and allow the disk to soak in DCM for 1 min. Then drain the DCM.
Load the disk with 5 mL methanol, apply a vacuum to draw most of the methanol through the disk, and leave a thin layer of methanol on the disk.
Load the disk with 10 mL of reagent water and apply a vacuum until leaving a thin layer of water on the disk.
Load 10 mL 0.05 N hydrochloric acid aqueous solution onto the disk and apply a vacuum until leaving a thin layer of acidic water on the disk.

Sample loading:
Load the above-mentioned 250-mL spiked water sample onto the disk, and control the vacuum to make a flow rate at 15~20 mL/min. Before the water sample loading completes, rinse the sample bottle with 10 mL of 0.05 N HCl solution and load it onto the disk.

Drying:
After draining the water sample, dry the disk under a high vacuum (e.g., -25 inHg) for 10 min. (Note: Dry for a well-controlled period. Eluting a wet disk may result in the back-extraction of some acidic compounds. Do not over-dry the disk to minimize the possible oxidation of some sensitive compounds

Eluting:
Turn the three-layer composite disk upside down with the activated carbon side facing up and the 8270 side down.

Elution Part 1: Elution of Acidic and Neutral Analytes
Wash the inner side of the sample bottle with 5 mL methanol/DCM solution (5/95) and load it onto the disk. Apply vacuum to pass 1/3 volume of the solvent through the disk to Collection Vial A. Soak the disk for 1 min, and collect the rest of the eluate dropwise to Collection Vial A.

Repeat the previous step.
Dry the eluate in Collection Vial A through 10 g anhydrous sodium sulfate and collect it into a concentration vial. Rinse the sodium sulfate with 3 mL DCM and combine it into the concentrate vial. (If the target analytes do not include phenolic species, this step can be overridden.)

Elution Part 2: Basification and Elution of Basic Analytes
Collect the next portion of the eluate with Collection Vial B. (If the target analytes do not include phenolic species, this replacing-collection-vial step can be overridden. Combine to Collection Vial A.)
Wash the sample bottle with 5 mL 95/5 DCM/0.35 N methanolic ammonia and load it onto the disk. Apply a vacuum to pass 1/3 volume of solvent through the disk to Collection Vial B. Soak the disk for 1 min. Collect the rest of the eluate dropwise to Collection Vial B.

Load 5 mL methanol/DCM solution (5/95) onto the disk and apply a vacuum to pass 1/3 volume of solvent through the disk to Collection Vial B. Soak the disk for 1 min, and collect the rest of the eluate dropwise to Collection Vial B.
Dry the eluate in Collection Vial B through sodium sulfate (the same drying column from Part 1) and collect and combine it with the dried eluate from Part 1. Rinse the sodium sulfate with 2x3 mL DCM and combine as above.

Concentrating:
Gently reduce the volume of the dried eluate at 45°C with nitrogen blowing to less than 1 mL (no less than 0.5 mL). The concentration cup is capped/sealed so that a narrow opening is left venting nitrogen and organic vapor. After adding the internal standard, bring the volume to 1.0 mL with DCM.

Results and Discussion:
A GC/MS chromatogram is shown in Figure 1 and the recovery data is shown in Table 1.
Overall recovery: With this relatively simple solid-phase extraction process, most compounds have a recovery of higher than 75%, and the RSD of most compounds is less than 15%.

After extraction, phentermine (α,α-Dimethylphenethylamine) showed chromatographic problems such as peak shape deformation and retention time change , which made quantification difficult.
Benzidine is listed as a special compound due to its probable oxidative loss, such as during concentration. The concentrator in this experiment minimized the sample loss by avoiding the contact of oxygen with the sample solution. However, the oxidation loss associated with the drying process of the extraction medium was still observed to an extent. Separate experiments were carried out to extract the three Benzidines.

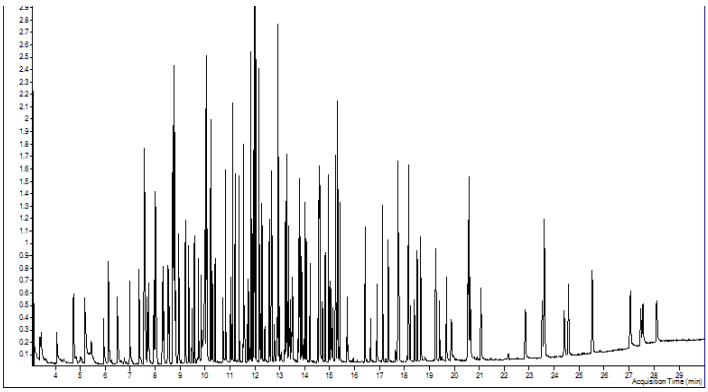


Figure 1 GC/MS chromatogram of the selected EPA 8270 compounds

Conclusions:
The application note developed a new EPA 8270E method by using CDS Empore 8270 disk to maximizes the advantages of the membrane solid-phase extraction medium, which include easy to stack and apply, easy reverse elution, and relatively shorter drying time, etc., and realizes the extraction process of quantitatively recovering a wide range of compounds with most compounds having recovery rates higher than 75%, and the RSDs less than 15%. This method provides a very versatile option for wastewater detection.

Table 1 The recovery data of the experiment

Compound (spiked level 20 ppb in 250 mL)	RT (min)	Ave Rec (%) n=3	RSD (%) n=3
1,4-Dioxane-d8 (IS)	3.380		
1,4-Dioxane	3.425	67.1	23.2
N-Nitrosodimethylamine	4.032	77.1	18.3
Pyridine	4.046	45.7	14.5
Ethyl methacrylate	4.700	64.9	21.2
2-Picoline	5.177	81.2	10.7
Methanesulfonic acid, ethyl ester	6.972	82.7	3.4
Benzaldehyde	7.343	172.1	7.1
Ethane, pentachloro-	7.540	58.5	16.6
Phenol-d6 (surr)	7.556	86.2	5.2
Aniline	7.570	77.1	5.6
Phenol	7.573	91.8	5.6
Bis(2-chloroethyl) ether	7.680	81.8	8.7
Phenol, 2-chloro-	7.727	82.0	6.0
Benzene, 1,4-dichloro-	7.938	62.2	14.2
1,4-Dichlorobenzene-D4 (IS)	7.996		
Benzene, 1,3-dichloro-	8.021	63.4	12.7
Benzyl Alcohol	8.278	100.4	1.9
Benzene, 1,2-dichloro-	8.316	65.2	11.8
Phenol, 2-methyl-	8.503	87.8	1.5
Propane, 2,2'-oxybis[1-chloro-	8.540	76.6	4.2
Pyrrolidine, 1-nitroso-	8.681	86.3	1.8
Acetophenone	8.694	99.5	7.8
Morpholine, 4-nitroso-	8.714	89.0	2.4
Phenol, 4-methyl-	8.734	94.3	2.7
N-Nitroso-di-n-propylamine	8.756	85.3	3.7
o-Toluidine	8.763	79.2	5.8
Ethane, hexachloro-	8.801	58.1	12.5
Nitrobenzene-D5 (surr)	8.924	80.4	4.7
Benzene, nitro-	8.952	86.5	3.8
Piperidine, 1-nitroso-	9.191	86.2	0.5
Isophorone	9.337	92.4	3.5
Phenol, 2-nitro-	9.466	84.3	8.8
Phenol, 2,4-dimethyl-	9.566	88.0	2.4
Methane, bis(2-chloroethoxy)-	9.722	85.8	6.1

Benzenecarboxylic acid	9.751	117.6	18.6
2,4-Dichlorophenol	9.842	86.2	2.4
Phentermine	9.925	52.8	16.9
Benzene, 1,2,4-trichloro-	9.976	70.3	7.8
Naphthalene-D8 (IS)	10.035		
Naphthalene	10.066	80.5	7.6
p-Chloroaniline	10.206	70.4	0.1
Phenol, 2,6-dichloro-	10.215	83.8	1.7
1-Propene, 1,1,2,3,3,3-hexachloro-	10.273	57.1	5.1
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	10.388	64.9	8.4
Caprolactam	10.698	95.5	7.4
1-Butanamine, N-butyl-N-nitroso-	10.811	84.6	3.6
Phenol, 4-chloro-3-methyl-	11.013	94.3	1.2
Safrole	11.085	79.8	4.0
Naphthalene, 2-methyl-	11.190	73.9	7.0
Naphthalene, 1-methyl-	11.363	75.2	6.6
Benzene, 1,2,4,5-tetrachloro-	11.528	71.2	3.6
Hexachlorocyclopentadiene	11.572	54.1	3.5
Phenol, 2,4,6-trichloro-	11.701	87.7	0.9
Phenol, 2,4,5-trichloro-	11.755	86.6	7.0
1,1'-Biphenyl, 2-fluoro-	11.835	77.0	3.6
Isosafrole	11.918	75.4	2.4
Naphthalene, 2-chloro-	11.970	73.7	5.3
Biphenyl	11.970	76.3	4.4
Naphthalene, 1-chloro-	12.022	72.9	5.3
Diphenyl ether	12.165	82.1	3.4
o-Nitroaniline	12.200	82.2	5.5
1,4-Naphthalenedione	12.263	113.2	25.2
Benzene, 1,4-dinitro-	12.380	78.6	8.4
Benzene, 1,3-dinitro-	12.568	79.6	5.1
Dimethyl phthalate	12.575	93.0	2.5
Acenaphthylene	12.651	75.6	5.5
Benzene, 2-methyl-1,3-dinitro-	12.663	88.0	1.4
Benzene, 1,2-dinitro-	12.765	85.1	3.4
m-Nitroaniline	12.877	76.3	3.4
Acenaphthene-d10 (IS)	12.906		
Acenaphthene	12.956	78.8	6.0
Phenol, 2,4-dinitro-	13.042	115.6	18.3
Phenol, 4-nitro	13.173	89.3	2.7

Phenol, 4-nitro	13.173	89.3	2.7
Dibenzofuran	13.217	78.4	6.4
Benzene, pentachloro-	13.259	75.9	4.5
Benzene, 1-methyl-2,4-dinitro-	13.293	86.5	5.7
1-Naphthalenamine	13.350	36.9	8.2
Phenol, 2,3,4,6-tetrachloro-	13.424	96.9	2.7
2-Naphthylamine	13.470	22.5	4.3
Phenol, 2,3,5,6-tetrachloro-	13.496	91.9	2.3
Diethyl Phthalate	13.735	96.7	3.1
Fluorene	13.777	80.3	5.6
Benzene, 1-chloro-4-phenoxy-	13.802	85.4	1.4
Benzenamine, 2-methyl-5-nitro-	13.853	77.8	1.7
p-Nitroaniline	13.876	72.6	3.0
Phenol, 2-methyl-4,6-dinitro-	13.946	105.0	13.2
Benzenamine, N-phenyl-	14.003	85.8	4.6
Azobenzene	14.054	78.4	6.5
Phenol, 2,4,6-tribromo-	14.196	95.9	5.4
1,3,5-Trinitrobenzene	14.496	82.4	11.7
Acetamide, N-(4-ethoxyphenyl)-	14.580	88.3	3.4
Benzene, 1-bromo-4-phenoxy-	14.587	89.0	2.1
Diallate	14.694	90.0	1.6
Benzene, hexachloro-	14.807	81.1	5.7
Atrazine	14.949	90.0	1.7
[1,1'-Biphenyl]-4-amine	15.021	32.0	7.0
Phenol, pentachloro-	15.100	94.2	5.9
Propyzamide	15.214	91.9	2.3
Benzene, pentachloronitro-	15.234	86.7	2.9
Phenanthrene-D10 (IS)	15.292		
Phenanthrene	15.328	80.4	5.8
Anthracene	15.403	77.5	5.9
Carbazole	15.679	107.5	7.2
Dibutyl phthalate	16.404	101.4	0.9
Quinoline, 4-nitro-, 1-oxide	16.628	80.7	11.4
Methapyrilene	16.877	79.8	10.7
Isodrin	17.111	48.9	7.8
Fluoranthene	17.337	81.4	5.5
Benzidine *	17.628	45.8	22.6
Pyrene-d10	17.720	80.2	5.6

Pyrene	17.757	80.4	6.0
p-Terphenyl-d14 (surr)	18.150	78.8	7.9
Aramite	18.214	106.0	3.1
p-Dimethylaminoazobenzene	18.493	82.6	4.0
Chlorobenzilate	18.641	97.6	1.7
3,3'-Dimethylbenzidine *	19.230	69.9	11.6
Kepone	19.240	68.4	2.4
Benzyl butyl phthalate	19.385	107.9	2.2
Benz[a]anthracene	19.487	69.7	10.8
DOA	19.663	100.9	2.1
N-2-Fluorenylacetamide	19.865	91.4	9.1
Chrysene-D12 (IS)	20.564		
3,3'-Dichlorobenzidine *	20.565	89.1	3.8
Chrysene	20.629	78.0	6.9
Bis(2-ethylhexyl) phthalate	21.053	116.5	3.5
Di-n-octyl phthalate	22.829	110.1	2.8
Benz[e]acephenanthrylene	23.507	81.6	5.3
Benzo(a)pyrene	23.575	80.5	8.7
Benz[a]anthracene, 7,12-dimethyl-	23.592	76.2	13.2
Benzo[k]fluoranthene	24.390	77.1	7.7
Perylene-D12 (IS)	24.555		
3-Methylcholanthrene	25.511	75.2	8.3
Dibenz[a,j]acridine	27.038	81.8	5.4
Indeno[1,2,3-cd]pyrene	27.450	81.5	4.2
Dibenz[a,h]anthracene	27.542	80.7	5.1
Benzo[ghi]perylene	28.090	82.6	1.9

* These three compounds were tested separately to avoid likely reactions with other compounds.