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Preliminary Studies on the Recovery of SVOC from Soil using Pressurized Fluid Extraction with Methanol/Water

E.A. Pfannkoch, R.J. Collins
*Gerstel, Inc., 701 Digital Drive, Suite J,
Linthicum, MD 21090, USA*

J. Thomas
*Roy F. Weston Inc., Sandia National Laboratories, PO Box 5800,
Albuquerque, NM 87185-1150, USA*

C.S. Chocas
*Sandia National Laboratories, PO Box 5800,
Albuquerque, NM 87185-1150, USA*

ABSTRACT

The analysis of contaminated soil and sludge samples for semi-volatile organic compounds (SVOC) has traditionally been performed using gas chromatography/mass spectrometry (GC/MS) (EPA SW-846, Method 8270). This method relies on the extraction of contaminants from the samples utilizing a variety of organic and chlorinated solvents. Pressurized fluid extraction (EPA SW-846, Method 3545) has been shown to efficiently extract SVOC contaminants from soil using methylene chloride as the extraction solvent. This technique minimizes the use of organic solvents but still requires a lengthy evaporation step.

The major areas of concern regarding traditional extraction techniques are: 1.) laboratory contamination resulting from the presence of organic solvents; 2.) health and environmental impact from the use of organic solvents; and 3.) extended processing times due to the need to evaporate the

solvent to concentrate the extract for analysis.

In response to these concerns and limitations, we report preliminary studies utilizing pressurized fluid extraction on a Dionex Accelerated Solvent Extractor 200 (ASE) with methanol/water as the extraction solvent for recovery of SVOC from soil samples. The soil samples were spiked with the SVOC listed in EPA SW-846, Method 8270 at the 167ppb level. The compounds in the aqueous extracts were then acidified and reconcentrated using Stir Bar Sorptive Extraction with PDMS-coated stir bars prior to analysis by thermal desorption GC/MS. The presence of polar solvents such as methanol, ethanol, or acetonitrile is compatible with partitioning of the SVOC into the stir bar PDMS phase, thus enabling the use of solvent blends with water to optimize extraction efficiency.

Extracting in the ASE with 20% methanol in water under moderate conditions (100C, 1500psi), compounds from phenol to benzo(g,h,I)perylene were recovered from the spiked soil. Generally, the lowest boiling 40 compounds (fluorene and below) showed the best recovery (>90% in the first extraction). The middle 15 compounds (fluorene to chrysene) showed recoveries of >75% in the first extraction. The highest boiling 7 compounds showed approximately equal recovery in two sequential ASE extractions. This suggests the extraction conditions should be optimized further. Detection limits in the mid ppt (pg/g) range appear to be attainable for most compounds.

INTRODUCTION

Gerstel, Inc. and Sandia National Laboratories, Environmental Restoration Chemistry Laboratory conducted a preliminary investigation to evaluate the application of polydimethylsiloxane (PDMS)-coated stir bars for the extraction of semi-volatile organic compounds (SVOC) in soil samples. PDMS coated stir bars have the potential to eliminate the need for chlorinated solvents in the extraction process, thereby reducing sample extraction time, laboratory contamination, environmental and health risks.

Background. EPA SW-846, Method 3545 uses pressurized fluid extraction with methylene chloride to recover SVOC from soil prior to GC analysis. Methylene chloride is effective at extracting the compounds of interest from the soil, and also is compatible with GC injection.

Previous reports [1-2] have shown that sub-critical water is capable of extracting PAH's and PCB's from soil samples. The conditions used (250-300°C, 50 bar) are fairly rigorous, and recovery of the analytes required solvent back-extraction into chloroform prior to GC analysis.

We have previously shown [3] that the presence of moderate levels of polar solvents (methanol, ethanol, acetone, acetonitrile) in an aqueous sample has minimal adverse effects on recovery of nonpolar compounds from solution using PDMS-coated stir bars. We hypothesized that the addition of a polar solvent to water would enhance the efficiency of SVOC extraction from soil and provide good recoveries at moderate extraction temperature and pressure. The extracts could then be easily concentrated onto a PDMS-coated stir bar for introduction onto a gas chromatograph/mass selective detector (GC/MSD).

EXPERIMENTAL

Apparatus. Dionex Accelerated Solvent Extractor 200 (ASE), Gerstel Twister™ PDMS-coated stir bars, Agilent Technologies Model 6890/5973 GC/MSD, Gerstel ModelsTDS2/TDSA Thermal Desorption Unit with autosampler, Gerstel Model CIS4 Programmable Temperature Vaporizing (PTV) inlet, SVOC stock standard containing compounds listed in EPA SW-846, Method 8270, Appendix 9.

Sample Preparation. ASE Extraction. Three samples containing 30g Ottawa sand and 25μL of 200ppm SVOC stock standard were placed into three separate 30mL ASE extraction cells. Samples were extracted with 20% methanol/water at 100°C and 1500psi for five minutes. The extracts were acidified with sulfuric acid to a pH of 2 or less. Each extract was split into two equal aliquots. A second extraction of each sample was then performed under the same conditions to assess the extraction efficiency.

Control samples were prepared by spiking 30mL water or 20% methanol/water with 25uL of 200ppm SVOC stock standard and acidifying to pH 2 or less.

Gerstel Twister™ Extraction. A Gerstel Twister™ stir bar was added to each aliquot and stirred at room temperature overnight. The stir bars were removed, rinsed in water, dried and placed into a clean 2mL vial for shipment to the lab for analysis. Within 3 days of receipt, the Gerstel Twisters™ were transferred to a conditioned thermal desorption tube for analysis.

Analysis Conditions.

TDS 2/TDS A: splitless
20°C; 60°C/min; 300°C (5 min)

PTV: 0.2 min solvent vent (50 mL/min)
split 30:1
-120°C; 12°C/s; 280°C (3 min)

Column: 30 m HP-5MS (Agilent)
$d_i = 0.25$ mm $d_f = 0.25$ µm

Pneumatics: He, constant flow = 1.0 mL/min

Oven: 40°C (4 min); 20°C/min;
50°C (3.25 min); 12°C/min;
290°C (6 min); 25°C/min; 325°C

RESULTS AND DISCUSSION

EPA SW-846, Method 8270 SVOC List. The EPA SW-846, method 8270 list of SVOC contains 62 compounds that are commonly analyzed for in contaminated soil and sludge samples. This list is a subset of the more extensive Appendix 9 list of 112 compounds. Table 1 provides the log octanol:water partition coefficients (Kow) for each compound predicted using SRC Kow-Win ver. 1.66.

Table 1. EPA SW-846, Method 8270 SVOC list.

No.	Compound	CAS-No.	log Kow	estimated % recovery
1	Phenol	108-95-2	1,51	5,31
2	Bis(2-chloroethyl)ether	111-44-4	1,56	5,92
3	2-Chlorophenol	95-57-8	2,16	20,03
4	1,3-Dichlorobenzene	541-73-1	3,28	76,76
5	1,4-Dichlorobenzene	106-46-7	3,28	76,76
6	1,2-Dichlorobenzene	95-50-1	3,28	76,76
7	2-Methylphenol	95-48-7	2,06	16,60
8	Bis(2-chloroisopropyl)ether	108-60-1	2,39	29,85
9	m/p-Methylphenol	106-44-5	2,06	16,60
10	n-Nitroso-di-n-propylamine	621-64-7	1,33	3,57
11	Hexachloroethane	67-72-1	4,03	94,89
12	Nitrobenzene	98-95-3	1,81	10,06
13	Isophorone	78-59-1	2,62	41,95
14	2-Nitrophenol	88-75-5	1,91	12,35
15	2,4-Dimethylphenol	105-67-9	2,61	41,39
16	Bis(2-chloroethoxy)methane	111-91-1	1,30	3,34
17	2,4-Dichlorophenol	120-83-2	2,8	52,24
18	1,2,4-Trichlorobenzene	120-82-1	3,93	93,65
19	Naphthalene	91-20-3	3,17	71,94
20	4-Chloroaniline	106-47-8	1,72	8,34
21	Hexachlorobutadiene	87-68-3	4,72	98,91
22	4-Chloro-3-methylphenol	59-50-7	2,7	46,49
23	2-Methylnaphthalene	91-57-6	3,72	90,10
24	Hexachlorocyclopentadiene	77-47-4	4,63	98,67
25	2,4,6-Trichlorophenol	88-06-2	3,45	83,01
26	2,4,5-Trichlorophenol	95-95-4	3,45	83,01
27	2-Chloronaphthalene	91-58-7	3,81	91,80
28	2-Nitroaniline	88-74-4	2,02	15,36
29	Dimethyl phthalate	131-11-3	1,66	7,34
30	Acenaphthylene	208-96-8	3,94	93,79
31	2,6-Dinitrotoluene	606-20-2	2,18	20,78
32	2,4-Dinitrotoluene	121-14-2	2,18	20,78
33	Acenaphthene	83-32-9	4,15	96,08
34	2,4-Dinitrophenol	51-28-5	1,73	8,52

Table 1 (cont.). EPA SW-846, Method 8270 SVOC list.

No.	Compound	CAS-No.	log Kow	estimated % recovery
35	Dibenzofuran	132-64-9	3,71	89,89
36	4-Nitrophenol	100-02-7	1,91	12,35
37	3-Nitroaniline	99-09-2	1,47	4,87
38	Diethyl phthalate	84-66-2	2,65	43,64
39	Fluorene	86-73-7	4,02	94,78
40	4-Chlorophenylphenylether	7005-72-3	4,69	98,84
41	4-Nitroaniline	100-01-6	1,47	4,87
42	n-Nitrosodiphenylamine	156-10-5	3,17	71,94
43	2-Methyl-4,6-dinitrophenol	534-52-1	2,27	24,40
44	4-Bromophenylphenylether	101-55-3	4,94	99,34
45	Hexachlorobenzene	118-74-1	5,86	99,92
46	Pentachlorophenol	87-86-5	4,74	98,96
47	Phenanthrene	85-01-8	4,35	97,49
48	Anthracene	120-12-7	4,35	97,49
49	Di-n-butyl phthalate	84-74-2	4,61	98,60
50	Fluoranthene	206-44-0	4,93	99,33
51	Pyrene	129-00-0	4,93	99,33
52	Butyl benzyl phthalate	85-68-7	4,84	99,17
53	Benz(a)anthracene	56-55-3	5,52	99,83
54	3-3-Dichlorobenzidine	91-94-1	3,21	73,76
55	Chrysene	218-01-9	5,52	99,83
56	Bis(2-ethylhexyl) phthalate	117-81-7	8,39	100,00
57	Di-n-octyl phthalate	117-84-0	8,54	100,00
58	Benzo(b)fluoranthene	205-99-2	6,11	99,96
59	Benzo(a)pyrene	50-32-8	6,11	99,96
60	Indeno(1,2,3-cd)pyrene	193-39-5	6,7	99,99
61	Dibenz(a,h)anthracene	215-58-7	6,7	99,99
62	Benzo(g,h,i)perylene	191-24-2	6,7	99,99
	Surrogates			
S1	2-Fluorophenol	367-12-4	1,71	8,16
S2	Phenol-d6	13127-88-3	1,51	5,31
S3	Nitrobenzene-d5	4165-60-0	1,81	10,06
S4	2-Fluorobiphenyl	321-60-8	3,96	94,05
S5	2,4,6-Tribromophenol	118-79-6	4,18	96,33

The partitioning of a compound between water and PDMS closely parallels the partitioning of the analyte between water and octanol, therefore the Kow can be used to predict the extraction efficiency of the PDMS-coated stir bar. Table 1 shows the predicted recovery of the Method 8270 list of compounds from a 15mL sample volume. Since most of the compounds are quite nonpolar and exhibit high octanol:water partition coefficients, the predicted extraction efficiency from water will be very high. Compounds that extract efficiently into the PDMS phase can usually be detected at ppt (pg/mL) levels in water. The typical minimum detection limits for soil SVOC are in the ppb range. Using the Gerstel Twister™ stir bar to concentrate analytes prior to GC/MSD analysis provides additional options for efficient extraction of soil SVOC.

Figure 1 shows the chromatogram obtained for a control sample consisting of the Appendix 9 SVOC stock standard spiked into water at 167ppb and acidified before extraction with the Gerstel Twister™. Note this sample was analyzed in the 30:1 split mode to prevent overloading either the column or the MSD. Although the most polar, early eluting compounds in this broad mix are not efficiently recovered, clearly the majority of compounds are easily detected.
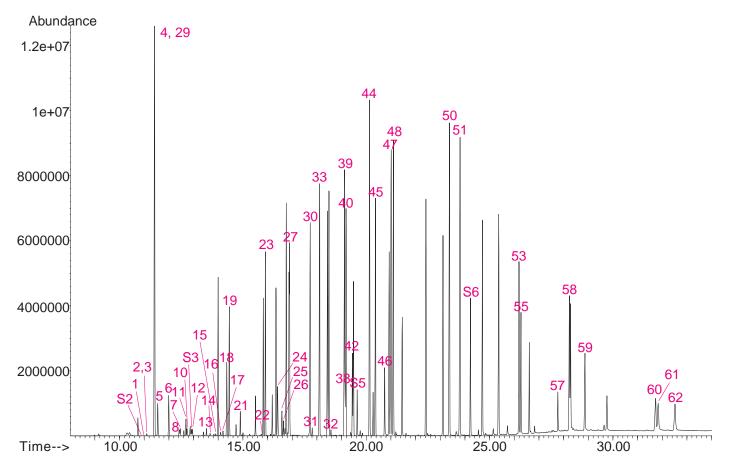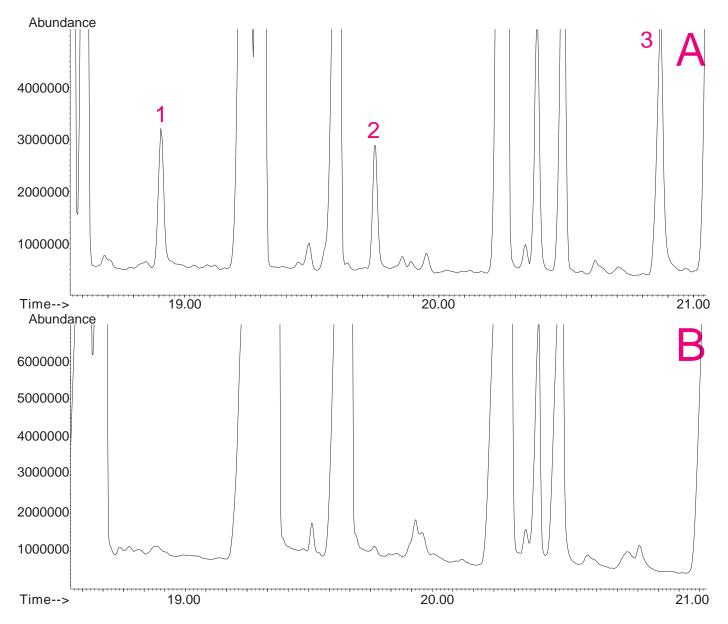

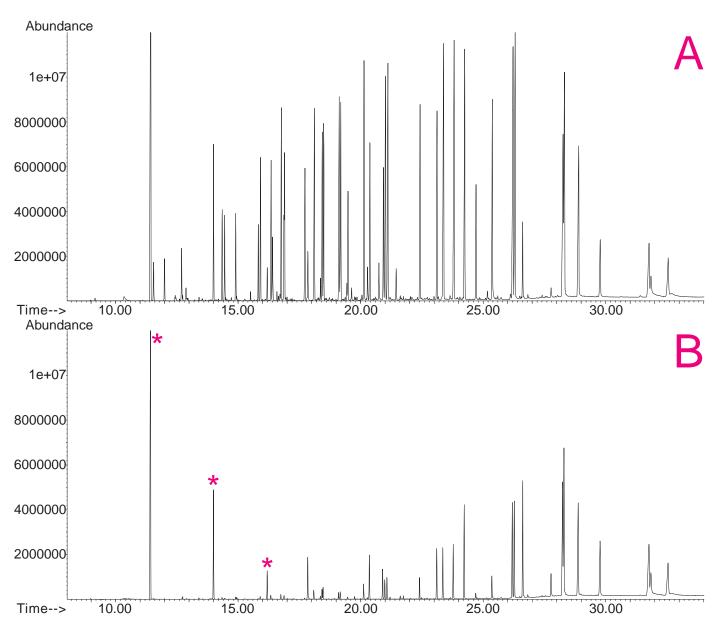**Figure 1.** Chromatogram of acidified control sample. See Table 1 for peak identities.

Extraction Optimization. Initial extraction studies showed poor recovery of the phenols from aqueous samples. Ionizable species have been shown to partition poorly into PDMS in their charged form. To try to improve recovery of phenols from the extract, the pH was adjusted to <2 with concentrated sulfuric acid prior to extraction with the Gerstel Twister™. Figure 2 shows a section of a chromatogram illustrating the improved recovery of phenolic species when the sample is acidified. All samples for the study were therefore acidified before stir bar extraction.

Figure 2. Water spiked with SVOC stock standard. (A) Acidified (B) non-acidified. Peak identities: 2,3,4,6-tetrachlorophenol (1); 2,4,6-tribromophenol (2); pentachlorophenol (3).

Soil Extraction Efficiency. The presence of moderate levels of polar solvents (methanol, ethanol, acetone, acetonitrile) in an aqueous sample has minimal adverse effect on recovery of nonpolar compounds from solution using PDMS coated stir bars. We therefore hypothesized that addition of 20% methanol would enhance soil extraction efficiency and allow recovery of SVOC under more moderate conditions. The resulting extract would be directly compatible with PDMS-coated stir bar extraction for recovery and introduction of the analytes into the GC with very low detection limits possible.

A standard soil (Ottawa sand) was spiked in triplicate and each sample was extracted twice with 20% methanol/water using the Dionex ASE system. The analytes were recovered from the extracts with the PDMS coated stir bars. Figure 3 shows a comparison of the chromatograms for the first and second extract from one sample. The entire range of compounds from phenol to benzo(g,h,I)perylene could be seen in the first extract, indicating the strategy of using water/solvent blends is promising. The higher boiling compounds are still present in the second extraction, suggesting the extraction conditions are not yet optimized.

Figure 3. Comparison of first (A) vs second (B) extraction of soil sample using the Dionex ASE system. *Indicates siloxane peak from PDMS on stir bar.

Figure 4 shows the average recovery of the compounds in the first and second extractions. For the earliest eluting 40 compounds, >90% of the recovered peak area is found in the first extract. Excluding the phthalates (that exhibit unusual behavior) only the five highest boiling compounds show substantial recovery in the second extraction.

The recovery of SVOC from soil was compared to the recovery of a control sample spiked directly with the same mass of analytes into water. This comparison provides only a rough estimate of extraction efficiency. Table 2 shows the comparison of recovery from the soil and the control samples. It is noteworthy that recovery estimates from the ASE are generally higher when compared to the more appropriate 20% methanol control. To adequately estimate recovery the PDMS/water distribution coefficients should be as similar as possible in samples and controls. The distribution coefficient can be influenced by the presence of solvent or inorganic species in the sample.

Table 2. Extraction-recovery and reproducibility.

No.	Compound (EPA 8270)	Water % rec.	20% MeOH % rec.	First extract % RSD	Total extract % RSD
1	Phenol	232	393	56.9	23.8
2	Bis(2-chloroethyl)ether	64	168	9.7	10.3
3	2-Chlorophenol	62	141	29.0	20.8
4	1,3-Dichlorobenzene	132	103	12.3	13.7
5	1,4-Dichlorobenzene	130	107	12.5	14.2
6	1,2-Dichlorobenzene	120	117	12.7	14.3
7	2-Methylphenol	60	85	19.5	14.5
8	Bis(2-chloroisopropyl)ether	70	141	9.7	9.4
9	m/p-Methylphenol	68	275	18.2	14.6
10	n-Nitrosodi-n-propylamine	31	82	17.8	13.8
11	Hexachloroethane	165	113	23.4	25.8
12	Nitrobenzene	57	126	22.3	14.0
13	Isophorone	24	78	16.7	13.6
14	2-Nitrophenol	53	101	36.2	18.6
15	2,4-Dimethylphenol	48	119	15.3	7.1
16	Bis(2-chloroethoxy)methane	48	157	4.4	4.9
17	2,4-Dichlorophenol	43	28	20.2	14.7
18	1,2,4-Trichlorobenzene	113	99	21.9	24.0
19	Naphthalene	81	112	10.5	10.9
20	4-Chloroaniline	0	0	NA	NA
21	Hexachlorobutadiene	159	82	36.0	40.0
22	4-Chloro-3-methylphenol	44	142	18.5	13.9
23	2-Methylnaphthalene	87	88	17.7	17.1
24	Hexachlorocyclopentadiene	78	63	57.0	57.5
25	2,4,6-Trichlorophenol	34	86	13.3	10.6
26	2,4,5-Trichlorophenol	32	84	11.6	8.8
27	2-Chloronaphthalene	79	114	19.4	16.6
28	2-Nitroaniline	0	0	NA	NA
29	Dimethyl phthalate	236	159	52.5	25.7
30	Acenaphthylene	65	99	15.7	11.5
31	2,6-Dinitrotoluene	40	93	22.4	16.9
32	2,4-Dinitrotoluene	39	80	28.3	17.3
33	Acenaphthene	85	108	20.5	14.2
34	2,4-Dinitrophenol	0	0	NA	NA
35	Dibenzofuran	84	107	20.0	12.2
36	4-Nitrophenol	0	0	NA	NA
37	3-Nitroaniline	0	0	NA	NA
38	Diethyl phthalate	72	184	141.0	99.8
39	Fluorene	87	116	22.6	12.4
40	4-Chlorophenylphenylether	99	126	28.5	19.5
41	4-Nitroaniline	0	0	NA	NA
42	(n-Nitroso)diphenylamine	0	0	NA	NA
43	2-Methyl-4,6-dinitrophenol	74	0	71.8	70.1
44	4-Bromophenylphenylether	96	124	52.9	38.1
45	Hexachlorobenzene	299	195	41.9	38.8
46	Pentachlorophenol	52	85	27.9	19.7

Table 2 (cont.). Extraction-recovery and reproducibility.

No.	Compound (EPA 8270)	Water % rec.	20% MeOH % rec.	First extract % RSD	Total extract % RSD
47	Phenanthrene	95	139	26.8	14.5
48	Anthracene	106	163	27.6	15.9
49	Di-n-butyl phthalate	115	162	25.5	8.7
50	Fluoranthene	121	183	31.8	21.5
51	Pyrene	121	183	31.8	21.5
52	Butyl benzyl phthalate	116	164	30.9	15.1
53	Benz(a)anthracene	271	404	37.4	34.3
54	3-3-Dichlorobenzidine	0	0	NA	NA
55	Chrysene	425	512	35.6	32.5
56	Bis(2-ethylhexyl) phthalate	250	308	34.4	27.6
57	Di-n-octyl phthalate	111	74	24.7	22.3
58	Benzo(b/k)fluoranthene	505	418	38.1	37.4
59	Benzo(a)pyrene	429	453	40.0	40.5
60	Indeno(1,2,3-cd)pyrene	422	286	41.4	35.3
61	Dibenz(a,h)anthracene	183	116	21.0	11.6
62	Benzo(g,h,i)perylene	352	200	32.9	19.4
	Surrogates				
S1	2-Fluorophenol	0	ND	NA	NA
S2	Phenol-d6	0	ND	NA	NA
S3	Nitrobenzene-d5	55	ND	22.5	14.2
S4	2-Fluorobiphenyl	95	ND	18.6	16.7
S5	2,4,6-Tribromophenol	32	ND	17.4	10.1
S6	Terphenyl-d14	339	ND	34.0	30.1

Soil Extraction Reproducibility. Table 2 shows the reproducibility of the first extraction and the total area from both extracts for the three spiked soil samples. Generally, total area from both extracts provides better precision than the first extraction alone. This suggests the conditions are not yet optimized. Based on results shown elsewhere [4-5], when extraction conditions are optimized precision in the range of 2-15% RSD are possible.
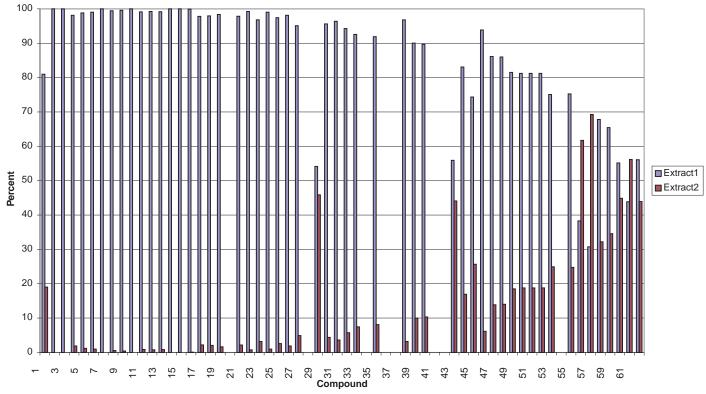
Figure 4. Comparison of average peak area obtained for first and second extraction of soil samples.

CONCLUSIONS

Soil SVOC can be extracted from methanol/water by stir bar sorptive extraction using the Gerstel Twister™ with minimum detection limits in the ppt (pg/mL) range for most compounds.

Acidification of sample solutions prior to transfer onto a Gerstel Twister™ helps to effectively recover acidic compounds (phenols). However acidification to pH levels of 2 or less prevents recovery of some basic compounds.

Pressurized fluid extraction of soil under relatively mild conditions (100°C, 1500 psi) with 20% methanol/water as extraction solvent can recover basically the full range of SVOC list in EPA Method 8270. Preliminary results indicate compounds up to chrysene are quite effectively extracted (>75% in the first extraction).

Precision for this sample set was reasonable (10-30% RSD) considering the extraction conditions are not yet optimized.

The recoveries of SVOC from soil samples versus the 20% methanol/water controls ranged between 80-160% (excluding a few compounds with significantly lower and higher recoveries).

Options to improve soil extraction efficiency include increasing temperature, adjusting methanol content, using other solvents (such as ethanol or acetonitrile), and optimizing pH.

ACKNOWLEDGEMENTS

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[4]   Extraction of BNA (Bases, Neutrals, and Acids) Using Accelerated Solvent Extraction (ASE), Dionex Application Note 317

[5]   Extraction of PAH's from Environmental Samples by Accelerated Solvent Extraction (ASE), Dionex Application Note 313

GERSTEL GmbH & Co. KG

Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany

☎ +49 (0) 208 - 7 65 03-0
🖨 +49 (0) 208 - 7 65 03 33
@ gerstel@gerstel.com
🌐 www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.

701 Digital Drive, Suite J
Linthicum, MD 21090
USA

☎ +1 (410) 247 5885
🖨 +1 (410) 247 5887
@ sales@gerstelus.com
🌐 www.gerstelus.com

GERSTEL LLP

10 Science Park Road
#02-18 The Alpha
Singapore 117684

☎ +65 6779 0933
🖨 +65 6779 0938
@ SEA@gerstel.com
🌐 www.gerstel.com

GERSTEL AG

Wassergrabe 27
CH-6210 Sursee
Switzerland

☎ +41 (41) 9 21 97 23
🖨 +41 (41) 9 21 97 25
@ swiss@ch.gerstel.com
🌐 www.gerstel.ch

GERSTEL (Shanghai) Co. Ltd

Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206

☎ +86 21 50 93 30 57
@ china@gerstel.com
🌐 www.gerstel.cn

GERSTEL K.K.

1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan

☎ +81 3 5731 5321
🖨 +81 3 5731 5322
@ info@gerstel.co.jp
🌐 www.gerstel.co.jp

GERSTEL Brasil

Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
☎ +55 (11)5665-8931
🖨 +55 (11)5666-9084
@ gerstel-brasil@gerstel.com
🌐 www.gerstel.com.br

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