

Application of Stir Bar Sorptive Extraction to Analysis of Volatile and Semivolatile Organic Chemicals of Potential Concern in Solids and Aqueous Samples from the Hanford Site

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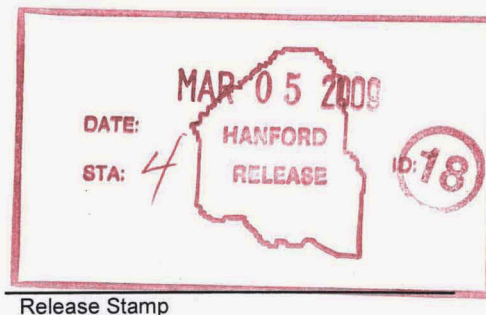
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Abstract: Stir bar sorptive extraction was applied to aqueous and solid samples for the extraction and analysis of organic compounds from the Hanford chemicals of potential concern list, as identified in the vapor data quality objectives. The 222-S Laboratory analyzed these compounds from vapor samples on thermal desorption tubes as part of the Hanford Site industrial hygiene vapor sampling effort.

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ABBREVIATIONS AND ACRONYMS

COPC	chemicals of potential concern
GC/MS	gas chromatography/mass spectrometry
LCS	laboratory control standard
MDL	method detection limit
PDMS	polydimethylsiloxane
SBSE	stir bar sorptive extraction
SVOA	semivolatile organic analysis
TDU	thermal desorption tubes
Terliq	Terminal Liquor Standard
Twister	GERSTEL® Twister
VOA	volatile organic analysis

1. INTRODUCTION

Stir bar sorptive extraction (SBSE) was applied to aqueous and solid samples for the extraction and analysis of organic compounds from the Hanford Site chemicals of potential concern (COPC) list, as identified in the vapor data quality objectives. The 222-S Laboratory analyzed these compounds from vapor samples on thermal desorption tubes (TDU) as part of the Hanford Site industrial hygiene vapor sampling effort. For this reason, these compounds were chosen for testing SBSE (interoffice memorandum 7S110-JMF-07-132, "Development of Stir Bar Sorptive Extraction as Applied to Hanford Tank Waste Liquids and Solids or Soils").

The extractions were performed by either immersing the SBSE in the aqueous sample for a set period of time and a set revolutions per minute, or by suspending it above the surface of the sample in a sealed headspace vial for a set period of time and temperature. Unlike classical extraction techniques in which the compounds of interest are extracted from a complicated matrix using liquid-liquid extraction, in SBSE the compound of interest is extracted into the solid sorbent phase, which is coated onto the surface of a glass stir bar. The SBSEs used for this test were GERSTEL-Twister® (Twister)¹ bars. Twisters are glass-covered magnetic stir bars that have a thick film (0.5 mm) of polydimethylsiloxane (PDMS). The PDMS is used to extract nonpolar compounds from polar matrices. It is possible to obtain an indication of how well a particular compound will extract into the Twister using the octanol/water coefficient (K_{ow}). Compounds with extremely low K_{ow} are less likely to be absorbed into the PDMS phase. SBSE technique was applied successfully to the less polar volatile organic analysis (VOA) compounds on the COPC list on both solids and liquids, and to semivolatile organic analysis (SVOA) compounds on the list from liquids.

Procedures ATS-LT-523-161, "222-S Laboratory Analysis of Semivolatile Organic Compounds Collected by Twister Stir-bar Sorptive Extraction by Gas Chromatography / Mass Spectrometry," and ATS-LT-523-162, "Analysis of Volatile Organic Compounds Collected on Twister Stir Bar Sorptive Extractors by Gas Chromatography/Mass Spectrometry," were developed as a result of this research. Experimental notes and results are documented in controlled notebook HNF-N-422, 2, *Analytical Development Projects*, pages 35 to 63 and 66 to 93. The compounds in Table 1 were successfully analyzed using this technique. The SVOA liquid method detection limits (MDL) were determined on two different gas chromatography/mass spectrometry (GC/MS) instruments, identified in the laboratory database as Spock and Sulu. The SVOA results obtained on these two different instruments were comparable. The MDL values determined for the same compounds from TDU tubes using a modified U.S. Environmental Protection Agency method are listed for comparison (Compendium Method TO-17, *Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes*). The TDU VOA MDLs were determined from Carbotrap™²300 tubes, and the TDU SVOA MDLs were determined from Carbotrap 150 tubes in 2007 from GC/MS Scotty and GC/MS Sulu. These MDLs are recalculated periodically and change.

¹ GERSTEL-Twister® is a registered trademark of Gerstel, Inc., Caton Research Center, Baltimore, Maryland.

² Carbotrap™ is a registered trademark of Supelco, Bellefonte, Pennsylvania.

Table 1. Method Detection Limit Comparison between Twister and Thermal Desorption Tubes Methods

Compound	VOA from Solid, MDL (ng)	VOA from Liquid, MDL (ng)	SVOA from Liquid, MDL (ng)	MDLs Using TDU Tubes (ng)
Instruments	Sulu	Sulu	--	Scotty
2-Methylfuran	10.78	20.57	NA	5.95
2,5-Dihydrofuran	10.75	16.00	NA	6.68
Butanal	34.43	31.92	NA	10.53
Benzene	6.98	9.99	NA	6.91
Butanenitrile	7.08	14.59	NA	20.32
3-Butene-2-one	11.32	NA	NA	6.49
1-Butanol	15.29	NA	NA	7.41
Pyridine	9.26	14.75	NA	16.83
2-Hexanone	9.66	11.74	NA	5.26
Pentanenitrile	14.48	12.09	NA	5.11
2,4-Dimethylpyridine	9.56	10.08	NA	12.60
Hexanenitrile	12.64	8.05	NA	3.82
Instruments	--	--	Spock, Sulu	Sulu
Biphenyl	NA	NA	3.73, 2.77	1.49
Diethylphthalate	NA	NA	6.20, 3.25	6.56
Dibutylbutylphosphonate	NA	NA	4.05, 2.39	1.03
Tributylphosphate	NA	NA	4.10, 4.06	1.26

Some VOA compounds like 3-Butene-2-one and 1-Butanol were too polar to be extracted from the aqueous phase with good repeatability into the PDMS phase of the Twister. Note that butanal, which is also a small polar compound, had an elevated MDL when compared to the other compounds. The SVOA compounds could not reliably be extracted from solids. The MDL values obtained for the less polar, longer chain VOA compounds, and the SVOA compounds are in the same range as those determined off of TDU tubes.

2. EXPERIMENTAL CONDITIONS

2.1 SEMIVOLATILE ORGANIC EXTRACTION AND ANALYSIS

2.1.1 Semivolatile Organic Analysis from Liquids Extraction

The SVOA from liquids were extracted by placing 10 mL of water in a 10-mL glass headspace vial. The water was adjusted to pH 10 with five drops of 0.125M NaOH. Calibration standards

were added to the vials along with a Twister stir bar extractor. The vials were capped and stirred at 1000 rpm for 60 minutes. After this extraction time, the Twisters were removed from the vial and placed in an empty glass TDU tube and desorbed on the GERSTEL TDS 3³ at 280 °C. The analysis was run on an Agilent⁴ 6890GC/Agilent 5973MSD equipped with a GERSTEL TDS 3, using the conditions listed in the following:

Initial column temperature:	40 °C for 1 minute
Column temperature program:	40-300 °C at 15 °/minute, 300-315 °C at 6 °/minute, hold 6 minutes
Final column temperature:	315 °C for 6 minutes
Column:	Agilent 122-5536 DB-5 ms, 30 m x 0.25mm x 0.5 µm, (or equivalent) max temperature 325 °C installed in back inlet.
Transfer line temperature:	300 °C
Back inlet, GERSTEL CIS 3:	Back inlet mode: solvent vent Initial temp: -30 °C Equilibration time: 0.20 minutes Initial time: 0.20 minutes Ramp rate: 12 °C/s Final temperature: 300 °C Hold time: 3.00 minutes
Carrier gas:	Helium at flow recommended by manufacturer.
GC run time:	29.83 minutes

³ GERSTEL Thermal Desorption Unit TDS 3 is a product of Gerstel, Inc., Baltimore, Maryland.

⁴ Agilent is a registered trademark of Agilent Technologies, Inc., Santa Clara, California.

The following conditions were used on the Gerstel TDS3.

TDS 3 parameters:	Sample mode: Sample remove
	Flow mode: Splitless
	Initial temp: 30 °C
	Initial time: 0.00 minutes
	Delay time: 0.50 minutes
	Purge time: 0.00 minutes
	Transfer temp: 300 °C
	1 st Rate: 60 °C/minutes
	1 st Final temp: 280 °C
	1 st Final time: 8.00 minutes
	2 nd Rate: 0 °C
	2 nd Final temp: 0 °C
	2 nd Final time: 0.00 minutes
Run parameters:	Run time: 15.00 minutes

Solutions were adjusted to pH 10 to mimic what might be encountered from Hanford radioactive tank waste samples, which are strongly basic. The pH 10 solutions did increase the number of siloxane type compounds present in the chromatograms. If the samples to be analyzed are not basic, then the calibration and samples could be run without adjusting the pH to 10. Tank simulant samples were extracted at pH values above pH 10, but fewer siloxane peaks were seen and better recovery of target compounds were obtained when the pH was adjusted back down to pH 10 with dilute nitric acid. For this comparison, an aliquot (1 mL) of tank simulant was added to 10 mL water in the Twister vial and spiked with a laboratory control standard (LCS). Another vial was prepared in the same way, but the pH was adjusted with 0.5 N nitric acid. The amount of nitric acid needed to bring the solution back down to pH 10 nearly doubled the volume in the vial. Extractions and analysis were performed in the same manner.

2.1.2 Semivolatle Organic Analysis from Solids Extraction

Efforts were made to determine if SVOA compounds could be extracted from a solid by suspending the Twister above the solid in a sealed headspace vial. Glass beads, 100 to 120 mesh size, were used to simulate a clean solid. These efforts were unsuccessful as the SVOA compounds had insufficient vapor pressure to be determined from a solid with the necessary accuracy, even when heated up to 200 °C dry or to 135 °C with a few drops of water added.

2.2 VOLATILE ORGANIC EXTRACTION AND ANALYSIS

2.2.1 Volatile Organic Analysis from Liquids Extraction Conditions

Liquids were extracted by placing 10 mL of water adjusted to pH 10 using five drops of 0.125M NaOH in a 10-mL Twister vial. Approximately 1 g of sodium sulfate, measured with a scoop, was added to the vials. The vials were spiked with 0.5 μL of calibration standards and 0.05 μL of internal standard solution. A Twister was added, and the vial was capped immediately. The vials were allowed to stir at room temperature at 1000 rpm for 60 minutes.

2.2.2 Volatile Organic Analysis from Solids Extraction Conditions

Approximately 1 g, measured volumetrically with a marked scoop, of 100- to 200-mesh glass beads were placed in a 20-mL headspace vial. The glass beads were spiked with calibration standards, a Twister was suspended above the glass beads, and the vial was sealed. The vials were heated at 65 °C in a block heater for 2 hours. The Twisters were then removed and placed in an empty glass TDU tube and desorbed at 250 °C. Initially in these studies the Twisters were heated to 75 °C for the extraction and 280 °C for the desorption. While this worked and produced usable calibration curves, it caused larger siloxane-type artifact peaks than using the lower temperature.

2.2.3 Volatile Organic Analysis Conditions

2.2.3.1 Gas Chromatography Conditions

Initial column temperature:	40 °C for 6 minutes
Column:	Restek Rtx-VMS, 60M x 0.25 mm with a 1.4-micron film thickness.
Column temperature program:	40-80 °C at 6 degrees/minute, hold for 5 minutes, 8 °C/minute to 95 °C, hold for 11 minutes, 12 °C/minutes, to 197 °C
Final column temperature:	197 °C for 5 minutes
Run time:	44.04 minutes
Transfer line temperature:	300 °C
Carrier gas:	Helium at flow recommended by manufacturer.

Back inlet: Gerstel CIS3	Back Inlet Mode: Solvent vent
	Initial temp: -30 °C
	Equilibration time: 0.20 min
	Initial time: 0.20 min
	Ramp rate: 12°C/s
	Final Temperature: 300°C
	Hold time: 3.00 min
TDS 3 parameters	
Initial temperature:	30 °C
Delay time:	0.50 minutes
Rate	60 °C/minute
End temperature:	250 °C
Hold time:	8 minutes

2.2.3.2 Mass Spectrometry Conditions

Electron energy:	70 V (nominal)
Mass range:	30-300 amu
Scan time:	Not to exceed 1 second/scan.

3. RESULTS

Initial evaluation of the K_{ow} values for the compounds on the COPC list is shown in Table 2.

In “New Concepts in Sorption Based Sample Preparation for Chromatography,” Baltussen (2000) notes that the K_{ow} value for a compound can be used to predict the K_{pdms} value for a compound. In other words, if the K_{ow} is low, the K_{pdms} is predicted to be low as well. Based on this prediction, compounds with very low K_{ow} values like acetonitrile, N-nitrosopyrrolidine, N-Nitrosodiethylamine, N-Nitrosomethyl ethylamine, and N-Nitrosodimethylamine would not be expected to work.

Table 2. Chemicals of Potential Concern Compound K_{ow} Values

Semivolatile Compound	CAS Number	Log KoW*
Biphenyl	92-52-4	3.76
Diethylphthalate	84-66-2	2.65
Dibutylbutylphosphonate	78-46-6	3.83
Tributylphosphate	126-73-8	3.82
N-Nitrosodimethylamine	62-75-9	-0.64
2,6-Di-tetra-butyl-p-cresol	128-37-0	5.03
Volatile compounds		
Acetonitrile	75-05-8	-0.15
Benzene	71-43-2	1.99
Butanal	123-72-8	0.82
1-Butanol	71-36-3	0.84
3-Buten-2-one	78-94-4	0.41
Butanenitrile	109-74-0	0.84
2,4-Dimethylpyridine	108-47-4	1.90
2,5-Dihydrofuran	1708-29-8	0.72
Furan	110-00-9	1.36
2-Hexanone	591-78-6	1.24
Hexanenitrile	628-73-9	1.82
2-Methylfuran	534-22-5	1.91
Pentanenitrile	110-59-8	1.33
Propionitrile	107-12-0	0.35
Pyridine	110-86-1	0.80
N-nitrosodimethylamine	62-75-9	-0.64
N-nitrosomethylethylamine	10595-95-6	-0.15
Methylene Chloride	75-09-2	1.34
N-Nitrosodiphenylamine	86-30-6	3.16
N-Nitrosodi-n-propylamine	621-64-7	1.33
N-Nitrosodiethylamine	55-18-5	0.34
N-Nitrosodi-n-butylamine	924-16-3	2.31
N-Nitrosopyrrolidine	930-55-2	0.23
N-Nitrosopiperidine	100-75-4	0.72
SVOA Internal Standards		
1,4-Dichlorobenzene-d4	3855-82-1	NA
Naphthalene-d8	1146-65-2	3.17
Acenaphthalene-d10	15067-26-2	NA
Phenanthrene-d10	1517-22-2	NA
Chrysene-d12	1719-03-5	NA
Perlene-d12	1520-96-3	NA
VOA Internal Standards		
Hexafluorobenzene	392-56-3	3.20
Trifluoromethylbenzene	98-08-8	2.96
1-Bromo-4-fluorobenzene	460-00-4	3.08
Bromobenzene-d5	4165-57-5	NA

* KowWin Program, Interactive LogKow (KowWin) Demo, Syracuse Research Corporation, Copyright 1999, http://www.syres.com/eSc/est_kowdemo.htm

In this work, the chemicals marked in bold in Table 2 were evaluated for analysis using Twisters to extract them from liquids or solids. Some of the other compounds listed on the COPC list were not available as standards. N-nitrosodimethylamine and Nitrosomethylethylamine were tried even though the K_{ow} values indicated that they might not work, and as expected, they did

not work. However, K_{ow} values are not a foolproof predictor for how well a compound will work. The 2,6-ditetra-butyl-p-cresol, and furan have high enough K_{ow} values that one would expect them to extract with Twister, but the laboratory was unable to get either of them to repeatedly extract from liquid or solid matrices. When examining a homologous series such as acetonitrile through hexanenitrile, it is seen that the K_{ow} values increase from acetonitrile, which has a K_{ow} of -0.15, to hexanenitrile, which has a K_{ow} of 1.82. The MDLs for these nitriles get progressively lower as the compounds get larger with higher K_{ow} values, indicating increased sensitivity for each compound in the series as the carbon chain gets progressively longer. Acetonitrile is recommended by the manufacturer of the Twister as a solvent of choice for cleaning the Twisters because of the low K_{ow} value. Propionitrile could not be extracted from liquids or solids using Twister, but butanenitrile, pentanenitrile, and hexanenitrile were successfully extracted and determined by the method.

Figure 1 is an example of a chromatogram of an LCS for the VOAs.

Figure 2 shows an example of a chromatogram of a LCS standard for SVOAs extracted and analyzed using Twister.

4. CONCLUSIONS

Repeatability studies were performed for VOA and SVOA compounds by analyzing replicate extractions of a mid-range standard from a source independent from the calibration standard, (LCS). Results of these studies are shown in Tables 3 and 4. All results are given in percent recovery.

The results of a SVOA LCS determination in diluted tank simulant are shown in Table 5. Terminal Liquor Standard (Terliq), a nearly saturated, extremely basic solution was used as a tank simulant. The Terliq standard is composed of a high concentration of aluminum, sodium nitrate, and sodium nitrite in 50% sodium hydroxide with lower quantities of sodium chloride, sodium fluoride, sodium sulfate, and sodium phosphate, tribasic decahydrate (LR-332-111, "Terminal Liquor Standards").

The results in the sample, adjusted to pH 10, were within the administrative limits for standard percent recovery of 65 to 135%.

The method was applied to analysis of tank simulants containing oil reported in interoffice memorandum WRPS-0800035, "Report for Hydraulic Fluid Interaction Study." The samples were successfully analyzed for SVOA compounds. Analysis of SVOA standards in pH 10 water and standards spiked into basic solutions of tank simulants can be successfully carried out using Twister stir bar sorptive extraction providing the pH of the solution is kept to about pH 10 or less. Volatile organic analysis compounds can be analyzed from solids or from pH 10 liquids.

Figure 1. Volatile Organic Analysis Chromatogram Example

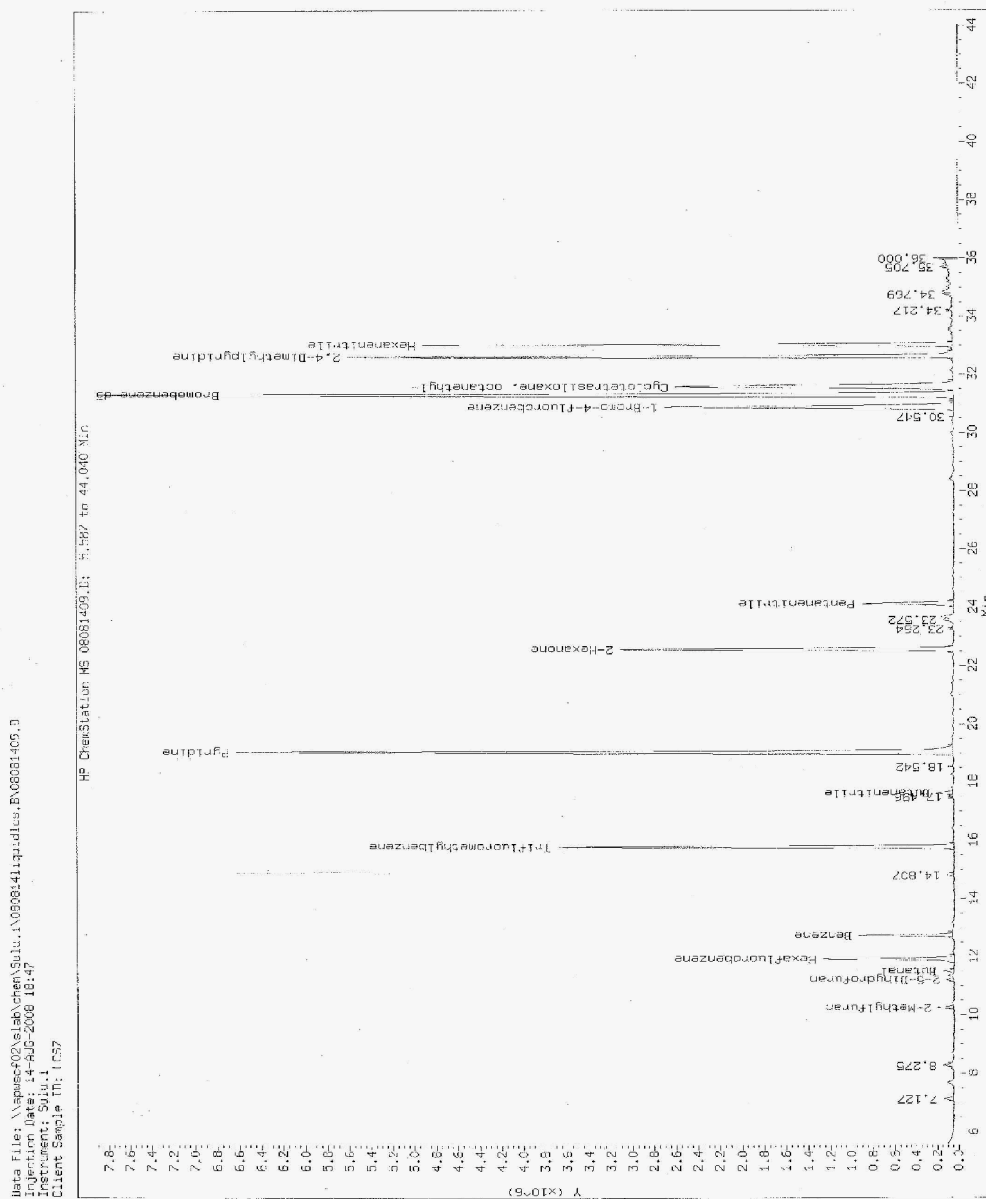


Figure 2. Semivolatile Organic Analysis Chromatogram Example

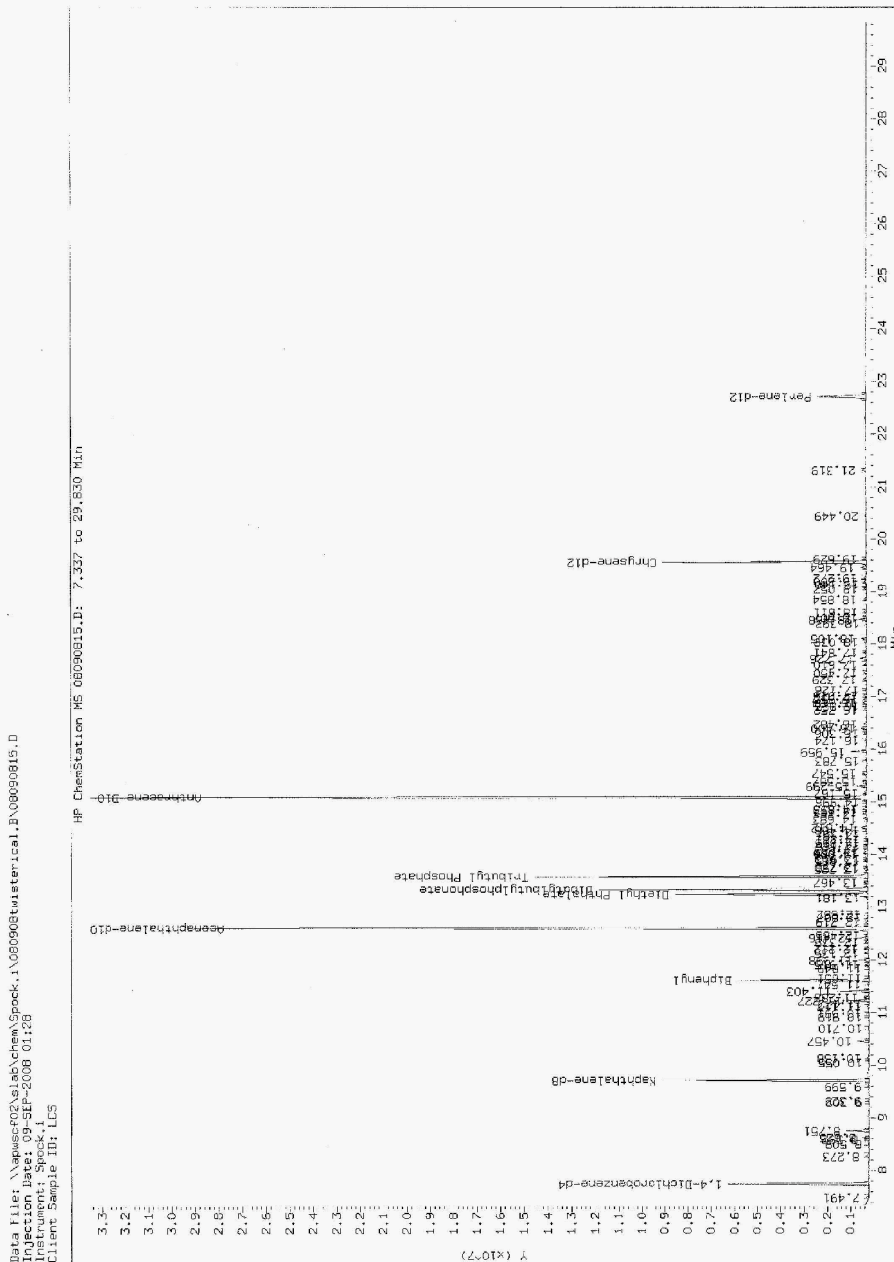


Table 3. Volatile Organic Analysis Repeatability

Compound from Solids	Number of Replicates	Average % Recovery	Standard Deviation	- 1 σ	+ 1 σ
2-Methylfuran	7	104.41	27.61	76.80	132.02
2,5-Dihydrofuran	7	103.55	10.13	93.42	113.69
Benzene	7	108.23	10.57	97.67	118.80
Pyridine	7	99.25	8.19	91.07	107.44
2-Hexanone	7	102.65	5.99	96.65	108.64
Pentanenitrile	7	120.51	7.10	113.41	127.61
Hexanenitrile	7	111.36	6.09	105.27	117.45
1-Butanol	7	111.90	16.54	95.36	128.44
Butanenitrile	7	97.23	4.56	92.67	101.80
2,4-Dimethylpyridine	7	101.58	6.03	95.55	107.61
Butanal	7	107.21	8.02	99.19	115.23
3-Buten-2-one	7	115.07	13.48	101.59	128.55
Compounds from Liquid					
2-Methylfuran	7	130.68	30.92	99.77	161.60
2,5-Dihydrofuran	7	89.54	17.92	71.61	107.46
Benzene	7	120.29	9.87	110.42	130.17
Pyridine	7	100.92	17.55	83.37	118.47
2-Hexanone	7	98.57	16.80	81.77	115.37
Pentanenitrile	7	111.69	12.48	99.20	124.17
Hexanenitrile	7	105.82	10.78	95.05	116.60
Butanenitrile	7	84.72	12.72	72.00	97.43
2,4-Dimethylpyridine	7	90.44	10.82	79.62	101.27
Butanal	7	91.54	11.70	79.84	103.24

Table 4. Semivolatile Organic Analysis Repeatability

Compounds from Liquid	Number of replicates	Average % Recovery	Standard Deviation	- 1 σ	+ 1 σ
Biphenyl	21	115.55	15.80	99.75	131.36
Diethylphthalate	21	92.03	26.75	65.28	118.78
Dibutylbutylphosphonate	21	98.77	35.22	63.55	133.99
Tributylphosphate	21	100.96	27.80	73.16	128.76

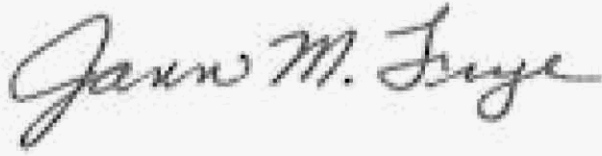
Table 5. Percent Recovery of LCS Standards in Terliq with Twister

Compound	1mL Terliq + LCS pH>10	1mL Terliq + LCS pH =10
Biphenyl	95.6	102.3
Diethyl phthalate	61.9	98.6
Dibutylbutyl phosphonate	69.0	74.8
Tributyl phosphate	63.9	82.5

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