Automated Sampling of Methanol Extractions

Application Note

Environmental

Author

Anne Jurek
Applications Chemist
EST Analytical
Cincinnati, OH

Abstract

The United States Environmental Protection Agency (USEPA) Method 8260 is used in order to ascertain volatile organic compounds in waters, soils and solid waste samples. Often times, soil and solid waste samples are so highly contaminated the sample needs to be dispersed in methanol. Sample collection for contaminated soils can be obtained in two ways. One, dispersing a bulk soil sample into a 40ml vial and adding methanol in the lab or two, sending pre-weighed vials with a septum sealed cap that already contains the pre-requisite methanol out in the field for soil sampling. No matter how the soil sample is dispersed in methanol, an aliquot of the methanol extract needs to be added to water and purged using USEPA Method 5030. This application will investigate automated sampling of methanol soil extractions.

Introduction:

Environmental labs are required to perform methanol extractions on highly contaminated solid waste samples. Additionally, these extractions are used for difficult matrices, for example oily waste samples, that are also soluble in methanol. Due to the variety of matrices that can be extracted with methanol there are assorted hurdles to cross in order to automate the sampling process. One of these obstacles is how the matrix can absorb the extraction solvent. For example, many soil samples require more methanol; due to the soil expanding with the solvent addition. Adding more methanol aids in rectifying this issue however, when automating sampling, the added methanol coupled with the soil expansion needs to be accommodated. For this reason, EST Analytical created software for the Centurion WS that allows the user to program the needle depth to different distances. In doing this, laboratories are able to sample soils at higher depths in order to adjust for sample absorption and at lower depths for samples that do not require the added solvent.

In order to test volatile compounds in methanol extractions, a portion of the extract needs to be sampled from the vial, diluted, and purged on a purge and trap concentrator. This examination will look at the automated sampling of three different soil matrices.

Experimental:

The Centurion WS autosampler with the syringe option and the Evolution purge and trap concentrator were set up to run methanol extractions. Since this is a volatile analysis, a Vocarb 3000 (K) trap was used for the analytical trap. The sampling system was configured to an Agilent 7890A Gas Chromatograph (GC) and an Agilent 5975C inert XL Mass Spectrometer (MS). The column selected for this analysis was a Restek Rxi®-624 Sil MS, with

dimensions of 30m x 0.25mm I.D. x 1.4μm film thickness. Experimental parameters used for this analysis are listed in Tables 1 and 2.

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	150°C
Transfer Line Temp.	150°C
Trap Temp.	35°C
Moisture Reduction Trap (MoRT) Temp.	39°C
Purge Time	11 min
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	1.0 min
Desorb Pressure Control	On
Desorb Pressure	6psi
Desorb Time	0.5 min
Desorb Preheat Delay	15 sec
Desorb Temp.	260°C
Moisture Reduction Trap (MoRT) Bake Temp.	210°C
Bake Temp	270°C
Sparge Vessel Bake Temp.	120°C
Bake Time	8
Bake Flow	85mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Type	Water
Water Volume	5ml
Sample Prime Time	5 sec
Loop Equilibration Time	5 sec
Sample Transfer Time	15 sec.
Syringe Rinse	On/6 ml
Number of Syringe Rinses	2
Sample Loop Rinse	On/15 sec
Sample Sweep Time	15 sec
Number of Sparge Rinses	On/2
Rinse Volume	5 ml
Rinse Transfer Time	15 sec
Rinse Drain Time	25 sec
Water Heater Temp.	85 sec
Internal Standard Vol.	5 μl
Extraction	MeOH Prep A (Sand and Clay)
Extraction	MeOH Prep B (Potting Soil)

Table 1: Evolution/Centurion Purge and Trap Experimental Parameters

GC/MS	Agilent 7890A/5975C inert XL
Inlet	Split/Splitless
Inlet Temp.	220°C
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	Rxi®-624Sil MS 30m x 0.25mm I.D. x 1.4μm film thickness
Oven Temp. Program	45°C hold for 1 min, ramp 15°C/min to 220°C, hold for 1.33 min, 14 min run time
Column Flow Rate	1mL/min
Gas	Helium
Total Flow	44mL/min
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Scan Range	m/z 35-300
Scans	5.2 scans/sec
Solvent Delay	0.7 min

Table 2: GC/MS Experimental Parameters

The EPA method 8260 standards were acquired from Restek while the purge and trap grade methanol was procured from JTBaker. A nine point methanol curve was established from 0.5 to 200μg/L. Next Method Detection Limits (MDLs) were found running seven replicates of the low point on the curve. Precision and accuracy was determined by examining seven replicates of the 50μg/L standard. Table 3 displays the curve, MDL and precision and accuracy results. A set of three spiked sand matrix samples were used to establish the accuracy of the automated extraction at a 50μg/L concentration, see Table 4. Finally, sand, clay and soil matrices were extracted in order to compare the chromatography of the automated extractions using different matrices. The matrix comparison required 5 grams of soil and 15mls of methanol due to the potting soils' absorption of the methanol. Thus, in order to make a direct comparison, all of the matrices were spiked with the same volume of standard and extracted with 15mls of methanol. Figure 1 displays a comparison of the three matrices and their respective interaction with the extraction solvent and Figure 2 shows the chromatograms of the three matrices.

Compound	Curve %RSD	Curve RF	MDL	Precision at 50µg/L	Recovery at 50µg/L	Compound	Curve %RSD	Curve RF	MDL	Precision at 50µg/L	Recovery at 50µg/L
Dichlorodifluoromethane	5.32	0.402	0.10	5.35	92.94	cis-1,3-Dichloropropene	4.33	0.618	0.09	2.39	99.57
Chloromethane	13.92	0.890	0.17	5.39	83.22	4-methyl-2-pentanone	7.12	0.373	0.08	2.87	95.05
Vinyl Chloride	5.92	0.881	0.08	5.17	91.09	Toluene-d8 SUR	5.87	1.402	0.06	3.63	100.73
Bromomethane	12.13	0.310	0.14	12.84	75.49	Toluene	4.56	0.962	0.07	3.59	99.95
Chloroethane	10.60	0.496	0.27	5.77	83.41	ethyl methacrylate	5.34	0.543	0.08	2.44	101.73
Trichlorofluoromethane	9.58	0.908	0.11	4.76	90.85	trans-1,3-Dichloropropene	5.38	0.574	0.06	2.06	99.59
diethyl ether	3.79	0.506	0.09	3.16	94.38	1,1,2-Trichloroethane	4.49	0.374	0.05	2.11	98.82
1,1,2-trichlorofluoroethane	10.45	0.558	0.11	4.76	90.85	Tetrachloroethene	14.64	0.528	0.10	10.65	111.05
1,1-Dichloroethene	7.35	0.535	0.10	5.02	94.19	1,3-Dichloropropane	2.71	0.618	0.05	2.03	98.94
Acetone	*0.998	0.212	2.38	6.30	105.86	Dibromochloromethane	7.65	0.418	0.06	2.17	102.42
Iodomethane	*0.997	0.341	0.20	9.09	115.06	2-Hexanone	6.86	0.264	0.12	3.40	97.52
Carbon Disulfide	9.96	1.483	0.09	4.53	90.88	1,2-Dibromoethane	3.34	0.386	0.08	2.13	101.24
allyl chloride	11.28	0.756	0.09	4.10	94.84	Chlorobenzene	6.15	1.044	0.05	2.46	97.24
Methylene Chloride	9.71	0.639	0.10	3.09	91.12	1,1,1,2-Tetrachloroethane	8.24	0.366	0.06	2.16	100.57
Tert Butyl Alcohol	3.59	0.366	0.19	3.02	95.00	Ethylbenzene	6.64	1.720	0.07	3.31	97.78
MTBE	2.62	1.944	0.06	3.20	94.76	Xylene (m + p)	6.95	1.329	0.08	3.34	196.87
cis-1,2-Dichloroethene	2.84	0.698	0.09	3.71	95.99	Styrene	7.40	1.135	0.05	2.33	100.12
acrylonitrile	10.23	0.260	0.10	4.37	91.97	Xylene (o)	5.69	1.375	0.07	2.94	98.44
Isopropylether	3.10	1.705	0.05	3.54	93.83	Bromoform	11.59	0.278	0.07	1.91	104.77
1,1-Dichloroethane	3.57	1.062	0.05	4.03	94.21	Isopropylbenzene	6.33	1.622	0.05	3.67	100.67
Ethyl Tert Butyl Ether	3.59	1.831	0.03	3.02	94.99	cis-1,4-dichloro-2-butene	7.61	0.151	0.11	2.83	101.10
trans-1,2-Dichloroethene	3.78	0.612	0.06	4.44	95.43	BFB SUR	11.19	0.801	0.06	2.40	89.94
2-Butanone	13.56	0.991	0.10	4.94	88.41	Bromobenzene	8.06	1.146	0.06	1.93	90.72
2,2-Dichloropropane	7.27	0.826	0.09	6.63	94.40	1,2,3-Trichloropropane	6.75	0.873	0.07	2.68	91.46
Bromochloromethane	4.65	0.408	0.09	3.23	95.73	1,1,2,2-Tetrachloroethane	7.31	0.728	0.08	4.04	91.72
propionitrile	10.83	0.096	0.31	4.75	94.31	n-Propylbenzene	6.55	3.131	0.07	3.68	94.14
methacrylonitrile	9.36	0.363	0.09	3.66	92.02	trans-1,4-dichloro-2-butene	12.47	0.218	0.10	2.99	89.79
THF	12.06	0.180	1.16	4.39	92.99	2-Chlorotoluene	4.45	0.666	0.10	2.81	95.77
Chloroform	9.12	1.119	0.06	3.80	92.32	4-Chlorotoluene	3.82	0.698	0.12	2.76	96.31
methyl acrylate	4.06	0.634	0.10	4.08	96.12	1,3,5-Trimethylbenzene	5.62	2.194	0.06	3.38	95.79
Dibromofluoromethane SUR	12.85	0.658	0.09	3.57	91.21	tert-Butylbenzene	9.59	1.942	0.06	5.37	97.16
1,1,1-Trichloroethane	13.84	0.985	0.09	4.38	89.87	sec-Butylbenzene	5.97	0.586	0.08	3.79	97.82
Carbon Tetrachloride	8.14	0.752	0.08	4.67	98.33	1,2,4-Trimethylbenzene	6.84	2.281	0.06	3.26	94.60
1,1-Dichloropropene	5.37	0.826	0.09	4.65	95.09	1,3-Dichlorobenzene	4.53	1.343	0.05	2.44	97.65
Tert Amyl Methyl Ether	1.59	1.848	0.04	3.22	96.11	1,4-Dichlorobenzene	7.92	1.436	0.06	2.26	93.09
Benzene	3.32	2.540	0.04	4.08	94.95	Isopropyltoluene	6.10	2.363	0.07	3.85	97.18
1,2-Dichloroethane	5.97	0.873	0.06	1.68	92.48	1,2,-Dichlorobenzene	5.03	1.329	0.04	2.29	96.30
Trichloroethene	7.54	0.431	0.08	3.98	102.45	n-Butylbenzene	9.34	2.105	0.04	4.09	93.80
1,2-Dichloropropane	3.77	0.368	0.04	3.00	97.73	1,2-Dibromo-3-chloropropane	8.60	0.138	0.15	3.17	90.83
methyl methacrylate	5.23	0.320	0.08	2.39	99.37	1,2,4-Trichlorobenzene	10.99	0.813	0.10	3.31	101.53
Dibromomethane	7.97	0.279	0.09	1.92	106.42	Naphthalene	9.07	2.274	0.08	2.83	95.82
Bromodichloromethane	4.43	0.508	0.08	2.51	99.08	Hexachlorobutadiene	14.10	0.318	0.11	5.37	102.29
2-nitropropane	6.03	0.109	0.17	3.73	97.27	1,2,3-Trichlorobenzene	11.96	0.750	0.09	2.99	101.78
						Average	7.32	0.756	0.18	4.37	94.35

Table 3: Curve, MDL and Precision and Accuracy Results

Compound	Accuracy of Extracted Sand Matrix	Compound	Accuracy of Extracted Sand Matrix
Dichlorodifluoromethane	89.30	cis-1,3-Dichloropropene	107.26
Chloromethane	90.88	4-methyl-2-pentanone	91.41
Vinyl Chloride	103.30	Toluene-d8 SUR	111.09
Bromomethane	129.50	Toluene	109.81
Chloroethane	111.24	ethyl methacrylate	100.55
Trichlorofluoromethane	108.71	trans-1,3-Dichloropropene	103.79
diethyl ether	94.80	1,1,2-Trichloroethane	98.89
1,1,2-trichlorofluoroethane	108.71	Tetrachloroethene	77.03
1,1-Dichloroethene	109.17	1,3-Dichloropropane	99.11
Acetone	99.13	Dibromochloromethane	103.52
Iodomethane	126.79	2-Hexanone	91.48
Carbon Disulfide	103.59	1,2-Dibromoethane	100.23
allyl chloride	106.38	Chlorobenzene	99.78
Methylene Chloride	97.68	1,1,1,2-Tetrachloroethane	103.46
Tert Butyl Alcohol	97.04	Ethylbenzene	102.98
MTBE	94.08	Xylene (m + p)	103.11
cis-1,2-Dichloroethene	104.95	Styrene	101.32
acrylonitrile	90.53	Xylene (o)	102.13
Isopropylether	99.22	Bromoform	99.17
1,1-Dichloroethane	103.21	Isopropylbenzene	105.70
Ethyl Tert Butyl Ether	97.04	cis-1,4-dichloro-2-butene	99.00
trans-1,2-Dichloroethene	105.85	BFB SUR	91.55
2-Butanone	82.63	Bromobenzene	91.39
2,2-Dichloropropane	122.20	1,2,3-Trichloropropane	88.25
Bromochloromethane	100.49	1,1,2,2-Tetrachloroethane	92.23
propionitrile	88.24	n-Propylbenzene	99.12
methacrylonitrile	89.13	trans-1,4-dichloro-2-butene	89.10
THF	85.99	2-Chlorotoluene	99.41
Chloroform	99.29	4-Chlorotoluene	97.69
methyl acrylate	93.09	1,3,5-Trimethylbenzene	99.20
Dibromofluoromethane SUR	99.27	tert-Butylbenzene	104.99
1,1,1-Trichloroethane	102.91	sec-Butylbenzene	100.19
Carbon Tetrachloride	115.02	1,2,4-Trimethylbenzene	96.20
1,1-Dichloropropene	109.04	1,3-Dichlorobenzene	95.85
Tert Amyl Methyl Ether	96.43	1,4-Dichlorobenzene	90.84
Benzene	104.23	Isopropyltoluene	98.20
1,2-Dichloroethane	94.87	1,2,-Dichlorobenzene	93.55
Trichloroethene	110.01	n-Butylbenzene	92.34
1,2-Dichloropropane	105.19	1,2-Dibromo-3-chloropropane	81.83
methyl methacrylate	98.96	1,2,4-Trichlorobenzene	90.93
Dibromomethane	108.46	Naphthalene	86.72
Bromodichloromethane	104.77	Hexachlorobutadiene	98.14
2-nitropropane	96.71	1,2,3-Trichlorobenzene	91.21
		Average	101.81

Table 4: Results of Automated Extraction of a Sand Matrix

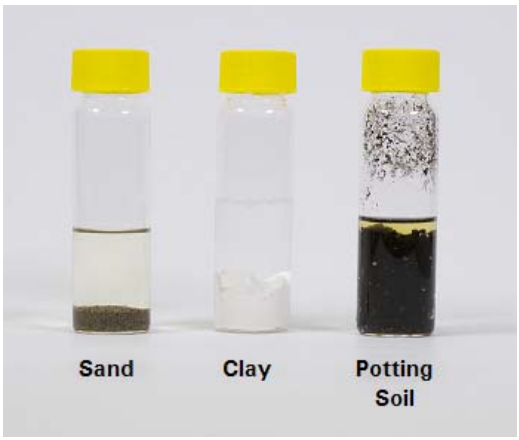

Figure 1: Image of 5g of soil matrices in 15mls of Methanol

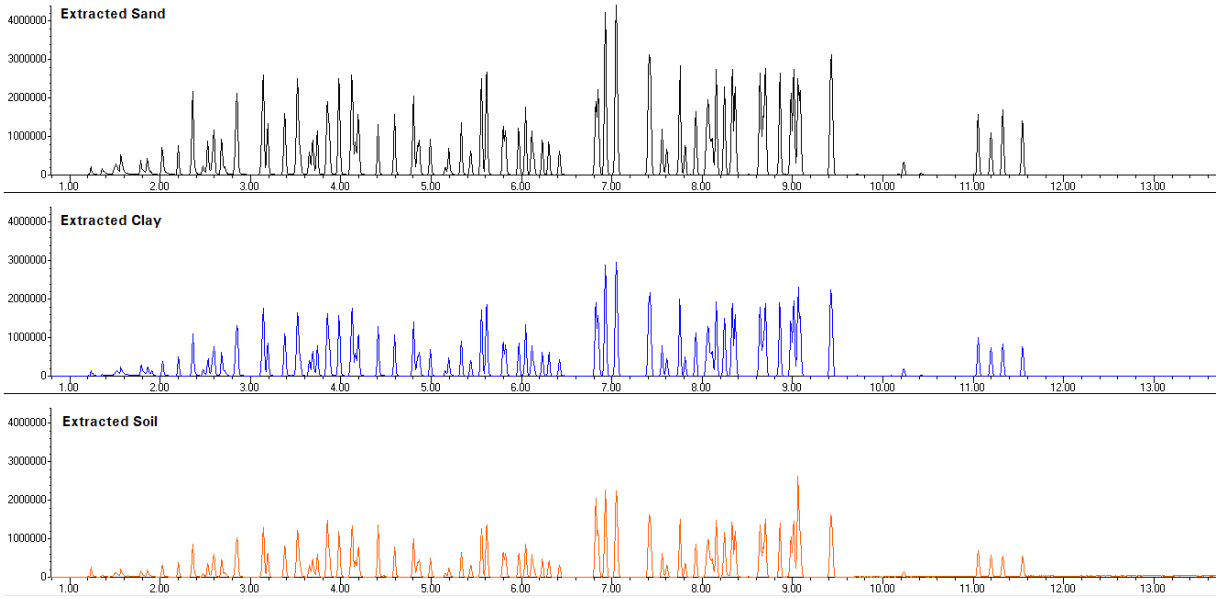

Figure 2: Chromatograms of Automated Extraction of Sand, Clay and Soil

Conclusions:

The system produced excellent results. The curve and the compound response factors met all of the method requirements. The overall precision was less than 5% RSD while the system showed an average recovery of 94%. When examining the expected analyte concentration to the extracted sand results, it was found that the average recovery was approximately 102%. Thus, the automated extraction performed extremely well. When comparing the three different matrices it was found that they all displayed similar recoveries, however the sand matrix did perform the best of the three as expected since sand tends not to absorb analytes as readily as other matrices. Finally, the ability to control the needle depth on extraction samples was a great benefit for the different matrices as the system exhibited no issues with needle clogging due to the higher needle depth when performing the potting soil extractions. As demonstrated from this study, the Centurion WS automated extraction capability would be an asset to any lab performing extractions.

References:

1. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); United States Environmental Protection Agency Method 8260B, Revision 2, December 1996.

2. Closed System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples; United States Environmental Protection Agency Method 5035, Revision 0, 1996.

For More Information

For more information on our products and services, visit our website www.estanalytical.com/products.