Automated Sampling of Methanol Extractions

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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**.

Table 1: Evolution/Centurion Purge and Trap **Experimental Parameters**

Purge Trap Type Valve Oven T Transfer Line Trap Temp. Moisture Redu Temp. Purge Time Purge Flow Dry Purge Ten Dry Purge Flo Dry Purge Tin **Desorb Pressu** Desorb Pressu Desorb Time **Desorb Prehe Desorb** Temp Moisture Red Bake Temp. Bake Temp Sparge Vesse Bake Time Bake Flow Purge And Tra Sample Type Water Volume Sample Prime Loop Equilibration Sample Trans Syringe Rinse Number Of Sy Sample Loop Sample Swee Number Of Sp **Rinse Volume Rinse Transfe**

Rinse Drain T

Water Heater Internal Stand Extraction Extraction

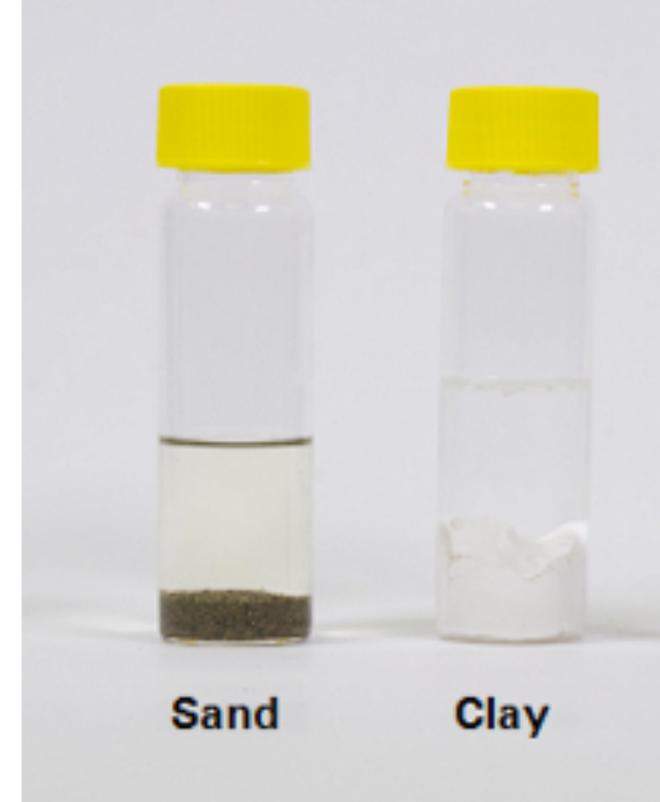
d Trap Concentrator	EST Evolution	
	Vocarb 3000	
Temp.	150°C	
e Temp.	150°C	
	35°C	
duction Trap (Mort)	39°C	
	11 min	
	40ml/min	
mn	Ambient	
emp.		
0W me	40ml/min 1.0 min	
me Control		
sure Control	On	
sure	6PSI	
)	0.5 min	
eat Delay	15 sec	
р.	260°C	
duction Trap (Mort)	210°C	
	270°C	
el Bake Temp.	120°C	
	8 85ml/min	
rap Auto-Sampler	EST Centurion WS	
9	Water	
ne	5ml	
ne Time	5 sec	
oration Time	5 sec	
nsfer Time	15 sec	
	On/6 ml	
Syringe Rinses	2 $Op/15$ coc	
o Rinse	On/15 sec	
ep Time	15 sec	
Sparge Rinses	On/2	
e	5 ml	
er Time	15 sec	
Time	25 sec	
r Temp.	85 sec	
ndard Vol.	5 ml	
	Meoh Prep A (Sand and Clay)	

Table 2: GC/MS Experimental Parameters

GC/MS	Ag
Inlet	Split/Splitles
Inlet Temp.	220°C
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	Rxi®-624Sil I thickness
Oven Temp. Program	45°C hold for hold for 1.33
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

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. 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 3.** 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.

Figure 1: Image of 5g of Soil Matrices in 15mls of Methanol



ent 7890A/5975C inert XL

I MS 30m x 0.25mm l.D. x 1.4µm film

or 1 min, ramp 15°C/min to 220°C, 8 min, 14 min run time



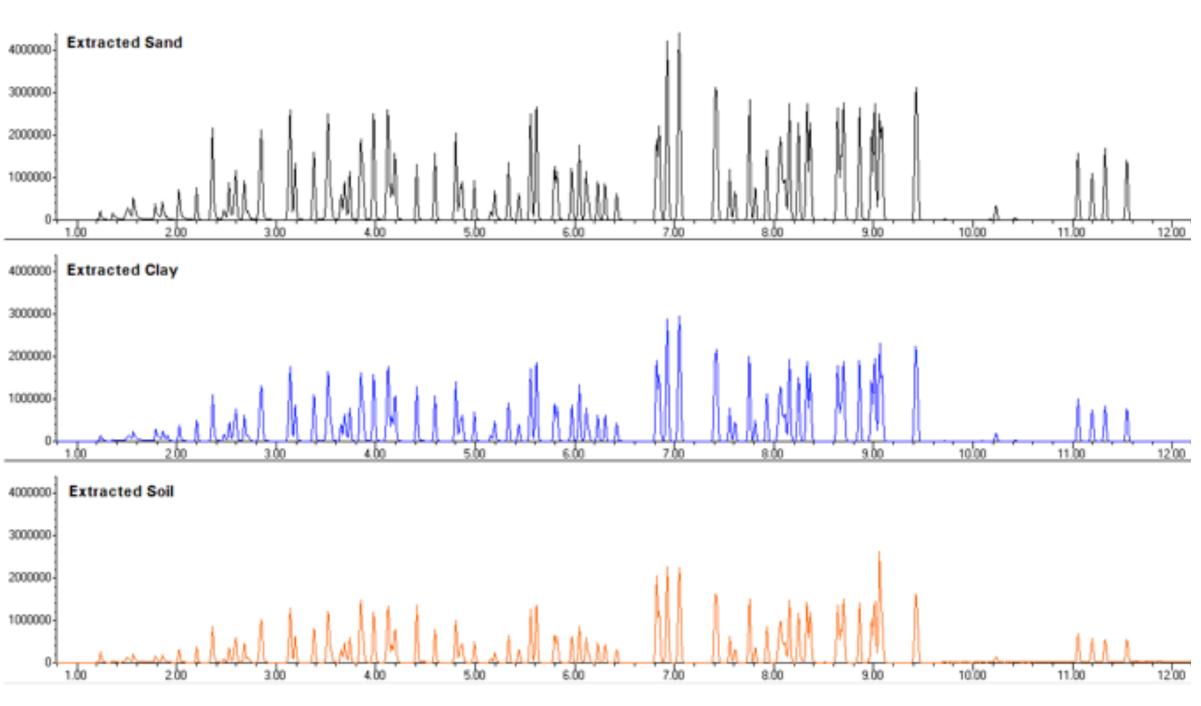
Potting Soil

Table 3: Results of Automated Extraction of a **Sand Matrix**

	Accuracy	
Compound	of Extracted	Compound
	Sand	
Dichlorodifluoromethane	Matrix 89.30	cis-1,3-Dichloropropene
Chloromethane	90.88	4-methyl-2-pentanone
Vinyl Chloride	103.30	Toluene-d8 SUR
Bromomethane	129.50	Toluene
Chloroethane	111.24	ethyl methacrylate
Trichlorofluoromethane	108.71	trans-1,3-Dichloropropen
diethyl ether	94.80	1,1,2-Trichloroethane
1,1,2-trichlorofluoroethane		Tetrachloroethene
	109.17	
1,1-Dichloroethene	99.13	1,3-Dichloropropane
Acetone		Dibromochloromethane
Iodomethane	126.79	2-Hexanone
Carbon Disulfide	103.59	1,2-Dibromoethane
allyl chloride	106.38	Chlorobenzene
Methylene Chloride	97.68	1,1,1,2-Tetrachloroethane
Tert Butyl Alcohol	97.04	Ethylbenzene
MTBE	94.08	Xylene (m+p)
cis-1,2-Dichloroethene	104.95	Styrene
acrylonitrile	90.53	Xylene (o)
Isopropylether	99.22	Bromoform
1,1-Dichloroethane	103.21	Isopropylbenzene
Ethyl Tert Butyl Ether	97.04	cis-1,4-dichloro-2-butene
trans-1,2-Dichloroethene	105.85	BFB SUR
2-Butanone	82.63	Bromobenzene
2,2-Dichloropropane	122.20	1,2,3-Trichloropropane
Bromochloromethane	100.49	1,1,2,2-Tetrachloroethane
propionitrile	88.24	n-Propylbenzene
methacrylonitrile	89.13	trans-1,4-dichloro-2-bute
THF	85.99	2-Chlorotoluene
Chloroform	99.29	4-Chlorotoluene
methyl acrylate	93.09	1,3,5-Trimethylbenzene
Dibromofluoromethane SUR	99.27	tert-Butylbenzene
1,1,1-Trichloroethane	102.91	sec-Butylbenzene
Carbon Tetrachloride	115.02	1,2,4-Trimethylbenzene
1,1-Dichloropropene	109.04	1,3-Dichlorobenzene
Tert Amyl Methyl Ether	96.43	1,4-Dichlorobenzene
Benzene	104.23	lsopropyltoluene
1,2-Dichloroethane	94.87	1,2,-Dichlorobenzene
Trichloroethene	110.01	n-Butylbenzene
1,2-Dichloropropane	105.19	1,2-Dibromo-3- chloropropane
methyl methacrylate	98.96	1,2,4-Trichlorobenzene
Dibromomethane	108.46	Naphthalene
Bromodichloromethane	104.77	Hexachlorobutadiene
2-nitropropane	96.71	1,2,3-Trichlorobenzene
		Average

Extrac 107.26 91.41 111.09 109.81 100.55 ne 103.79 98.89 77.03 99.11 103.52 91.48 100.23 99.78 103.46 102.98 103.11 101.32 102.13 99.17 105.70 99.00 91.55 91.39 88.25 92.23 99.12 ene 89.10 99.41 97.69 99.20 104.99 100.19 96.20 95.85 90.84 98.20 93.55 92.34 81.83 90.93 86.72 98.14 91.21 101.81

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

. 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.

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