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Automated Methanol Extraction of High-Level Soil Samples Using the Teledyne Tekmar Atomx XYZ and Agilent 7890B GC/5977A MSD

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Abstract

US EPA Method 5035 was used to determine the concentration of volatile organic compounds (VOCs) in high-level soil samples using purge and trap concentration. For this study, a Teledyne Tekmar Atomx XYZ purge and trap (P&T) system and Agilent 7890B Gas Chromatograph (GC)/5977A Mass Spectrometer (MS) was used to generate a working linear calibration curve, method detection limits (MDLs), recovery and carryover data for high-level soil samples. Additionally, the study will demonstrate the Atomx XYZ's ability to automate the methanol extraction process, as well as the system's ability to reduce carryover. It should also be noted, that US EPA 5035 includes the handling of soils which exceed normal VOC concentration levels (>200 ppb).[1]

Introduction

US EPA Method 5035 allows for two soil sample collection options that can be used in accordance with US EPA Method 8260C: "The first option is to collect an appropriate sample volume in a pre-weighed vial with a septum-sealed screw-cap that contains a water-miscible organic solvent (e.g., methanol). At the time of analysis, an aliquot of the solvent is removed from the vial and diluted into water along with the internal standards and surrogates, then purged using Method 5030 and analyzed by an appropriate determinative method. The second option is to collect a bulk sample in a VOA vial without the use of a chemical preservative. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method." [1,2]

For this study, 5 and 7 gram (g) baked sand samples were placed in 40 mL VOA vials with methanol, spiked with standard, a stir bar added and then sealed. The methanol extraction process was then conducted by the 84-position Atomx XYZ automated system including: addition of methanol via the system's 3-stage needle, mixing of the sample to release VOCs from the sample into the methanol, extraction of a methanol aliquot, and the addition of 5 mL of DI water to that aliquot for sparging. The remaining analysis used normal P&T conditions.

Sample Preparation

A 50 ppm working calibration standard was prepared in methanol from a six compound Restek® BTEX standard. The water method calibration curve was prepared from 1 ppb to 200 ppb. The relative response factor (RF) was calculated for each compound using one internal standard: Fluorobenzene. Surrogate standards consisted of: 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb. Ten 1 ppb standards were prepared for MDL, accuracy and precision calculations. The Atomx XYZ conditions for all calibration and MDL standards are shown in Table I.

A set of ten 5 g baked sand samples and ten 7 g baked sand samples were prepared in 40 mL VOA vials. 1 mL of methanol was added to the 5 g samples and 2 mL to 7 g samples. A spike of 50 ppm BTEX standard was then added to each, along with a stir bar, and the vials sealed. Each set was then run using a separate methanol extraction method. The method conditions for the 5 g samples are shown in Table II while those for the 7 g samples are shown in Table III. After the automated methanol extraction process, a sample aliquot was taken by the system and diluted 1:50 by adding 5 mL of DI water, for a final

concentration of 100 ppb.

When analyzing high-level soil samples, system carryover can be a concern. To evaluate carryover of the Atomx XYZ's automated methanol extraction system, five vials containing 5 g of baked sand sample along with 1 mL of methanol, 50 ppm BTEX standard spike and stir bar were run. After the automated methanol extraction process, a sample aliquot was taken by the system and diluted 1:50 by adding 5 mL of DI water, for a final concentration of 200 ppb. Immediately following the spiked 200 ppb baked sand samples, an un-spiked 5 g baked sand sample was run and evaluated for system carryover. The carryover evaluation used the Atomx XYZ conditions found in Table II.

Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Water Method Conditions

Standby	Variable	Desorb	Variable
Valve Oven Temp	140 ºC	Water Needle Rinse Volume	7.0 mL
Transfer Line Temp	140 ºC	Sweep Needle Time	0.25 min
Sample Mount Temp	90 ºC	Desorb Preheat Temp	245 ºC
Water Heater Temp	90 ºC	Desorb Time	1.00 min
Soil Valve Temp	100 ºC	Drain Flow	300 mL/min
Standby Flow	10 mL/min	Desorb Temp	250 ºC
Purge Ready Temp	40 ºC	Methanol Needle Rinse	Off
Purge	**Variable**	GC Start Signal	Begin Desorb
Sample Equilibrate Time	0.00 min	**Bake**	**Variable**
Presweep Time	0.25 min	Methanol Glass Rinse	Off
Prime Sample Fill Volume	3.0 mL	Number of Water Bake Rinses	1
Sample Volume	5.0 mL	Water Bake Rinse Volume	7.0 mL
Sweep Sample Time	0.25 min	Bake Rinse Sweep Time	0.25 min
Sweep Sample Flow	100 mL/min	Bake Rinse Sweep Flow	100 mL/min
Purge Time	11.00 min	Bake Rinse Drain Time	0.40 min
Purge Flow	40 mL/min	Bake Time	2.00 min
Purge Temp	20 ºC	Bake Flow	200 mL/min
MCS Purge Temp	20 ºC	Bake Temp	280 ºC
Dry Purge Time	0.50 min	MCS Bake Temp	180 ºC
Dry Purge Flow	100 mL/min	**Trap**	9
Dry Purge Temp	20 ºC	**Chiller Tray**	Off
		Purge Gas	Helium

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Table II Teledyne Tekmar Atomx XYZ Methanol Extraction Method Conditions (5 g)			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	140 ºC	Water Needle Rinse Volume	7.0 mL
Transfer Line Temp	140 ºC	Sweep Needle Time	0.50 min
Sample Mount Temp	90 ºC	Desorb Preheat Temp	245 ºC
Water Heater Temp	90 ºC	GC Start Signal	Begin Desorb
Soil Valve Temp	125 ºC	Desorb Time	1.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40 ºC	Desorb Temp	250 ºC
Purge	**Variable**	**Bake**	**Variable**
Presweep Time	0.25 min	Methanol Glass Rinse	On
Methanol Volume	9.0 mL	Number of Methanol Glass Rinses	1
Sample Mix Speed	Medium	Methanol Glass Rinse Volume	3.0 mL
Sample Mix Time	2.00 min	Number of Water Bake Rinses	1
Sample Mix Settle Time	1.00 min	Water Bake Rinse Volume	7.0 mL
Sample Sweep Time	0.25 min	Bake Rinse Sweep Time	0.25 min
Sample Sweep Flow	100 mL/min	Bake Rinse Sweep Flow	100 mL/min
Purge Time	11.00 min	Bake Rinse Drain Time	0.40 min
Purge Flow	40 mL/min	Bake Time	2.00 min
MCS Purge Temp	20 ºC	Bake Flow	200 mL/min
Dry Purge Time	0.50 min	Bake Temp	280 ºC
Dry Purge Flow	100 mL/min	MCS Bake Temp	200 ºC
Dry Purge Temp	20 ºC		
Desorb	**Variable**	**Trap**	9
Methanol Needle Rinse	On	**Chiller Tray**	Off
Methanol Needle Rinse Volume	2.0 mL	**Purge Gas**	Helium

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Table III Teledyne Tekmar Atomx XYZ Methanol Extraction Method Conditions (7 g)			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	140 ºC	Water Needle Rinse Volume	7.0 mL
Transfer Line Temp	140 ºC	Sweep Needle Time	0.50 min
Sample Mount Temp	90 ºC	Desorb Preheat Temp	245 ºC
Water Heater Temp	90 ºC	GC Start Signal	Begin Desorb
Soil Valve Temp	125 ºC	Desorb Time	1.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40 ºC	Desorb Temp	250 ºC
Purge	**Variable**	**Bake**	**Variable**
Presweep Time	0.25 min	Methanol Glass Rinse	On
Methanol Volume	5.0 mL	Number of Methanol Glass Rinses	1
Sample Mix Speed	Medium	Methanol Glass Rinse Volume	3.0 mL
Sample Mix Time	2.00 min	Number of Water Bake Rinses	1
Sample Mix Settle Time	1.00 min	Water Bake Rinse Volume	7.0 mL
Sample Sweep Time	0.25 min	Bake Rinse Sweep Time	0.25 min
Sample Sweep Flow	100 mL/min	Bake Rinse Sweep Flow	100 mL/min
Purge Time	11.00 min	Bake Rinse Drain Time	0.40 min
Purge Flow	40 mL/min	Bake Time	2.00 min
MCS Purge Temp	20 ºC	Bake Flow	200 mL/min
Dry Purge Time	0.50 min	Bake Temp	280 ºC
Dry Purge Flow	100 mL/min	MCS Bake Temp	200 ºC
Dry Purge Temp	20 ºC		
Desorb	**Variable**	**Trap**	9
Methanol Needle Rinse	On	**Chiller Tray**	Off
Methanol Needle Rinse Volume	2.0 mL	**Purge Gas**	Helium

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Table IV Agilent 7890B GC and 5977A MSD System Conditions	
Agilent 7890B GC Conditions	
Column	Restek®-VMS, 20 m x 0.18 mm, 1µm Film, Helium – 1 mL/min
Oven Profile	35 ºC, 4 min, 15 ºC/min to 85 ºC, 30 ºC/min to 225 ºC, 2 min hold, Run Time 14.00 min
Inlet	180 ºC, 120:1 Split, 19.752 psi
Agilent 5977A MSD Conditions	
Temp	Transfer Line 225 ºC; Source 230 ºC; Quad 150 ºC
Scan	Range 35 m/z to 260 m/z, Solvent Delay 0.50 min, Normal Scanning
Gain	Gain Factor 10.00, Autotune

Results

The relative standard deviation (%RSD) of the response factors (RF) for the calibration curve, MDL and accuracy and precision data are shown in Table V.

Accuracy and precision data for the 5 g and 7 g sets of baked sand 100 ppb BTEX methanol extraction samples is shown in Table VI and Table VII, respectively. Example chromatograms of 5 g and 7 g samples are shown in Figure 1 and Figure 2 respectively.

Accuracy and precision data for the set of five 5 g baked sand 200 ppb BTEX carryover evaluation samples, along with carryover data from the un-spiked 5 g sample, is shown in Table VIII.

Table V BTEX Calibration, Accuracy, and Precision Data						
Compound	Calibration			Accuracy and Precision (n=10, 1.0 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (%)	Precision (%RSD)
Fluorobenzene (IS)						
Benzene	6.40	0.21	0.839	1.00	99.80	6.6
Toluene	8.15	0.12	0.957	1.01	100.8	3.9
Ethylbenzene	12.9	0.17	1.025	1.03	102.8	5.4
m,p-Xylene	19.4	0.31	0.783	2.10	105.1	4.7
o-Xylene	11.6	0.18	0.805	1.00	99.90	5.8
4-Bromofluorobenzene (Surr)	5.86		0.225	24.7	98.84	1.8
1,2-Dichlorobenzene (Surr)	4.99		0.388	24.3	97.11	5.0

Table VI BTEX Methanol Extraction Accuracy and Precision Data (5 g)		
Compounds	Accuracy (%)	Precision (%RSD)
Benzene	107.1	7.8
Toluene	98.75	7.9
Ethylbenzene	96.64	7.6
m,p-Xylene	96.22	6.5
o-Xylene	99.10	8.2

Figure 1 Total Ion Chromatogram of a Methanol Extraction Method 5 g Baked Sand Sample Containing a Final Concentration of 100 ppb BTEX Standard.

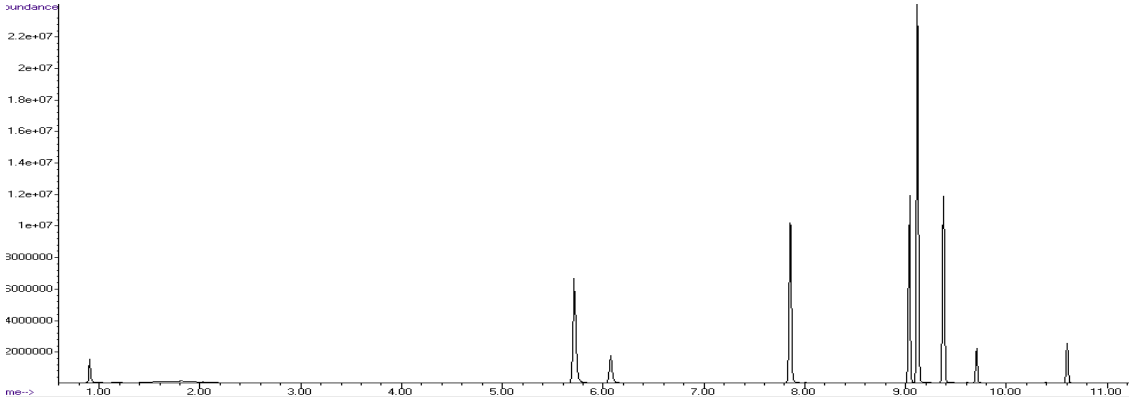

Table VII BTEX Methanol Extraction Accuracy and Precision Data (7 g)		
Compounds	**Accuracy (%)**	**Precision (%RSD)**
Benzene	105.0	10.0
Toluene	95.97	9.4
Ethylbenzene	94.04	9.3
m,p-Xylene	94.67	8.7
o-Xylene	95.20	9.2

Figure 2 Total Ion Chromatogram of a Methanol Extraction Method 7 g Baked Sand Sample Containing a Final Concentration of 100 ppb BTEX Standard.

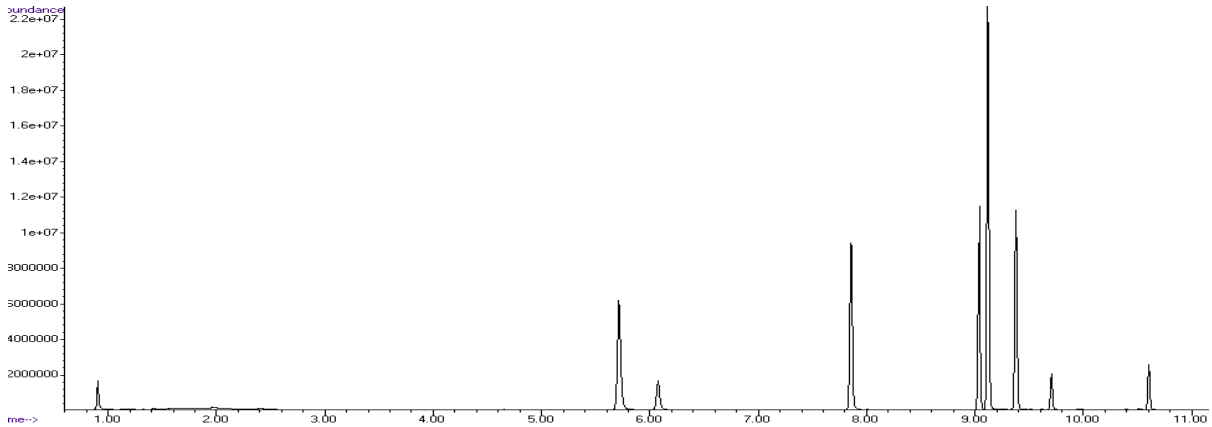

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Table VIII Carryover Study - BTEX Methanol Extraction Accuracy and Precision Data and Avg Carryover			
Compounds	**Accuracy (%)**	**Precision (%RSD)**	**Average Carryover (%)**
Benzene	93.95	2.8	0.25
Toluene	89.42	2.6	0.41
Ethylbenzene	92.05	1.5	0.53
m,p-Xylene	93.09	1.7	0.65
o-Xylene	91.52	2.7	0.43

Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in high-level soil samples using automated methanol extraction, following US EPA Method 5035 and 8260C, with detection by an Agilent 7890B GC/5977A MS. The %RSD of the calibration curve passed all method requirements. Furthermore, the Atomx XYZ's automated methanol extraction was able to process the high-level soil samples with a 94% recovery or better for both 5 g and 7 g sample sets, with less than 10% RSD over 10 replicates. Finally, the Atomx XYZ showed less than 0.65% system carryover for the five high-level soil samples spiked with 50 ppm BTEX standard, followed by an un-spiked 5 g sample.

It should also be noted that by making additional, appropriate changes to the GC oven temperature program, the GC/MS cycle time may also be reduced, increasing laboratory throughput in a 12-hour period.

References

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