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Automated Methanol Extraction of High-Level Soil Samples Using the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ 7000 MS System with an ExtractaBrite Source

Amy Nutter, Applications Chemist; Teledyne Tekmar

Abstract

US EPA Method 5035 was used to determine the concentration of volatile organic compounds (VOCs) in high-level soil and waste samples using purge and trap technology. This includes the handling of soils which exceed normal VOC concentration levels (>200 parts per billion [ppb] or microgram per liter [µg/L]). For this study a Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) and ISQ™ 7000 Mass Spectrometer (MS) with an ExtractaBrite source was used to generate a working linear calibration curve, initial demonstration of capability (IDC) and carryover study for high-level soil samples. Additionally, this study will demonstrate the Atomx XYZ's ability to automate the methanol extraction process, as well as the system's ability to reduce carryover.

Introduction

US EPA Method 5035 allows for two sample collection options that can be used in accordance with US EPA Method 8260.[1,2,3] The first option is to collect 5 grams (g) of soil into a pre-weighed vial containing a prescribed amount of a water-miscible solvent (methanol). An aliquot of the sample is then taken and purged using US EPA Method 5030.[4] The second option is to collect a bulk soil sample on site. Once in the lab, the bulk soil is separated into individual samples containing a water-miscible solvent (methanol). An aliquot of the sample is then taken and purged using US EPA Method 5030.[4]

The Atomx XYZ is Teledyne Tekmar's most advanced P&T system and based on the time-tested Atomx instrument platform. Spiked, baked sand samples were placed in 40 milliliter (mL) VOA vials with methanol. The vials were then placed in the 84-position autosampler. When a high-level soil sample was ready for analysis, the vial was raised onto the three-stage needle where the Atomx XYZ added the prescribed amount of methanol to the sealed vial. The Atomx XYZ vial mixing option was turned ON to release the VOCs from the soil into the methanol solution. An aliquot of the methanol solution was added to 5 mL of de-ionized (DI) water and analyzed under normal P&T conditions.

The Atomx XYZ was designed to automate the time-consuming steps of the methanol extraction process and reduce over-all analysis time. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 18% over the previous model. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

Sample Preparation

A 1000 parts per million (ppm) or milligram per liter (mg/L) working calibration standard was prepared in methanol from a 9-compound Restek® PVOC/GRO Mix (Wisconsin) standard. A 5-point methanol extraction calibration curve was prepared from 200 ppb to 1000 ppb. The relative response factor (RF) was calculated for each compound using one of the four internal standards: Pentafluorobenzene, 1,4-Difluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of: Dibromofluoromethane, 1,2-Dichloroethane-d4, Toluene-d8 and 4-Bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 (microliter) µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 5 g, spiked, baked sand samples were prepared for the IDC accuracy and precision calculations. Five grams of baked sand was weighed and placed in a 40 mL VOA vial with a stir bar. These replicates of baked sand were then spiked with the 1000 ppm PVOC/GRO Mix (Wisconsin) standard. The methanol extracted samples were then diluted 1:50 in 5 mL of DI water by the Atomx XYZ for a final concentration of 600 ppb. Atomx XYZ conditions for all calibration and IDC samples are shown in Table I. GC-MS conditions are shown in Table II.

When analyzing high-level soil samples, system carryover can be a concern. Carryover from the Atomx XYZ's automated methanol extraction method (Table I) was evaluated with 3 replicates of a 5 g, un-spiked, baked sand sample analyzed directly after the last 600 ppb IDC, spiked, baked sand sample.

Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Methanol Extraction Method Conditions

Standby	Variable	Desorb	Variable
Valve Oven Temp	140 ºC	Methanol Needle Rinse	On
Transfer Line Temp	140 ºC	Methanol Needle Rinse Volume	2.0 mL
Sample Mount Temp	90 ºC	Water Needle Rinse Volume	7.0 mL
Water Heater Temp	90 ºC	Sweep Needle Time	0.25 min
Soil Valve Temp	100 ºC	Desorb Preheat Temp	245 ºC
Standby Flow	10 mL/min	GC Start Signal	Begin Desorb
Purge Ready Temp	40 ºC	Desorb Time	2.00 min
Purge	**Variable**	Drain Flow	300 mL/min
Presweep Time	0.25 min	Desorb Temp	250 ºC
Methanol Volume	10.0 mL	**Bake**	**Variable**
Sparge Vessel Heater	Off	Methanol Glass Rinse	On
Sample Mix Speed	Medium	Methanol Glass Rinse Volume	3.0 mL
Sample Mix Time	2.00 min	Number of Methanol Glass Rinses	1
Sample Mix Settle Time	2.00 min	Number of Water Bake Rinses	1
Sample Sweep Time	0.25 min	Water Bake Rinse Volume	7.0 mL
Sample Sweep Flow	100 mL/min	Bake Rinse Sweep Time	0.25 min
Purge Time	11.00 min	Bake Rinse Sweep Flow	100 mL/min
Purge Flow	40 mL/min	Bake Rinse Drain Time	0.40 min
Purge Temp	20 ºC	Bake Time	2.00 min
MCS Purge Temp	20 ºC	Bake Flow	200 mL/min
Dry Purge Time	1.00 min	Bake Temp	280 ºC
Dry Purge Flow	100 mL/min	MCS Bake Temp	180 ºC
Dry Purge Temp	20 ºC	**Trap**	9
		Chiller Tray	Off
		Purge Gas	Helium

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Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System	
Thermo Scientific TRACE 1310 GC	
Column	TG VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 0.8 mL/min
Oven Profile	35 ºC, 3 min, 12ºC/min to 85 ºC, 25 ºC/min to 225 ºC, 2 min Hold, Run Time 14.767 min
Inlet	200 ºC, 50:1 Split, Purge Flow 0.5 mL/min
ISQ 7000 MS Conditions	
Temp	Transfer Line 230 ºC; Ion Source 280 ºC
Scan	Range 35 *amu* to 260 *amu*, Solvent Delay 0.50 min, Dwell/Scan Time 0.15 sec
Gain	Emission Current 25 µA, Gain 3.00E+005

Results

The relative standard deviation (%RSD) of the response factors (RF) for the calibration curve, and IDC precision and accuracy data are shown in Table III. Table IV displays the system carryover data after a 600 ppb (final concentration), spiked, baked sand sample. Figure 1 displays a methanol extracted, spiked, baked sand sample containing 200 ppb of PVOC/GRO Mix (Wisconsin) (final concentration) standard. Results indicate excellent peak resolution with minimal water interference for all VOCs. Figure 2 displays 1,2,4-trimethylbenzene, methanol extracted from a 5 g, spiked, baked sand sample containing a final concentration of 600 ppb PVOC/GRO Mix (Wisconsin).

Table III PVOC/GRO Mix (Wisconsin) Calibration and Initial Demonstration of Capability (IDC) Data

Compound	Calibration (5-point curve)				Initial Demonstration of Capability (n=7, 600 ppb [µg/L])	
	Retention Time	Quant Ion	Linearity RF (%RSD)	Average RF	Accuracy (≤20%)	Precision (±30%)
Methyl tert-butyl ether	3.47	73	6.2	0.254	6.0	114
Dibromofluoromethane (SURR)	4.89	111	16.4	0.130	6.6	85
Benzene	5.25	78	10.3	0.346	4.4	91
Pentafluorobenzene (IS)	5.37	168				
1,2-dichloroethane-d4 (SURR)	5.40	65	12.9	0.061	4.9	82
1,4-difluorobenzene (IS)	5.88	114				
Toluene-d8 (SURR)	7.24	98	8.4	0.431	3.7	103
Toluene	7.29	91	8.8	0.628	6.1	104
Chlorobenzene-d5 (IS)	8.57	117				
Ethylbenzene	8.62	91	13.3	0.724	6.4	106
m,p-Xylene	8.74	106	13.8	0.304	8.0	103
o-Xylene	9.06	106	10.8	0.162	8.2	109
4-bromofluorobenzene (Surr)	9.48	95	3.1	0.422	2.4	103
1,3,5-trimethylbenzene	9.73	105	9.7	0.383	4.4	117
1,2,4-trimethylbenzene	9.99	105	8.8	0.409	5.3	114
1,4-dichlorobenzene-d4 (IS)	10.26	152				
Naphthalene	11.74	128	13.6	0.537	6.9	105

Table IV PVOC/GRO Mix (Wisconsin) Methanol Extraction Carryover Data	
Compound	**Average Carryover (%)**
Methyl tert-butyl ether	0.002
Benzene	0.01
Toluene	0.08
Ethylbenzene	0.2
m,p-Xylene	0.2
o-Xylene	0.1
1,3,5-trimethylbenzene	0.1
1,2,4-trimethylbenzene	0.2
Naphthalene	0.4

Figure 1 Total Ion Chromatogram of a Methanol Extracted, 5 g, Spiked, Baked Sand Sample Containing a Final Concentration of 200 ppb (µg/L) PVOC/GRO Mix (Wisconsin). Results Display Excellent Peak Separation and Minimal Water Interference for all VOCs: 1. Methyl tert-butyl ether; 2. Dibromofluoromethane (Surr); 3. Benzene; 4. Pentafluorobenzene (IS); 5. 1,2-dichloroethane-d4 (Surr); 6. 1,4-difluorobenzene (Surr); 7. Toluene-d8 (Surr); 8. Toluene; 9. Chlorobenzene-d5; 10. Ethylbenzene; 11. m,p-Xylene; 12. o-Xylene; 13. 4-Bromofluorobenzene (Surr); 14. 1,3,5-trimethylbenzene; 15. 1,2,4-trimethylbenzene; 16. 1,4-dichlorobenzene-d4 (IS); and 17. Naphthalene.

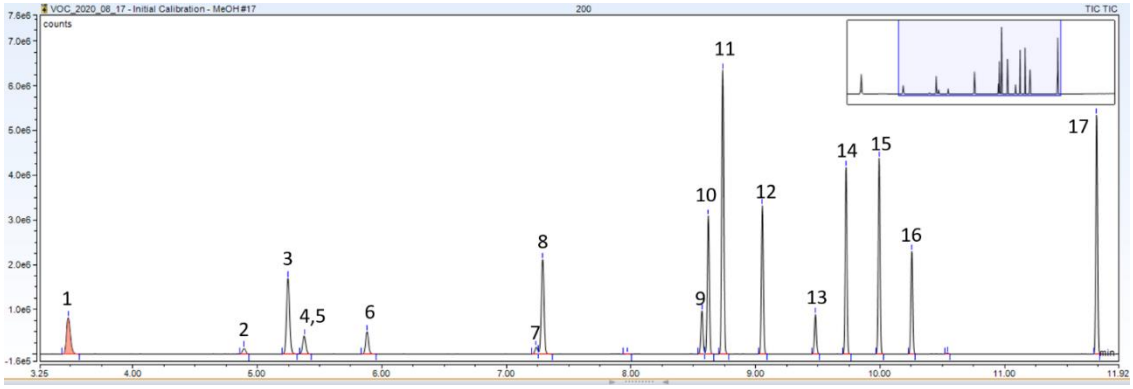
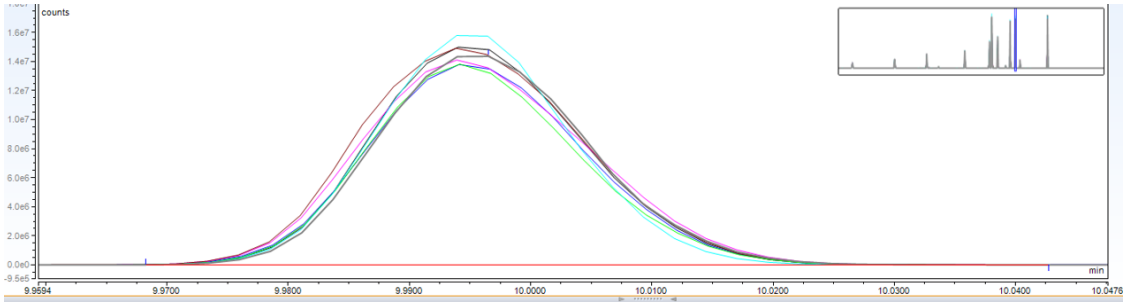


Figure 2 Total Ion Chromatogram of (n=7 replicates) 1,2,4-trimethylbenzene, Methanol Extracted from a 5 g, Spiked, Baked Sand Sample Containing a Final Concentration of 600 ppb (µg/L) PVOC/GRO Mix (Wisconsin). Results Display Excellent Reproducibility with a 5.3% RSD and a 114% Recovery.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in high-level soil and waste samples using automated methanol extraction following US EPA Method 5035, and in accordance with US EPA Method 8260. Detection was performed by a Thermo Scientific TRACE 1310 GC and ISQ 7000 MS system with an ExtractaBrite source. The %RSD of the calibration curve passed all method requirements. The Atomx XYZ's automated methanol extraction function was able to process high-level soil samples with a 91% or better recovery and with less than 8% RSD over 7 replicates. Additionally, the Atomx XYZ demonstrated a system carryover of less than 0.4% average (n=3 replicates) for high-level soil samples spiked with a final concentration of 600 ppb PVOC/GRO Mix (Wisconsin) standard.

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