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Analysis of Volatile Organic Compounds in Water and Soil by EPA Method 8260 with the Atomx Concentrator/Multimatrix Autosampler

Application Note

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Abstract

In order to determine the amount of Volatile Organic Compounds (VOCs) in water and soil matrices the USEPA developed Method 8260 in conjunction with preparative Method 5030 and 5035[1]. Since this method encompasses a wide range of matrices with an extensive range of concentration limits for VOCs, it is necessary to have an analytical system that is sensitive for enough for the lower restrictions and robust enough for the higher concentrations of VOC components. A widely used technique for VOC analysis is Purge and Trap (P&T) concentration in conjunction with Gas Chromatography and Mass Spectrometry (GC/MS) analysis. This paper discusses soil and water analysis using Teledyne Tekmar's Atomx, a combination P&T Concentrator (PTC) and multi-matrix autosampler system,

Introduction

Teledyne Tekmar has consistently been at the cutting edge of P&T technology. In keeping with this tradition, Teledyne Tekmar has developed a new combination P&T concentrator/autosampler. The Atomx offers our proprietary #9 U-shaped trap and utilizes an 80 position autosampler that is capable of sampling multiple matrices. The Atomx, in conjunction with the Agilent 7890A GC and 5975C inert XL MS proved to be excellent tools in the detection of Method 8260 compounds.

In this study, a linear calibration was performed for both the water and the soil matrices for 95 analytes. The range for the water study was 0.5- 200ppb and the soil range was 1.0-200ppb. A 5.0 milliliter (mL) purge volume was used for the water curve, for the soil curve a 5g sample with 10mLs of reagent water was simulated. Conditions and specifications outlined in USEPA Method 8260 were utilized for both matrices.

Experimental-Instrument Conditions

As stated previously, the Atomx, an Agilent 7890A GC and a 5975C inert XL MSD were used for this study. The trap used for this analysis was a #9 adsorbent trap. Tables 1, 2, 3 and 4 display the GC, MSD, and P&T conditions for both the water and soil matrices.

GC Parameters	
GC:	Agilent 7890A
Column:	J&W Scientific DB-VRX 30m x 0.250mm x1.4um
Oven Program:	35°C for 4 min,16°C/min to 85°C for 0 min, 30°C /min to 210°C for 3 min, 14.29 min runtime
Inlet:	220°C
Column Flow	1.02mL/min
Gas:	Helium
Split:	80:1
Pressure:	20.14 psi
Inlet:	Split/Splitless

MSD Parameters	
MSD:	5975C inert XL
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Scan Range:	m/z 35-300
Scans:	5.19 scans/sec
Threshold:	400
MS Transfer Line Temp.:	230°C

Tables 1 & 2 GC and MSD Parameters

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Atomx Water Parameters			
Variable	**Value**	**Variable**	**Value**
Valve Oven Temp	140°C	Dry Purge Flow	100mL/ min
Transfer Line Temp	140°C	Dry Purge Temp	20°C
Sample Mount Temp	90°C	Methanol Needle Rinse	Off
Water Heater Temp	90°C	Methanol Needle Rinse Volume	3.0mL
Sample Vial Temp	20°C	Water Needle Rinse Volume	7.0mL
Sample Equilibrate Time	0.00 min	Sweep Needle Time	0.50 min
Soil Valve Temp	125°C	Desorb Preheat Temp	245°C
Standby Flow	10mL/ min	GC Start Signal	Start of Desorb
Purge Ready Temp	40°C	Desorb Time	2.00 min
Condensate Trap Standby	45°C	Drain Flow	300mL/min
Presweep Time	0.50 min	Desorb Temp	250°C
Prime Sample Fill Volume	3.0mL	Methanol Glass Rinse	Off
Sample Volume	5.0mL	Number of Methanol Glass Rinses	1
Sweep Sample Time	0.25 min	Methanol Glass Rinse Volume	3.0mL
Sweep Sample Flow	100mL/min	Number Of Bake Rinses	1
Sparge Vessel Heater	Off	Water Bake Rinse Volume	7.0mL
Sparge Vessel Temp	20°C	Bake Rinse Sweep Time	0.25 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100mL/min
Prepurge Flow	0mL/min	Bake Rinse Drain Time	0.40 min
Purge Time	11.00 min	Bake Time	4.00 min
Purge Flow	40mL/min	Bake Flow	200mL/min
Purge Temp	20°C	Bake Temp	280°C
Condensate Purge Temp	20°C	Condensate Bake Temp	200°C
Dry Purge Time	1.00 min		

Table 3. Atomx Water Parameters (parameters highlighted in yellow were not used.)

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ATOMX Soil Parameters			
Variable	**Value**	**Variable**	**Value**
Valve Oven Temp	140°C	Purge Time	11.0 min
Transfer Line Temp	140°C	Purge Flow	40mL/min
Sample Mount Temp	90°C	Purge Temp	20°C
Water Heater Temp	90°C	Condensate Purge Temp	20°C
Sample Vial Temp	40°C	Dry Purge Time	1.00 min
Prepurge Time	0.00 min	Dry Purge Flow	100mL/ min
Prepurge Flow	0mL/min	Dry Purge Temp	20°C
Preheat Mix Speed	Off	Methanol Needle Rinse	Off
Sample Preheat Time	2.00 min	Methanol Needle Rinse Volume	3.0mL
Soil Valve Temp	125°C	Water Needle Rinse Volume	7.0mL
Standby Flow	10mL/min	Sweep Needle Time	0.50 min
Purge Ready Temp	40°C	Desorb Preheat Temp	245°C
Condensate Temp Standby	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.50 min	Desorb Time	2.00 min
Water Volume	10mL	Drain Flow	300mL/min
Sweep Water Time	0.25 min	Desorb Temp	250°C
Sweep Water Flow	100mL/min	Bake Time	4.00 min
Sparge Vessel Heater	Off	Bake Flow	200mL/min
Sparge Vessel Temp	20°C	Bake Temp	280°C
Purge Mix Speed	Medium	Condensate Bake Temp	200°C

Table 4. Atomx Soil Parameters (parameters in yellow were not used.)

Calibration

A 50ppm working calibration standard was prepared in methanol. Calibration standards were prepared in a 50mL volumetric flask and filled to volume with de-ionized water. The water calibration range was 0.5-200ppb while the soil calibration range was 1.0-200ppb. The water standards were transferred to headspace free 40mL vials for analysis while the soil standards were transferred to 40mL vials in 5mL aliquots. A 25ppm Internal Standard (IS) was prepared in methanol and transferred to the standard vessel on the Atomx. The Atomx, using the Standards Addition feature, then transferred the IS in 5µl aliquots to the samples in order to hold the IS concentration at a constant 25ppb.

The calibration data was processed using Agilent Chemstation software. The relative response factors of all of the analytes of interest were evaluated for linearity and response. The soil and water calibration curves both met the USEPA Method 8260 performance criteria. The calibration results are listed in Table 5.

Method Detection Limit (MDL) Determination

A statistical determination of the MDL's was determined for each analyte. Seven replicate standards of a low calibration point were analyzed in order to determine the MDL's for each compound. The detection limits for the compounds are listed in Table 5.

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MDL according to 40 CFR 136, Appendix B, Revision 1.11										
	Water					Soil				
Compound	Spike Level	MDL	50ppb CCV (%DEV)	Ave. RF	Calibration %RSD	Spike Level	MDL	50ppb CCV (%DEV)	Ave. RF	Calibration %RSD
pentafluorobenzene (IS)	25					25				
dichlorodifluoromethane	1	0.36	86.66	0.54	10.38	1	0.19	84.01	0.55	9.65
Chloromethane (SPCC)	1	0.3	98.65	0.46	11.19	1	0.23	98.45	0.46	7.48
vinyl chloride	1	0.3	103.2	0.53	7.14	1	0.21	101.89	0.52	6.8
bromomethane	1	0.21	101.43	0.41	12.38	1	0.19	101.73	0.39	12.69
chloroethane	1	0.22	103.6	0.28	4.49	1	0.31	113.91	0.27	7.4
trichlorofluoromethane	1	0.32	122.87	0.99	7.18	1	0.16	127.24	1	10.45
diethyl ether	1	0.2	106.74	0.45	5.75	1	0.19	111.94	0.36	6.01
1,1-dichloroethene	1	0.27	111.24	0.89	5.83	1	0.19	117.24	0.9	6.4
carbon disulfide	1	0.19	100.93	1.31	9.76	1	0.2	111.73	1.49	6.77
1,1,2-trichlorofluoroethane (Freon)	1	0.32	101.1	0.34	5.89	1	0.3	105.13	0.35	8.54
iodomethane	1	0.33	96.76	0.51	11.44	1	0.21	121.75	0.41	10.33
allyl chloride	1	0.14	100.48	0.9	9.32	1	0.45	104.63	0.88	7.41
methylene chloride	1	0.22	108.22	0.74	6.18	1	0.25	109.62	0.71	9.95
acetone	5	0.73	103.43	0.29	7.6	5	2.64	100.87	0.89	0.998
trans-1,2-dichloroethene	1	0.15	106.25	0.86	9.05	1	0.18	114.75	0.87	7.48
methyl acetate	1	0.52	98.25	0.56	9.86	5	0.58	103.81	0.42	10.75
MTBE	1	0.18	111.29	1.87	3.11	1	0.16	115.91	1.48	6.25
TBA	5	1.11	100.02	0.09	8.43	5	0.37	115.64	0.08	5.04
diisopropyl ether	1	0.25	101.13	1.9	8.49	1	0.15	105.97	1.68	9.69
chloroprene	1	0.23	111.03	1.14	8.81	1	0.16	116.42	1.17	9.23
1,1-dichloroethane (SPCC)	1	0.21	110	1.08	7.12	1	0.13	116.14	1.04	6.44
acrylonitrile	1	0.44	100.86	0.23	8.91	1	0.74	108.03	0.16	7.11
vinyl acetate	1	0.17	105.29	1.16	6.32	5	0.18	99.46	1.04	10.29
ETBE	1	0.21	107.08	2.01	6.63	1	0.15	108.11	1.72	6.51
cis-1,2-dichloroethene	1	0.13	109.11	0.86	7.26	1	0.3	117.59	0.81	5.14
2,2-dichloropropane	1	0.16	124.6	0.88	8.31	1	0.18	114.18	1.04	9.55
bromochloromethane	1	0.35	105.84	0.52	7.43	1	0.26	108.89	0.44	8.87
Chloroform	1	0.24	114.62	1.2	8.44	1	0.18	119.19	1.07	11.85
carbon tetrachloride	1	0.32	117.36	0.98	9.32	1	0.16	117.88	0.99	7.57
1,1,1-trichloroethane	1	0.22	114.63	1.13	6.99	1	0.2	117.9	1.11	4.52
THF	5	0.88	95.14	0.2	11.93	5	0.65	98.13	0.17	9.63
dibromofluoromethane (Surrogate)	1	0.21	112.88	0.59	10.58	1	0.29	114.71	0.55	9.55
methyl acrylate	1	0.18	99.86	0.66	7.69	1	0.24	101.85	0.48	11.88
1,1-dichloropropene	1	0.35	103.83	0.81	10.37	1	0.18	107.86	0.86	9.99
2-butanone (MEK)	5	1.54	98.05	0.35	9.38	5	1.07	101.21	0.24	11.88
benzene	1	0.16	107.43	1.99	5.04	1	0.14	107.24	1.96	6.56
propionitrile	1	0.24	102.78	0.86	4.75	1	0.38	111.42	0.64	10.28
tert amyl methyl ether (TAME)	1	0.16	104.5	1.75	4.8	1	0.13	104.34	1.47	7.48
1,2-dichloroethane	1	0.21	114.23	1.25	7.88	1	0.16	118.07	1.01	10.17
isobutyl alcohol	1	0.25	107.04	0.71	6.1	1	0.23	106.81	0.6	11.8
isopropyl acetate	1	0.29	101.88	1.31	7.83	1	0.33	101.2	1	8.62
trichloroethene	1	0.26	107.25	0.66	8.72	1	0.18	114.5	0.64	8.73
1,4-difluorobenzene (IS)	25					25				
dibromomethane	1	0.18	107.6	0.23	3.74	1	0.26	108.33	0.19	4.37
1,2-dichloropropane	1	0.33	96.51	0.31	9.94	1	0.25	99.45	0.28	10.45
bromodichloromethane	1	0.18	107.25	0.55	8.82	1	0.14	106.67	0.51	7.17

Table 5. Experimental Results

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MDL according to 40 CFR 136, Appendix B, Revision 1.11										
	Water					Soil				
Compound	Spike Level	MDL	50ppb CCV (%DEV)	Ave. RF	Calibration %RSD	Spike Level	MDL	50ppb CCV (%DEV)	Ave. RF	Calibration %RSD
methyl methacrylate	1	0.16	97.64	0.43	6.16	1	0.36	94.67	0.34	8.84
n-propyl acetate	1	0.19	93.08	0.54	9.57	1	0.27	96.89	0.41	9.96
2-cleve	1	0.17	96.57	0.23	5.94	1	0.45	98.92	0.17	11.45
cis-1,3-dichloropropene	1	0.18	98.56	0.53	5.65	1	0.15	96.86	0.49	9.9
toluene-d8 (Surrogate)	1	0.16	99.49	1.03	4.29	1	0.16	99.92	1.04	8.18
Toluene	1	0.19	100.96	1.21	5.6	1	0.15	101.81	1.2	6.15
2-nitropropane	1	0.37	94.05	0.18	9.22	1	0.54	92.43	0.14	9.36
tetrachloroethene	1	0.23	93.24	0.45	11.7	1	0.23	101.85	0.36	10.1
4-methyl2-pentanone	1	0.44	96.41	0.05	9.99	5	0.91	97.93	0.04	9.81
1,1,2-trichloroethane	1	0.3	98.1	0.29	7.24	1	0.18	101.2	0.23	11.03
ethyl methacrylate	1	0.17	94.82	0.26	7.95	1	0.38	98.32	0.19	6.15
dibromochloromethane	1	0.19	100.55	0.4	9.74	1	0.36	100.4	0.33	9.15
1,3-dichloropropane	1	0.14	101.33	0.52	5.47	1	0.16	101.97	0.42	7.32
1,2-dibromoethane	1	0.16	98.83	0.34	7.94	1	0.18	106.65	0.24	9.8
n-butyl acetate	1	0.19	97.23	0.56	9.14	1	0.2	94.61	0.44	7.98
2-hexanone	1	0.18	96.52	0.26	3.32	1	0.28	99.3	0.21	7.36
chlorobenzene-d5 (IS)	25.00					25.00				
Chlorobenzene (SPCC)	1	0.19	98.71	0.87	6.07	1	0.14	99.8	0.93	10.75
Ethylbenzene	1	0.14	98.34	1.66	6.18	1	0.12	100.77	1.79	9.71
1,1,1,2-tetrachloroethane	1	0.17	98.76	0.38	9.76	1	0.14	100.64	0.37	8.28
m&p xylene	2	0.21	101.37	1.34	10.21	2	0.17	103.42	1.44	8.86
ortho xylene	1	0.18	98.18	1.42	9	1	0.17	104.16	1.43	7.28
styrene	1	0.16	97.06	0.95	10.36	1	0.14	103.8	0.93	6.01
Bromoform (SPCC)	1	0.16	95.7	0.27	6.38	1	0.29	99.54	0.21	7.41
isopropylbenzene	1	0.19	98.16	1.57	8.62	1	0.12	102.07	1.69	8.35
n-amyl acetate	1	0.26	100.28	0.55	11.68	1	0.18	96.53	0.46	11.37
BFB (Surrogate)	1	0.27	99.95	0.54	10.25	1	0.3	101.68	0.55	11.49
n-propylbenzene	1	0.16	101.49	1.86	8.44	1	0.18	103.47	2.09	8.85
trans-1,4-dichloro-2-butene	1	0.17	102.49	0.19	9.66	1	0.26	92.26	0.16	10.29
nitrobenzene	5	1.37	87.27	0.04	11.94	5	1.12	83.51	0.04	11.53
bromobenzene	1	0.18	98.58	0.72	9.18	1	0.13	101.26	0.7	10.88
1,1,2,2-tetrachloroethane (SPCC)	1	0.16	96.05	0.42	9.13	1	0.19	101.21	0.33	6.69
1,3,5-trimethylbenzene	1	0.21	98.71	1.36	8.58	1	0.19	103.5	1.42	7.75
2-chlorotoluene	1	0.15	98.75	1.23	9.02	1	0.18	103.83	1.25	8.32
cis-1,4-dichloro-2-butene	1	0.35	99.02	0.17	9.11	1	0.2	88.38	0.14	7.43
4-chlorotoluene	1	0.16	99.13	1.27	7.67	1	0.26	101.87	1.33	10.67
tertbutylbenzene	1	0.12	97.94	1.09	10.04	1	0.13	106.02	1.14	5.88
1,2,4-trimethylbenzene	1	0.15	100.9	1.35	6.89	1	0.19	102.27	1.42	8.7
sec-butylbenzene	1	0.15	102.63	1.59	5.54	1	0.12	103.64	1.82	8.26
p-isopropyltoluene	1	0.11	98.2	1.38	9.39	1	0.13	100.75	1.52	10.57
1,3-dichlorobenzene	1	0.19	96.42	0.65	10.93	1	0.18	98.31	0.66	10.36
1,4-dichlorobenzene-d4 (IS)	25.00					25.00				
1,4-dichlorobenzene	1	0.19	97.88	0.65	9.01	1	0.16	98.5	0.66	9.56
n-butylbenzene	1	0.19	104.01	1.36	5.38	1	0.18	103.65	1.59	7.92
1,2-dichlorobenzene	1	0.16	96.8	0.64	11.49	1	0.22	100.85	0.6	7.6
1,2-dibromo-3-chloropropane	1	0.54	90.84	0.09	7.62	5	0.27	91.04	0.08	6.52
hexachlorobutadiene	1	0.26	96.73	0.17	7.6	1	0.34	89.65	0.21	8.31
1,2,4-trichlorobenzene	1	0.15	92.15	0.43	8.49	1	0.19	91.42	0.4	9.43
naphthalene	1	0.17	98.38	1.44	3.76	1	0.19	99.64	1.13	8.84
1,2,3-trichlorobenzene	1	0.19	94.75	0.42	6.26	1	0.17	93.08	0.38	10.34

Table 5. Experimental Results (continued)

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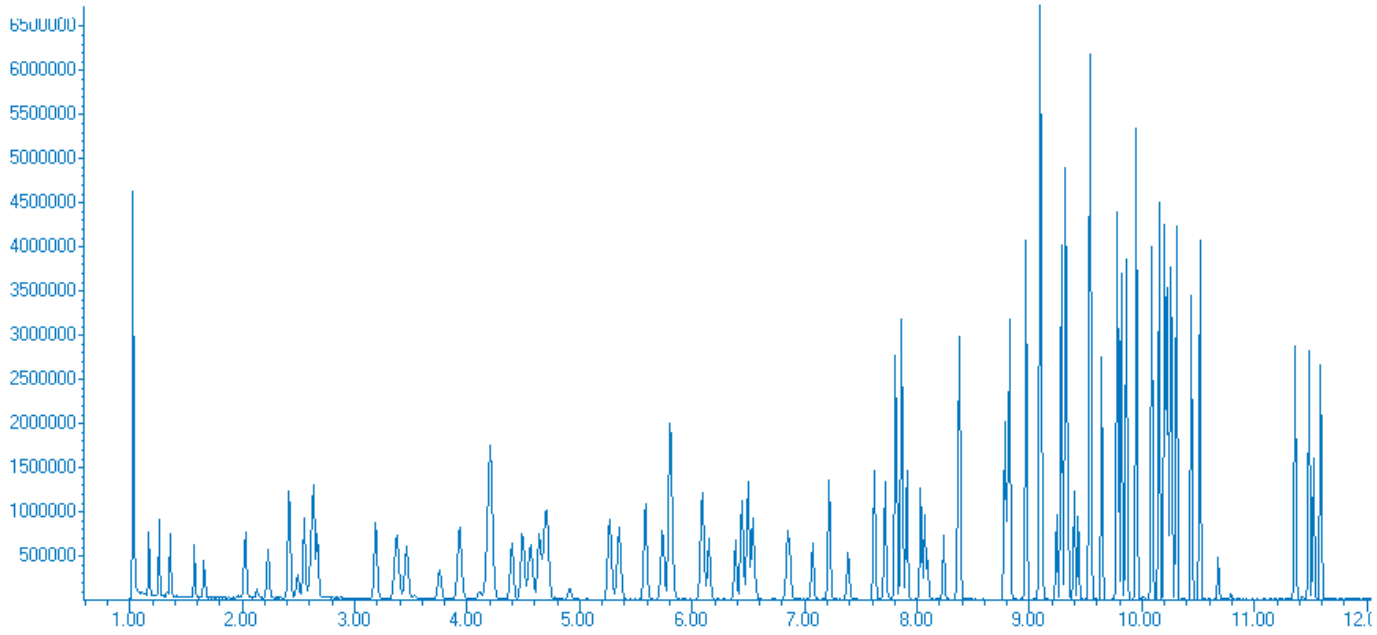

Figure 1. 50ppb Water Chromatogram

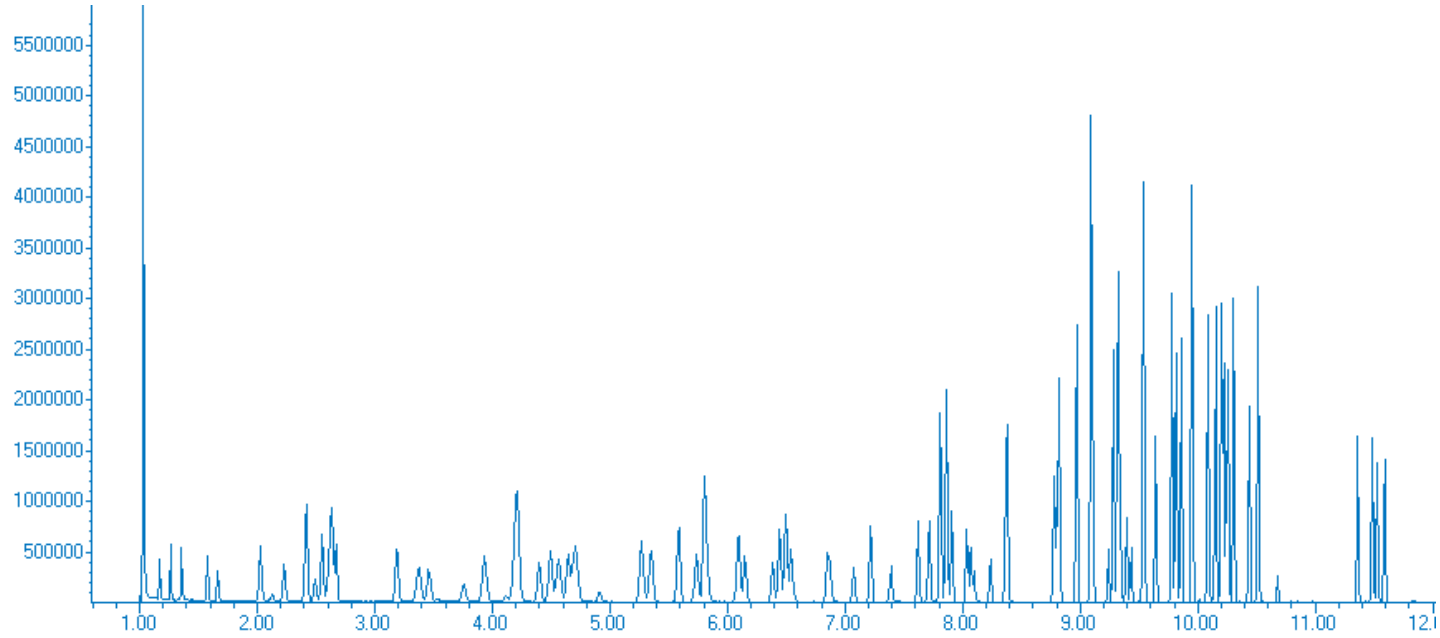

Figure 2. 50ppb Soil Chromatogram

Conclusions

Teledyne Tekmar's new Atomx offers the best of both worlds, combining a multi-matrix autosampler and a PTC into one system in order to streamline communication between the autosampler and the PTC. This combination also simplifies the electronics and enables easier installation. The concentrator is equipped with Tekmar's innovative #9 proprietary U–shaped trap. This trap is excellent in the removal of water that is so crucial in P&T analysis. The system contains a

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Siltek™ coated sample pathway which is important in the reduction of carryover. Linearity was demonstrated for both a water curve from 0.5- 200ppb and for a soil curve from 1.0- 200ppb. The autosampler offers 80 sample vial positions with a carrousel drive mechanism to enhance system reliability. The system also has three standard vessels capable of delivering variable volumes independently offering greater spiking versatility. Finally, the autosampler offers several rinse options for carryover reduction these options include hot water bake rinses, needle rinses, and a methanol rinse option (patent pending) that reduces carryover to some of the lowest levels on the market, these options are investigated further in another application note. Teledyne Tekmar has once again displayed excellence in the development of a PTC and multi-matrix autosampler system.

References

1. USEPA Method 8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, December 1996.

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