USEPA Method 8260C using the Tekmar Atomx Automated VOC Sample Prep System and a Thermo Focus/DSQ™ II GCMS

Application Note

By Roger Bardsley

Abstract

The United States Environmental Protection Agency (USEPA) developed Method 8260 to determine the concentration of Volatile Organic Compounds (VOCs) in water and soil matrices. USEPA Methods 5030 and 5035[1] are used to prepare water, soil and waste samples for analysis by USEPA Method 8260. USEPA Method 8260 was recently updated from 8260B to 8260C[2]. In this study water and soil sample analysis will be performed using USEPA Method 8260C[3] guidelines.

A calibration curve and Method Detection Limits (MDLs) for a target compound list will be performed on the Atomx, an Automated VOC Sample Prep System in conjunction with a Thermo Focus/DSQ II Gas Chromatography-Mass Spectrometry (GC/MS). A 5mL purge volume will be utilized for the water study, while an in-vial purge will be utilized for the soil samples. All conditions outlined in Method 8260C will be followed.

Image 1: Atomx, Automated VOC Sample Prep System

Introduction

Teledyne Tekmar developed the Atomx, an Automated VOC Sample Prep System that integrates both a purge and trap concentrator with an 80-postion autosampler to allow for sampling of multiple matrices such as water, soil and methanol extraction with a single instrument. This “all-in-one” instrument allows for increased throughput and efficiency through the features that it provides.

The Atomx utilizes the #9 U-shape trap and three standard addition vessels. The Atomx, in conjunction with a Thermo Focus GC with the optional Purge and Trap adapter inlet and a Thermo DSQ II MS is an exceptional instrument to meet the new requirements for the detection of the target analytes by USEPA Method 8260C.

In this study, a calibration curve and MDLs were preformed for both water and soil matrices. The water samples employed a calibration curve from 0.5ppb to 200ppb, while the soil samples used a calibration curve from 1.0ppb to 200ppb. A 5mL purge volume was used for the water samples, and the soil samples utilized 5g of sample with 10mL of reagent water added by the Atomx. The conditions that are outlined in USEPA Method 8260C were followed for both water and soil matrices.

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Experimental-Instrument Conditions

The instrument conditions for both the waters and soils application developments and results are listed in Tables 1 through 4.

GC Parameters	
GC	Thermo Scientific Focus GC
Column	Restek Rtx®-VMS 20m x 0.18mmID x 1um
Oven Program	40°C for 4 min; 16°C/min to 100°C for 0 min; 25°C /min to 200°C for 3 min, 14.75 min runtime
Inlet	220°C
Column Flow	1.0mL/min
Gas	Helium
Split	50mL/min
Inlet	Thermo optional Purge and Trap adapter

MS Parameters	
MSD	Thermo DSQ II
Source	230°C
MS Transfer Line Temp	230°C
Solvent Delay	0.5 min
Scan Range	35.0 m/z to 270 m/z
Scans	5.5586 scans/sec
Chrom Filter	2.5 Sec

Tables 1 and 2: Thermo Scientific GC and MS Parameters

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	0.25min
Soil Valve Temp	100°C	Desorb Preheat Time	245°C
Standby Flow	10mL/min	GC Start Signal	Start of Desorb
Purge Ready Temp	40°C	Desorb Time	2.00 min
Condensate Ready Temp	45°C	Drain Flow	300mL/min
Presweep Time	0.25 min	Desorb Temp	250°C
Prime Sample Fill Volume	3.0mL	Methanol Glass Rinse	On
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	2.00 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	0.50 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	150°C	Purge Time	11.00 min
Transfer Line Temp	150°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	2.00 min
Prepurge Time	0.00 min	Dry Purge Flow	100mL/min
Prepurge Flow	0mL/min	Dry Purge Temp	20°C
Preheat Mix Speed	Slow	Methanol Needle Rinse	Off
Sample Preheat Time	2.00 min	Methanol Needle Rinse Volume	3.0mL
Soil Valve Temp	120°C	Water Needle Rinse Volume	10.0mL
Standby Flow	20mL/min	Sweep Needle Time	0.50 min
Purge Ready Temp	40°C	Desorb Preheat Time	245°C
Condensate Ready Temp	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.25 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	2.00 min
Sparge Vessel Heater	Off	Bake Flow	400mL/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 highlighted in yellow were not used.)

Calibration and Sample Preparation

A stock standard solution was prepared at 50ppm (µg/mL) utilizing 6 Restek Stock standards to provide 94 compounds related to USEPA method 8260C and other state environmental methods. The Restek standards include those listed in Table 5. The amounts listed in Table 5 were transferred to a 10mL volumetric flask containing P&T methanol. The flask was diluted to volume with P&T methanol.

Cat#	Name	Concentration	Amount	Vol.	Final Conc.
30633	8260B MegaMix®	2000µg/mL	250µL	10mL	50ppm
30489	8260B Acetate Mix	2000µg/mL	250µL	10mL	50ppm
30465	California Oxygenates Mix	2000 – 10,000µg/mL	250µL	10mL	50ppm
30042	502.2 Calibration Mix (Gases)	2000µg/mL	250µL	10mL	50ppm
30265	2-Chloroethyl Vinyl Ether	2000µg/mL	250µL	10mL	50ppm
30006	VOA Calibration Mix (Ketones)	5000µg/mL	100µL	10mL	50ppm

Table 5: Stock Standard Solution Preparation

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Working standards were prepared ranging from 0.5ppb to 200ppb for the water analysis and 1ppb to 200ppb for the soil analysis by diluting the stock standard to a final volume in reagent water. This method of standard preparation creates varying amounts of methanol in the samples to ensure that the higher methanol concentration does not interfere with the mass spectrometer.

A 0.5ppb solution for the water analysis and a 1.0ppb solution for the soil analysis were used to calculate the minimum detectable limits of the compounds.

A 125ppm Internal Standard (IS) and Surrogate Standard (SS) solution was prepared by diluting 500µL of both the Restek 8260 Internal Standard Mix and 8260 Surrogate Mix to 10mL with P&T methanol. This was placed in the standard vessel on the Atomx. 2µL of the IS/SS solution was automatically added to each sample by the Atomx system.

Minimum Detection Limits

The water analysis standard curve and MDL samples were prepared by filling a standard 40mL VOA vial with the appropriate standard. Seven samples at 0.5ppb were used for the calculation of the MDL for the water assay.

The soil analysis standard curve and MDL samples were prepared by transfer 5mL of the appropriate standard of sample to a 40mL VOA vial, Teflon stir bar added and the vial capped. Seven samples at 1.0ppb were used for the MDL calculation.

The samples were placed on the Atomx automated VOC instrument which purged either 5mL of the water sample in the standard purge and trap vessel or added 10mL of water to each soil sample along with IS/SS solution to perform an in vial purge and trap of the soil samples. The trapped VOC's were rapidly desorbed from the trap and transferred to the Focus/DSQ II GC/MS for analysis.

Results and Discussion

Thermo Scientific EnviroLab Forms™ 3.0 GC/MS analysis and reporting software was used to process the calibration standards and MDL sample data. The relative response factors (RF) of all target analytes were evaluated for average RF and calibration %RSD. The minimum detection limit was calculated for the water and the soil samples. These results are presented in Table 6.

Example chromatograms of a 50ppb water standard and a 50ppb soil standard are presented in Figures 1 and 2.

	Water				Soil			
Compound	Spike Level	MDL	Avg. RF	Calibration %RSD	Spike Level	MDL	Avg. RF	Calibration %RSD
Dichlorodifluoromethane	0.5	0.169	0.633	9.49	1	0.329	0.436	11.24
Chloromethane	0.5	0.107	2.348	7.60	1	0.121	1.975	9.24
Vinyl Chloride	0.5	0.061	0.750	5.57	1	0.142	0.684	9.44
Bromomethane	0.5	0.110	0.334	8.89	1	0.395	0.293	7.97
Chloroethane	0.5	0.228	0.236	5.86	1	0.187	0.205	11.87
Trichloromonofluoromethane	0.5	0.150	0.432	11.57	1	0.086	0.414	9.14
Diethyl Ether	0.5	0.112	0.284	8.11	1	0.196	0.278	3.68
1,1-Dichloroethene	0.5	0.125	0.311	4.26	1	0.169	0.288	7.05
Carbon disulfide	0.5	0..296	1.251	7.98	1	0.120	1.389	16.63
1,1,2-Trichlorotrifluoroethane	0.5	0.149	0.169	8.19	1	0.104	0.170	10.13
Iodomethane*	0.5	0.054	0.410	13.58	1	0.035		0.9997
Allyl chloride	0.5	0.102	0.264	6.77	1	0.321	0.240	4.86
Methylene Chloride	0.5	0.107	0.299	6.21	1	0.181	0.298	7.00
Acetone*	0.5			0.9987	1			0.9994

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	Water				Soil			
Compound	Spike Level	MDL	Avg. RF	Calibration %RSD	Spike Level	MDL	Avg. RF	Calibration %RSD
trans-1,2-Dichloroethene	0.5	0.070	0.352	7.82	1	0.186	0.347	7.15
Methyl Acetate	0.5	0.450	0.831	5.23	1	0.154	0.570	1.77
Methyl-tert-butyl Ether (MTBE)	0.5	0.65	1.298	7.03	1	0.136	1.244	3.59
tert-Butyl Alcohol (TBA)	2.5	0.441	0.060	11.50	5	1.237	0.049	7.84
Acetonitrile	0.5	0.222	0.685	5.98	1	0.132	0.654	5.32
Diisopropyl Ether (DIPE)	0.5	0.0435	4.083	5.16	1	0.096	3.925	4.45
Chloroprene	0.5	0.099	0.794	4.61	1	0.156	0.671	7.55
1,1-Dichloroethane	0.5	0.074	1.297	4.37	1	0.114	1.154	6.10
Acrylonitrile	0.5	0.124	0.264	5.97	1	0.150	0.168	2.84
Ethyl-tert-butyl Ether (ETBE)	0.5	0.047	2.165	4.7	1	0.124	2.036	4.84
Vinyl Acetate	0.5	0.051	3.434	5.94	1	0.195	2.508	16.29
cis-1,2-Dichloroethene	0.5	0.125	0.752	3.16	1	0.130	0.696	4.73
2,2-Dichloropropane	0.5	0.081	1.093	3.35	1	0.195	0.855	6.41
Bromochloromethane	0.5	0.051	0.419	5.58	1	0.145	0.359	8.02
Chloroform	0.5	0.085	1.044	4.31	1	0.105	0.934	4.71
Carbon Tetrachloride	0.5	0.093	0.799	6.25	1	0.161	0.636	6.52
1,1,1-Trichloroethane	0.5	0.076	0.894	4.06	1	0.109	0.744	7.05
Dibromofluoromethane (Surrogate)	25	2.264	0.605	4.27	25	1.683	0.624	2.19
Methyl Acrylate	0.5	0.098	0.672	6.84	1	0.168	0.509	11.74
Tetrahydrofuran	0.5	0.099	0.139	6.51	1	0.207	0.100	4.52
Ethyl Acetate	0.5	0.356	0.036	6.82	1	1.312	0.027	7.47
1,1-Dichloropropene	0.5	0.143	1.029	4.29	1	0.103	0.857	8.47
2-Butanone (MEK)	0.5	0.097	0.149	8.52	1	0.449	0.108	16.21
Benzene	0.5	0.089	3.516	3.65	1	0.124	3.085	5.79
Methacrylonitrile	0.5	0.132	1.026	7.00	1	0.199	0.727	2.69
Pentafluorobenzene (IS)	25			2.48	25			3.43
tert-Amyl Methyl Ether (TAME)	0.5	0.078	2.540	4.40	1	0.137	2.281	4.09
1,2-Dichloroethane	0.5	0.075	0.888	3.63	1	0.123	0.770	4.89
Isopropyl Acetate	0.5	0.057	0.185	6.76	1	0.192	0.148	2.76
Trichloroethylene	0.5	0.112	0.690	5.04	1	0.159	0.587	7.84
Dibromomethane	0.5	0.049	0.468	5.91	1	0.127	0.365	6.91
1,2-Dichloropropane	0.5	0.078	0.747	4.60	1	0.131	0.683	3.41
Bromodichloromethane	0.5	0.075	0.767	2.99	1	0.129	0.699	3.72
Methyl Methacrylate	0.5	0.085	0.680	4.86	1	0.157	0.523	4.44
n-Propyl acetate	0.5	0.128	2.491	6.23	1	0.133	1.968	6.97
2-Chloroethyl Vinyl Ether	0.5	0.100	0.297	7.37	1	0.102	0.208	7.77
cis-1,3-Dichloropropene	0.5	0.055	0.728	5.75	1	0.140	0.596	6.17
Toluene-d8 (Surrogate)	25	2.049	1.312	2.63	25	1.958	1.321	2.25
Toluene	0.5	0.079	0.964	3.10	1	0.113	0.801	8.18
2-Nitropropane*	0.5	1.137		0.9970	1	2.652		0.9972
Tetrachloroethylene	0.5	0.140	0.323	9.35	1	0.347	0.201	8.41
4-Methyl-2pentanone	0.5	0.172	0.139	8.12	1	0.204	0.106	5.30
trans-1,3-Dichloropropene	0.5	0.095	0.650	6.26	1	0.117	0.515	5.29
1,1,2-Trichloroethane	0.5	0.054	0274	5.40	1	0.131	0.214	5.20
Ethyl Methacrylate	0.5	0.068	0.666	7.35	1	0.108	0.514	5.20
Dibromochloromethane	0.5	0.031	0.443	8.39	1	0.126	0.362	7.43
1,3-Dichloropropane	0.5	0.066	0.748	5.22	1	0.125	0.592	4.63
1,2-Dibromoethane (EDB)	0.5	0.047	0.413	5.67	1	0.114	0.303	6.86

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Compound	Spike Level	MDL	Avg. RF	Calibration %RSD	Spike Level	MDL	Avg. RF	Calibration %RSD
Butyl Acetate	0.5	0.078	1.485	9.58	1	0.093	1.104	6.63
2-Hexanone	0.5	0.065	0.727	9.94	1	0.339	0.524	9.56
Chlorobenzene-d5 (IS)	25			5.50	25			1.91
Chlorobenzene	0.5	0.069	1.131	4.04	1	0.142	0.927	5.53
Ethylbenzene	0.5	0.071	1.594	3.45	1	0.179	1.296	6.99
1,1,1,2-Tetrachloroethane	0.5	0.064	0.400	4.13	1	0.088	0.341	5.42
m-,p-Xylene	1	0.121	0.748	3.73	2	0.331	0.582	8.04
o-Xylene	0.5	0.062	0.759	3.94	1	0.119	0.599	5.40
Bromoform	0.5	0.101	0.205	7.88	1	0.150	0.156	6.56
Styrene	0.5	0.062	1.139	5.79	1	0.172	0.936	6.06
Isopropylbenzene (Cumene)	0.5	0.073	1.679	3.92	1	0.206	1.288	7.69
n-Amyl Acetate	0.5	0.084	1.535	10.28	1	0.116	1.146	5.56
Bromofluorobenzene (Surrogate)	25	1.550	0.487	3.11	25	1.889	0.483	2.10
Bromobenzene	0.5	0.112	1.010	6.86	1	0.206	0.844	6.73
cis-1,4-Dichloro-2-butene	0.5	0.150	0.371	5.34	1	0.403	0.595	6.57
n-Propylbenzene	0.5	0.093	5.319	7.94	1	0.233	4.092	8.77
1,1,2,2-Tetrachloroethane	0.5	0.067	1.344	5.13	1	0.188	1.022	7.24
2-Chlorotoluene	0.5	0.079	3.484	4.29	1	0.196	2.669	6.57
1,2,3-Trichloropropane	0.5	0.116	1.552	5.35	1	0.237	1.098	5.52
1,3,5-Trimethylbenzene	0.5	0.101	4.779	4.96	1	0.206	3.546	7.02
trans-1,4-dichloro-2-Butene	0.5	0.148	0.358	12.26	1	0.376	0.234	10.06
4-Chlorotoluene	0.5	0.134	3.547	6.25	1	0.226	2.732	6.80
tert-Butylbenzene	0.5	0.095	4.404	4.64	1	0.189	3.613	6.21
Pentachloroethane	0.5	0.287	0.292	24.61	1	0.583	0.400	10.10
1,2,4-Trimethylbenzene	0.5	0.090	4.794	5.52	1	0.178	3.504	6.63
sec-Butylbenzene	0.5	0.092	5.315	7.28	1	0.225	4.065	8.20
p-Isopropyltoluene (p-Cymene)	0.5	0.094	4.563	8.75	1	0.187	3.311	7.67
1,3-Dichlorobenzene	0.5	0.131	1.733	5.68	1	0.234	1.307	7.78
1,4-Dichlorobenzene-d4 (IS)	25			7.78	25			7.96
1,4-Dichlorobenzene	0.5	0.161	1.749	5.97	1	0.248	1.308	9.83
n-Butylbenzene	0.5	0.157	3.252	11.20	1	0.234	2.390	9.63
1,2-Dichlorobenzene	0.5	0.074	1.697	5.10	1	0.176	1.269	4.49
1,2-Dibromo-3-chloropropane	0.5	0.116	0.410	5.24	1	0.232	0.257	3.70
Hexachlorobutadiene	0.5	0.166	0.412	4.66	1	0.384	0.304	11.82
1,2,4-Trichlorobenzene	0.5	0.153	1.128	11.38	1	0.297	0.686	9.51
Naphthalene	0.5	0.081	5.418	9.62	1	0.334	3.621	4.61
1,2,3-Trichlorobenzene	0.5	0.094	1.143	11.00	1	0.341	0.730	6.15

Table 6: Minimum Detection Limit, Method Minimum Response Factor, Method Response Factor, and Calibration %RSD for the Water and Soil Analysis

* The %RSD value was greater than the 20% allowed by the method. The alternate linear regression curve passed the method requirement of greater than 0.99.

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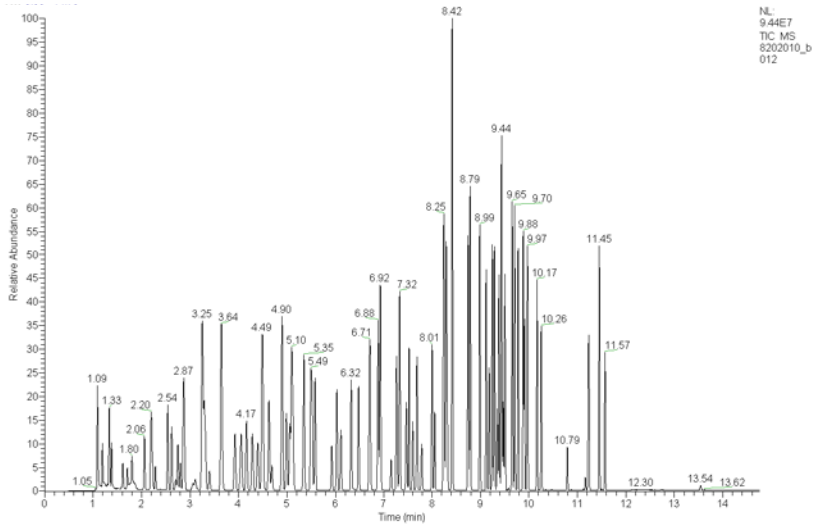

Figure 1: 50ppb Water Chromatogram

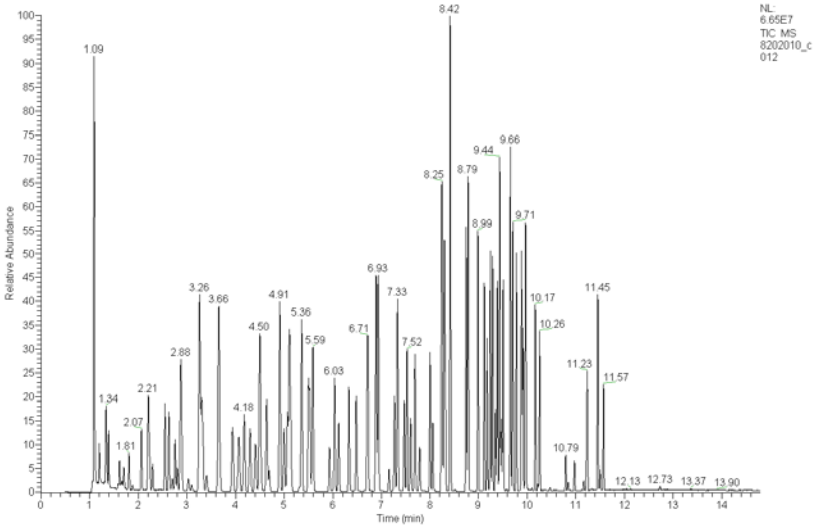

Figure 2: 50ppb Soil Chromatogram

Conclusions

The Atomx, purge and trap concentrator with a multi-matrix autosampler in conjunction with Thermo Scientific Focus/DSQ II GC/MS was shown to be an excellent system for detection for the analytes by USEPA Method 8260C. In this study all analytes have met and pass the requirements set forth by this method.

References

1. USEPA Method 5030 Purge-And-Trap For Aqueous Samples Revision 3, May 2003
2. USEPA Method 5035 Closed-System Purge-And Trap and Extractions For Volatile Organics In Soil and Waste Samples Revision 1, July 2002
3. USEPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3, August 2006

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