A Comparison of Volatile Organic Compound Response When Using Nitrogen as a Purge Gas

Abstract

For many years Helium has been the gas of choice for purging Volatile Organic Compounds (VOCs). However, in the past few years, the price and demand for helium gas has increased substantially, thus making the use of Helium for the purge gas in Purge and Trap (P&T) very expensive. The expense of Helium has provoked interest in finding a viable alternative purge gas. This application note investigates VOC compound responses when purged using Helium and Nitrogen in order to validate Nitrogen as a possible alternative to Helium for P&T applications.

Introduction

Teledyne Tekmar developed a combination P&T Concentrator/ Vial Autosampler, the Atomx. The Atomx was developed to fully automate water, soil, and methanol extraction in accordance with the USEPA methods for volatile analyses. One of the beneficial features of the Atomx highlighted in this study is the use of an electronic mass flow controller that is calibrated for either Nitrogen or Helium. The controller is employed for both fritted glass sparging used for aqueous samples and in vial sparging used in soil applications. Since the mass flow controller is electronic, flow rates can be programmed via the software interface for various modes of operation. This patent pending ability allows for the end user to simplify the potential switch by simply changing the configuration rather than manually adjusting pressures and flows as seen in traditional regulator/needle flow controller systems.

In this study, data was collected to evaluate compound response when using Nitrogen as a purge gas as opposed to the traditional Helium purge gas. Furthermore, as water samples are purged in the sparge vessel and soils are purged in the sample vial, an additional comparison was done to see if the analytes responded differently when purged in the vial with Nitrogen in contrast to a Helium purge.

Experimental-Instrument Conditions

The Atomx, an Agilent 7890A GC and a 5975C inert XL MSD were used for this analysis. The Atomx was equipped with a #9 adsorbent trap. Tables 1 and 2 display the GC, MSD conditions while Tables 3 and 4 display the P&T Concentrator/Autosampler conditions for water and soil matrices respectively.

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	1.2mL/min
Gas:	Helium
Split:	80:1
Pressure:	9.3psi
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:	4.51 scans/sec
Threshold:	400
MS Transfer Line Temp:	230°C

Tables 1 & 2: GC and MSD Parameters

Calibration

A 50ppb working calibration stock standard was prepared in methanol. Calibration standards were prepared in a 50mL volumetric flask and filled to volume with de-ionized water. 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. 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 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.

The calibration data was analyzed using Agilent Chemstation software. The average compound response for the water and soil matrices with the Helium and Nitrogen purge gases is outlined in Table 5. The relative response factors of all of the analytes of interest were evaluated for linearity and response and the average %RSD of the respective curves are summarized in Table 6.

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	0.25 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	4.00 min
Purge Flow	40mL/min	Bake Flow	250mL/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.)

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	On
Sample Preheat Time	0.00 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	0.25 min
Purge Ready Temp	40°C	Desorb Preheat Temp	245°C
Condensate Temp Standby	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.25 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	4.00 min
Sparge Vessel Heater	Off	Bake Flow	250mL/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.)

Method Detection Limit (MDL)

A statistical determination of the MDL's was determined for all of the compounds by analyzing seven replicate standards of a low calibration standard. The average detection limits are provided in Table 6.

Compound	Water		Soil	
	Ave. Response N2 Purge	Ave. Response He Purge	Ave. Response N2 Purge	Ave. Response He Purge
Pentafluorobenzene (IS)	N/A	N/A	N/A	N/A
Dichlorodifluoromethane	0.337	0.517	0.807	0.507
Chloromethane	0.551	0.655	0.993	0.692
Vinyl Chloride	0.675	0.620	1.194	0.763
Bromomethane	0.379	0.393	0.717	0.660
Chloroethane (Ethyl Chloride)	0.461	0.415	0.693	0.501
Trichlorofluoromethane	0.962	0.735	1.526	1.035
Diethyl Ether	0.604	0.484	0.783	0.540
1,1-Dichloroethene	0.839	0.686	1.416	0.528
Carbon Disulfide	1.069	1.417	2.423	1.111
1,1,2-Trichlorofluoroethane (Freon)	0.283	0.349	0.805	0.366
Iodomethane	0.469	0.475	0.801	0.462
Allyl Chloride	0.713	0.615	0.859	0.441
Methylene Chloride	0.694	0.614	1.067	0.377
Acetone	0.263	0.203	0.252	0.194
trans-1,2-Dichloroethene	0.675	0.712	0.874	0.768
Methyl Acetate	0.493	0.494	0.336	0.187
MTBE	1.507	1.827	2.721	1.780
TBA	0.088	0.078	0.098	0.046
Diisopropyl Ether	1.394	1.668	1.711	1.565
Chloroprene	0.671	0.851	0.945	0.878
1,1-Dichloroethane	0.874	0.953	1.996	1.119
Acrylonitrile	0.308	0.263	0.299	0.104
Vinyl acetate	0.855	0.636	1.146	1.025
ETBE	1.462	1.776	1.520	1.596
cis-1,2-Dichloroethene	0.617	0.704	1.390	0.855
2,2-Dichloropropane	0.682	0.485	0.928	0.915
Bromochloromethane	0.397	0.392	0.476	0.422
Chloroform	0.915	1.005	1.094	0.974
Carbon Tetrachloride	0.571	0.727	0.710	0.715
1,1,1-Trichloroethane	0.726	0.892	0.880	0.844
THF	0.143	0.169	0.105	0.125
Dibromofluoromethane (Surrogate)	0.464	0.502	0.502	0.510
Methyl Acrylate	0.511	0.576	0.438	0.466
1,1-Dichloropropene	0.614	0.706	0.740	0.807
2-Butanone (MEK)	0.209	0.217	0.208	0.158
Benzene	1.977	2.214	2.316	2.243
Propionitrile	0.591	0.637	0.612	0.567
tert Amyl Methyl Ether (TAME)	1.449	1.787	1.216	1.524
1,2-Dichloroethane	0.729	0.815	0.777	0.728
Isobutyl Alcohol	0.451	0.193	0.458	0.148
Isopropyl Acetate	0.931	1.134	0.813	0.873
Trichloroethene	0.482	0.617	0.588	0.619
1,4-Difluorobenzene (IS)	N/A	N/A	N/A	N/A
Dibromomethane	0.160	0.197	0.148	0.172
1,2-Dichloropropane	0.253	0.300	0.275	0.270
Dibromomethane	0.160	0.197	0.148	0.172
1,2-Dichloropropane	0.253	0.300	0.275	0.270
Bromodichloromethane	0.330	0.466	0.391	0.393
Methyl Methacrylate	0.227	0.317	0.180	0.238
n-Propyl Acetate	0.347	0.411	0.270	0.323
2-Cleve	0.162	0.192	0.110	0.149
cis-1,3-Dichloropropene	0.377	0.460	0.370	0.444
Toluene-d8 (surr)	0.830	1.092	0.790	1.089
Toluene	0.999	1.249	1.034	1.276
2-Nitropropane	0.339	0.425	0.270	0.323
Tetrachloroethene	0.266	0.493	0.235	0.300
4-methyl2-pentanone	0.036	0.050	0.068	0.034
1,1,2-Trichloroethane	0.230	0.301	0.205	0.235
Ethyl Methacrylate	0.192	0.255	0.124	0.177
Dibromochloromethane	0.207	0.329	0.213	0.248
1,3-Dichloropropane	0.420	0.506	0.354	0.410
1,2-Dibromoethane	0.230	0.301	0.187	0.233
n-Butyl Acetate	0.361	0.463	0.272	0.339
2-Hexanone	0.174	0.213	0.128	0.149
Chlorobenzene-d5 (IS)	N/A	N/A	N/A	N/A
Chlorobenzene	0.739	0.908	0.803	0.949
Ethylbenzene	1.207	1.550	1.321	1.573
1,1,1,2-Tetrachloroethane	0.242	0.336	0.270	0.287
M&P Xylene	0.961	1.264	1.042	1.300
Ortho Xylene	1.014	1.314	1.115	1.290
Styrene	0.675	0.920	0.747	0.913
Bromoform	0.131	0.240	0.143	0.164
Isopropylbenzene	1.200	1.502	1.218	1.541
n-Amyl Acetate	0.471	0.533	0.399	0.401
BFB (surr)	0.364	0.501	0.390	0.501
n-Propylbenzene	1.335	1.720	1.452	1.924
trans-1,4-Dichloro-2-Butene	0.104	0.116	0.085	0.091
Nitrobenzene	0.016	0.041	0.017	0.020
Bromobenzene	0.536	0.675	0.555	0.661
1,1,2,2-Tetrachloroethane	0.413	0.429	0.381	0.366
1,3,5-Trimethylbenzene	0.917	1.260	0.972	1.262
2-Chlorotoluene	0.869	1.113	0.914	1.127
cis-1,4-Dichloro-2-Butene	0.143	0.152	0.109	0.125
4-Chlorotoluene	0.886	1.113	0.933	1.223
Tertbutylbenzene	0.756	1.035	0.813	1.050
1,2,4-Trimethylbenzene	0.930	1.259	0.961	1.260
sec-Butylbenzene	1.216	1.578	0.388	1.717
p-Isopropyltoluene	0.992	1.281	1.081	1.367
1,3-Dichlorobenzene	0.506	0.629	0.546	0.671
1,4-Dichlorobenzene-d4 (IS)	N/A	N/A	N/A	N/A
1,4-Dichlorobenzene	0.552	0.678	0.580	0.691
n-Butylbenzene	0.936	1.159	1.127	1.360
1,2-Dichlorobenzen	0.507	0.642	0.481	0.600
1,2-Dibromo-3-Chloropropane	0.070	0.097	0.049	0.061
Hexachlorobutadiene	0.125	0.169	0.157	0.199
1,2,4-Trichlorobenzene	0.313	0.439	0.293	0.413
Naphthalene	1.098	1.461	0.685	1.026
1,2,3-Trichlorobenzene	0.318	0.442	0.264	0.364

Table 5: Average Compound Response Summary

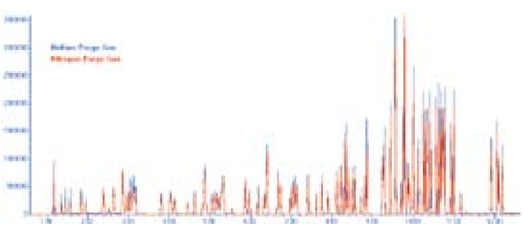

Figure 1: Overlay of 50ppb water standard purged in He and in N2

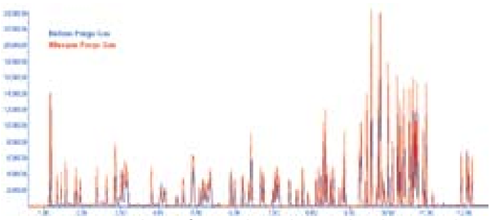

Figure 2: Overlay of 50ppb soil standard purged in He and in N2

Matrix	Average %RSD N2 Purge	Average %RSD He Purge	Average MDL N2 Purge	Average MDL He Purge	Average Compound Response N2 Purge	Average Compound Response He Purge
Water	10.08	8.30	0.32	0.33	0.602	0.708
Soil	10.30	8.10	0.48	0.53	0.718	0.689

Table 6: Experimental Results Summary

Conclusions

The Atomx Purge and Trap Concentrator Multimatrix Autosampler in conjunction with an Agilent GC/MS system performed very well for both the water and the soil calibration range, as seen in Figures 1 and 2. These findings support the option of moving to Nitrogen as an alternative to Helium. Considering Helium can cost as much as three times the price of Nitrogen, this switch can save companies performing typical USEPA methodologies considerable amounts of costs over the long term. In addition the use of Nitrogen generators capable of producing 99.999 or greater purity offer yet another solution to the cost associated with the analysis by removing the need for cylinders.