

Application Note

Abstract

Due to regional shortages and increasing costs of helium, the preferred carrier gas in gas chromatography, alternative carrier gas options are increasing in demand. This study will evaluate the Teledyne Tekmar Atomx VOC Sample Prep System in conjunction with a Thermo Scientific TRACE 1310 / ISQ GCMS while employing hydrogen GC carrier gas and nitrogen purge gas to perform EPA method 8260C. A working linear calibration curve, Method Detection Limits (MDLs), and a BFB tuning evaluation will be presented to determine the validity of alternative helium gases for VOC analysis by USEPA 8260C.



Introduction

The EPA developed method 8260C to determine volatile organic compounds (VOCs) in soil and water.¹ Helium is the preferred GC carrier gas, as well as the most widely used purge gas. Unfortunately, helium is a nonrenewable gas which has caused issues with supply and increasing costs.

Conversely, alternative carrier gases such as hydrogen and nitrogen are renewable and can be derived from generators. Many laboratories are making the conscious effort to cut costs and shift to helium free instruments and methodologies, but must also be able to produce reliable results.

This study will evaluate using these renewable gas sources - hydrogen for the GC/MS and nitrogen for the Atomx - as substitutes for helium in EPA Method 8260C. Calibration standards will be evaluated by linear calibration curves per the method criteria. A calibration curve will be generated from 0.5 ppb to 200 ppb, and must meet the criteria of %RSD below 20% or a linear regression value (r^2) of at least 0.99.¹ The minimum average response factor is also defined in EPA Method 8260C. MDLs will be assessed for 100% or 1 ppb variance of the actual concentration.

Teledyne Tekmar's Atomx is a VOC sample prep system that integrates a Purge and Trap Concentrator with a Multi-Matrix Autosampler. It employs an 80-position vial autosampler capable of running water, soil and automated methanol extractions, and also has the capability of prepping samples ahead, while the previous sample is being analyzed by GC, allowing for faster analysis time. The Atomx has the ability to automatically add Internal Standards (IS) and Surrogate Sample (SS) from three separate standard addition vessels, with volume increment variables of 1, 2, 5, 10, and 20 μ l.

Experimental-Instrument Conditions

For this study, the Atomx VOC Sample Prep System was coupled to a Thermo Scientific TRACE 1310 GC with ISQ MS Detector. The analytical trap used was a #9 (proprietary). Hydrogen was used as the carrier gas and nitrogen as the purge gas. The GC was equipped with a Rtx®-VMS 20m x 0.18mm x 1 μ m column. The GC/MS parameters are outlined in Tables 1 and 2. Table 3 outlines the Atomx conditions.

GC Parameters	
GC:	Thermo Scientific TRACE 1310
Column:	Rtx®-VMS 20 m x 0.18 mm ID x 1.0 µm
Oven Program:	35 °C for 3 min; 14 °C/min to 100 °C; 25 to 210; hold for 2 min
Inlet:	200 °C
Column Flow:	0.8 mL/min
Gas:	Hydrogen
Split:	60:1
Pressure:	5 psi
MS Transfer Line:	230 °C

MS Parameters	
MS:	ISQ
Ion Source:	280 °C
Solvent Delay:	0.8 min
Scan Range:	35 - 260
Dwell Time:	0.15 sec
Emission Current:	40 µA
Detector Gain:	3.00e ⁵
Chrom Filter Width:	2.0 sec

Tables 1 & 2: GC and MS Parameters

Atomx 8260C Water Parameters			
Variable	Value	Variable	Value
Valve oven Temp	140 °C	Dry Purge Flow	100 mL/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	3.0 mL
Sample Vial Temp	20 °C	Water Needle Rinse Volume	7.0 mL
Sample Equilibrate Time	0.00 min	Sweep Needle Time	0.25 min
Soil Valve Temp	50 °C	Desorb Preheat Time	245 °C
Standby Flow	10 mL/min	GC Start Signal	Start of Desorb
Purge Ready Temp	40 °C	Desorb Time	2 min
Condensate Ready Temp	45 °C	Drain Flow	300 mL/min
Presweep Time	0.25 min	Desorb Temp	250 °C
Prime Sample Fill Volume	3.0 mL	Methanol Glass Rinse	Off
Sample Volume	5.0 mL	Number of Methanol Glass Rinses	1
Sweep Sample Time	0.25 min	Methanol Glass Rinse Volume	3.0 mL
Sweep Sample Flow	100 mL/min	Number of Water Bake Rinses	1
Spurge Vessel Heater	OFF	Water Bake Rinse Volume	7.0 mL
Spurge Vessel Temp	20 °C	Bake Rinse Sweep Time	0.25 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100 mL/min
Prepurge Flow	0 mL/min	Bake Rinse Drain Time	0.40 min
Purge Time	11.00 min	Bake Time	2.00 min
Purge Flow	40 mL/min	Bake Flow	400 mL/min
Purge Temp	20 °C	Bake Temp	280 °C
Condensate Purge Temp	20 °C	Condensate Bake Temp	200 °C
Dry Purge Time	0.5 min		

Table 3: Atomx 8260C Parameters (items in yellow were not used)

Calibration and Method Detection Limits

A 50 ppm stock standard was brought to volume with methanol. The stock standard was diluted in deionized water to generate calibration standards from 0.5 ppb to 200 ppb. These standards were transferred to headspace free 40 mL VOA vials. A chromatogram of a 10 ppb calibration standard can be found in Figure 1.

Internal Standard (IS) and Surrogate standards (SS) were made in methanol at 50 ppm. IS/SS were dispensed by the internal standard vessels in 5 µL aliquots for a final concentration of 50 ppb. Thermo TraceFinder software was used to process the calibration data for each compound using extracted ion mode. The primary and secondary characteristic ions are prescribed in method 8260C. The relative response factors (RRF) were used to calculate the percent relative standard deviation (%RSD). Full calibration data can be found in Table 4.

MDLs were determined by running a 1 ppb standard in seven repetitions. The MDL must be less than 1. The results can be found in table 4.

Compound	Avg RRF	% RSD	MDL	Compound	Avg RRF	% RSD	MDL
Dichlorodifluoromethane	0.275	8.37	0.217	2-Chloroethylvinyl ether	0.313	8.65	0.152
Chloromethane	0.657	7.2	0.105	cis-1,3-Dichloropropene	0.853	11.17	0.155
Bromomethane*		0.998	0.207	Toluene	2.389	5.93	0.134
Chloroethane	0.314	6.08	0.296	Tetrachloroethylene	0.576	7.91	0.373
Trichlorofluoromethane	0.631	11.95	0.239	2-Hexanone	1.207	13.23	0.132
Ethyl ether	0.542	11.42	0.148	4-Methyl-2-pentanone	1.155	11.8	0.151
1,1-Dichloroethene	0.838	8.47	0.143	trans 1,3-Dichloropropene	0.782	12.1	0.105
Vinyl Chloride	0.355	6.57	0.251	1,1,2-Trichloroethane	0.4	10.19	0.131
Carbon Disulfide	2.132	7.59	0.204	Ethyl Methacrylate	0.691	14.5	0.112
1,1,2-Trichlorotrifluoroethane	0.607	11.22	0.139	Dibromochloromethane	0.241	11.9	0.181
Acetonitrile	3.106	12.59	0.433	1,3-Dichloropropane	1.015	7.82	0.158
Allyl chloride	3.14	12.49	0.428	1,2-dibromoethane	0.469	9.25	0.19
Methylene Chloride	2.726	6.99	0.204	Butyl acetate	1.552	13.54	0.155
Acetone	0.642	17.62	0.438	Chlorobenzene	1.304	5.29	0.084
trans-1,2-Dichloroethene	1.032	7.22	0.09	Ethylbenzene	2.456	5.94	0.095
Methyl acetate	1.768	8.27	0.222	1,1,1,2-Tetrachloroethane	0.611	11.64	0.12
Methyl-tert-butyl-Ether	2.49	9.33	0.122	m, p-Xylene	1.995	5.6	0.171
Propionitrile	0.093	9.58	0.322	Isopropylbenzene	0.383	6.26	0.124
tert-Butyl Alcohol	0.246	11.28	0.159	o-Xylene	2.054	5.87	0.113
Ethyl-tert-butyl-Ether	0.256	6.45	0.136	Bromoform	0.206	14.72	0.164
Chloroprene	0.766	9.25	0.061	Styrene	1.49	6.83	0.075
1,1-Dichloroethane	1.253	5.55	0.143	Amyl acetate	1.65	13.27	0.075
Acrylonitrile	0.254	9.8	0.225	Bromobenzene	1.165	5.25	0.141
Vinyl acetate	3.249	10.23	0.288	n Propylbenzene	2.823	5.99	0.196
cis-1,2-Dichloroethene	0.881	7.16	0.092	1,1,2,2-Tetrachloroethane	0.576	9.66	0.13

2,2-Dichloropropane	0.959	7.51	0.1	4-Chlorotoluene	2.865	6.21	0.069
Bromochloromethane	1.483	8.33	0.118	1,2,3-Trichloropropane	0.323	8.87	0.151
Trichloroethene	0.075	8.2	0.152	1,2,3-Trimethylbenzene	3.434	6.16	0.138
Chloroform	1.132	6.58	0.095	trans-1,4-dichloro-2-butene	0.238	14.58	0.105
Carbon Tetrachloride	0.515	12.21	0.149	2-Chlorotoluene	1.777	6.18	0.161
1,1,1-Trichloroethane	0.85	9.68	0.148	Pentachloroethane	2.42	8.02	0.23
Ethyl Acetate	1.558	10.01	0.352	sec-Butylbenzene	4.085	7.44	0.277
Tetrahydrofuran	0.575	11.85	0.176	1,2,4-Trimethylbenzene	0.124	8.96	0.438
Isobutanol	0.978	8.28	0.446	tert-Butylbenzene	2.799	7.75	0.303
Isopropyl acetate	0.986	7.07	0.378	p-Isopropyltoluene	2.835	7.69	0.293
1,1-Dichloropropene	0.962	6.11	0.122	1,3-Dichlorobenzene	1.879	8.18	0.209
2-Butanone	0.43	6.85	0.192	1,4-Dichlorobenzene	1.93	7.24	0.181
Benzene	2.137	4.08	0.143	n-Butylbenzene	3.371	7.91	0.318
tert-Amyl-Methyl Ether	2.176	8.77	0.16	1,2-dichlorobenzene	1.844	7.77	0.129
1,2-Dichloroethane	0.508	5.37	0.206	1,2-Dibromo-3-chloropropane	0.158	11.57	0.212
Dibromomethane	0.277	6.15	0.139	Nitrobenzene	0.054	12.28	0.953
1,2-Dichloropropane	0.455	5.23	0.101	Hexachlorobutadiene	0.194	7.52	0.256
Brodichloromethane	0.42	8.59	0.098	1,2,4-Trichlorobenzene	1.138	9.8	0.48
Methyl Methacrylate	1.17	10.51	0.218	Naphthalene	2.478	8.85	0.14
Propyl acetate	1.256	8.27	0.134	1,2,3 Trichlorobenzene	1.09	9.98	0.399

Table 4: Calibration Data for EPA Method 8260C using Hydrogen Carrier Gas (*denotes linear regression)

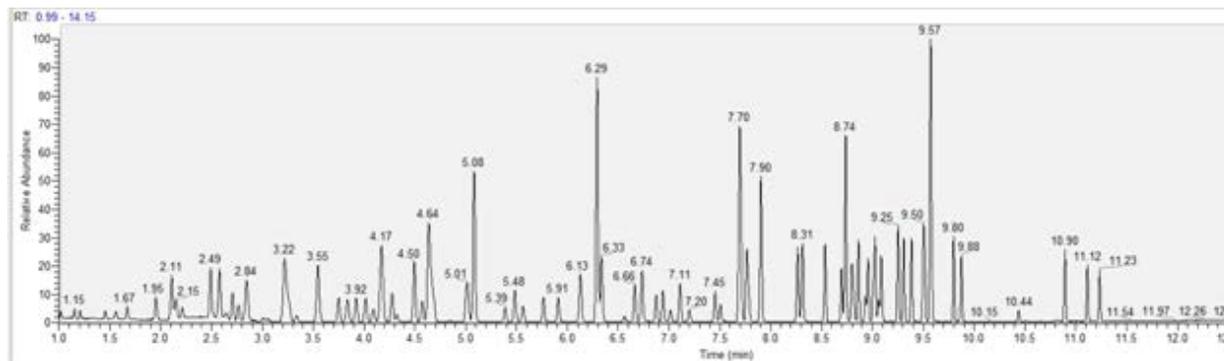


Figure 1: Total Ion Chromatogram (TIC of 10 ppb Calibration Standard.)

4-bromofluorobenzene (BFB) tuning requirements met all the ion abundance criteria for EPA Method 8260¹ (see Figure 2).

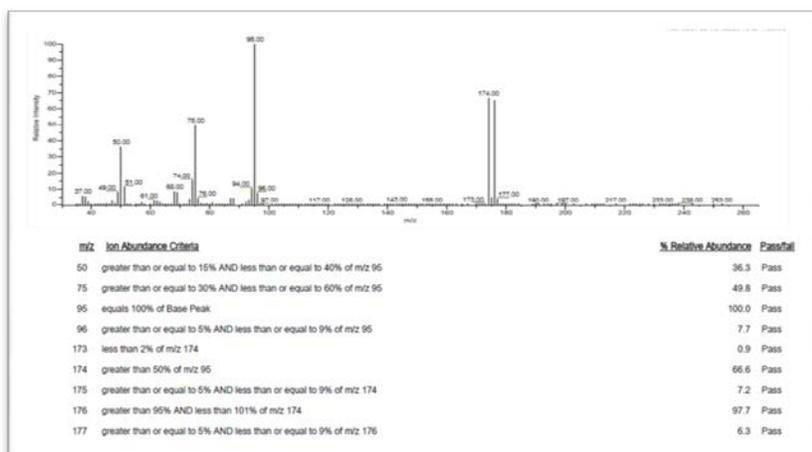


Figure 2: Passing BFB Tune using Hydrogen Carrier Gas.

Conclusions

The Atomx VOC Sample Prep System, used in conjunction with a Thermo Scientific TRACE 1310 / ISQ GCMS, was able to pass all performance requirements of US EPA method 8260C using hydrogen carrier gas and nitrogen purge gas. This is both a budget and environmentally friendlier way to analyze VOCs. As this study demonstrates, these readily available gases are viable alternatives for this analysis, although the method itself must be further evaluated and updated to allow for their use.

Acknowledgement

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References

1. USEPA Method 8260C, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)," Revision 3, August 2006.