Using Alternative Carrier Gases for US EPA VOC Drinking Water Methods

Application Note

Abstract

Limited supplies and the rising cost of helium have spurred the need for analytical methods allowing more economical alternatives. With this in mind, new purge and trap VOC methods are being developed and evaluated using nitrogen purge gas, replacing helium. Building upon this new methodology, replacing the helium carrier gas with hydrogen or nitrogen offers the potential for additional cost savings, eliminating the need for helium altogether.

This application note will use a Teledyne Tekmar Atomx multimatrix autosampler to examine the use of alternative carrier gases for the GC/MS system. Comparisons to previous EPA purge and trap methodology using helium and nitrogen will be made. Calibration data and Method Detection Limits (MDLs) will be presented for all compounds using alternative carrier and purge gases per each method.

Introduction

Helium has been the mobile phase of choice in gas chromatography due to its inertness and flexibility to work with a variety of detectors. These properties as a nonflammable noble gas are also vital to its use in mass spectrometry. As the second smallest element, helium is very efficient and offers excellent separation across a diverse range of applications. This versatility has also driven the demand for, and the increased cost of, helium in many parts of the world.

Unfortunately, the helium supply on Earth is fixed, rendering it essentially a fossil fuel. Most helium is actually produced, or extracted, as a byproduct of natural gas drilling and production. Unlike other gases - nitrogen and hydrogen - the capability for onsite generation is not possible. The corresponding supply/demand issues have driven the need for alternative gases for GC applications. This application note will examine the viability of using hydrogen and nitrogen as replacements for helium in EPA methods 524.2[1] and 8260C[2].

This application note utilizes an Atomx multimatrix autosampler integrated with a purge and trap concentrator. This set-up allows for complete automation of sample preparation for the analysis of liquid, soil and methanol extracted samples for purge and trap. 5 mL or 25 mL samples (depending on the method) were transferred to the sparging tube and purged onto a sorbent trap using nitrogen. The trap is then heated and analytes are desorbed to the GC/MS for analysis. A linear calibration was performed and Percent Relative Standard Deviation (%RSD), MDLs, and percent carryover were determined.

Experimental-Instrument Conditions

The Atomx multimatrix autosampler was coupled to an Agilent 7890/5975 GC/MS with Triple Axis Detector for this analysis. A Vocarb 3000 trap was the analytical trap of choice. The GC was configured with a J&W DB-624 20 m x 0.18 mm x 1.0 µm column. The GC/MS parameters are outlined in Tables 1 and 2. Table 3 outlines the Atomx conditions for each method.

GC Parameters	
GC:	Agilent 7890A
Column:	J&W DB-624 20m x 0.18 mmID x 1.0 µm
Oven Program:	35 °C for 4 min; 15 °C/min to 240 °C 0.33 min
Inlet:	200 °C
Column Flow:	0.33094 mL/min
Gas:	Hydrogen
Split:	8260C - 80:1, 524.2 - 150:1
Pressure:	5.1555 psi

MSD Parameters	
MSD:	5975C inert XL with TAD
Source:	250 °C
Quad:	200 °C
Solvent Delay:	Method Dependent
Scan Range:	35-300 m/z
Scans:	5.19 scans/sec
Threshold:	100
MS Transfer Line Temp:	250 °C

Tables 1 & 2: GC and MSD Parameters

Atomx 524.2 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	40 °C	Methanol Needle Rinse	Off
Water Heater Temp	80 °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	0.50 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	25.0 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 Bake Rinses	1
Sparge Vessel Heater	Off	Water Bake Rinse Volume	27.0 mL
Sparge Vessel Temp	20 °C	Bake Rinse Sweep Time	0.40 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100 mL/min
Prepurge Flow	0 mL/min	Bake Rinse Drain Time	0.60 min
Purge Time	11.00 min	Bake Time	6.00 min
Purge Flow	40 mL/min	Bake Flow	200 mL/min
Purge Temp	20 °C	Bake Temp	280 °C
Condensate Purge Temp	20 °C	Condensate Bake Temp	200 °C
Dry Purge Time	2.00 min		

Table 3: Atomx 524.2 Parameters (items in yellow were not used)

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	40 °C	Methanol Needle Rinse	Off
Water Heater Temp	80 °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	0.50 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 Bake Rinses	1
Sparge Vessel Heater	On	Water Bake Rinse Volume	7.0 mL
Sparge Vessel Temp	40 °C	Bake Rinse Sweep Time	0.40 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100 mL/min
Prepurge Flow	0 mL/min	Bake Rinse Drain Time	0.60 min
Purge Time	11.00 min	Bake Time	6.00 min
Purge Flow	40 mL/min	Bake Flow	200 mL/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 8260C Parameters (items in yellow were not used)

Calibration and Results

A 50 ppm stock standard was prepared in methanol for each representative method. Calibration curves were generated over a range of 0.2 to 50 ppb for method 524.2 and 1 to 200 ppb for method 8260C. Samples were transferred to headspace free 40 mL VOA vials for analysis. The Internal Standard (IS) and Surrogates (SS) were prepared in methanol at a 50ppm concentration. After transferring to the standard vessel on the Atomx, the IS was added to each sample, bringing the final concentration of 5 ppb for 524.2 and 50 ppb for 8260C, factoring in the sample volumes.

Agilent Chemstation software was used to process the calibration data. Relative response factors were evaluated for %RSD and coefficient of determination (r^2) with results for all compounds listed in Tables 4 and 5. Of note, some compounds required quadratic regression when using hydrogen (noted by ^{1} in the table below). Further investigation would be required to determine if matrix matched calibration standards would improve the linearity of these compounds. MDLs were also established for all by analyzing seven replicates at a concentration of 0.5 ppb for 524.2 and 1 ppb for 8260C. Percent carryover was determined by running blank samples after the highest calibration standard. Example chromatograms for each method can be found in Figures 1 through 3.

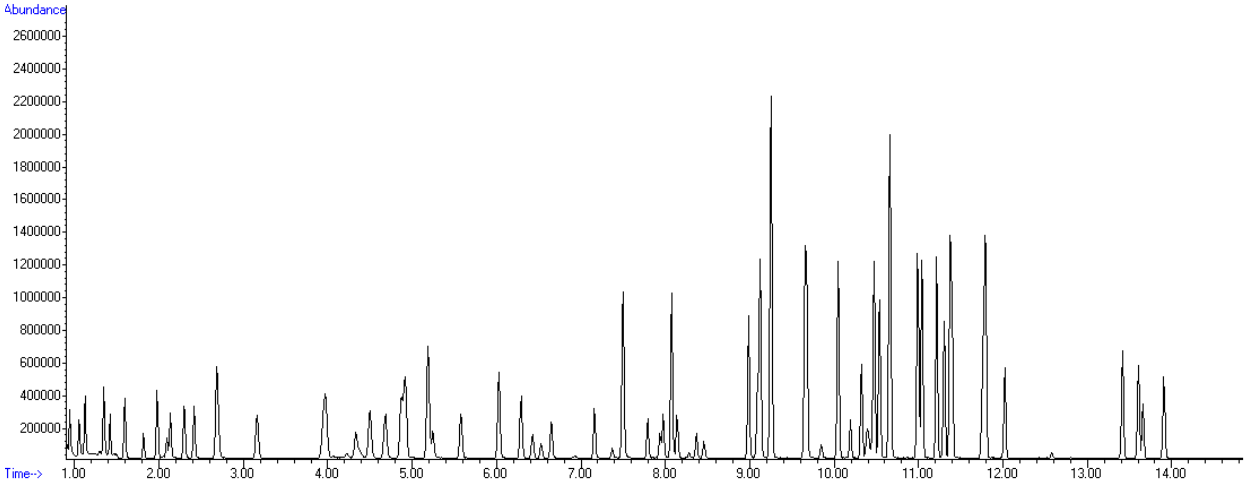


Figure 1: 10 ppb Standard using Hydrogen Carrier Gas for Method 524.2

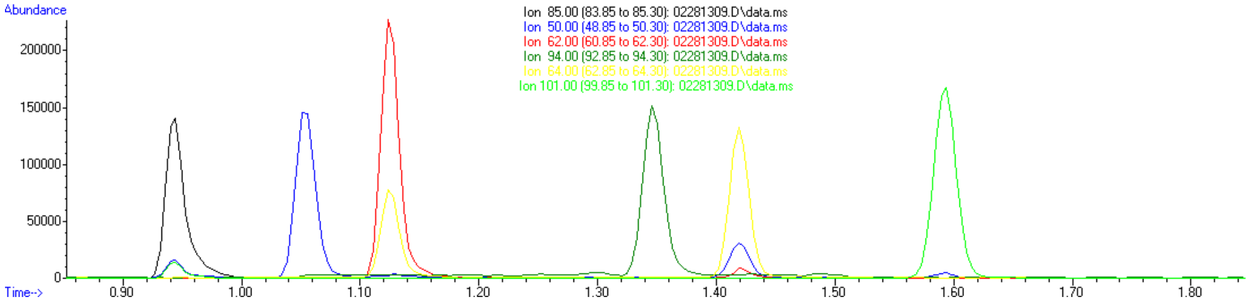


Figure 2: 10 ppb Extracted Chromatogram for Gaseous Compounds for Method 524.2

Compound Name	Avg RRF	% RSD	MDL
Dichlorodifluoromethane	0.277	10.79	0.05
Chloromethane	0.293	5.31	0.08
Vinyl Chloride	0.424	6.67	0.05
Bromomethane	0.349	14.30	0.07
Chloroethane	0.259	5.78	0.04
Trichlorofluoromethane*	0.347	0.999*	0.12
Diethyl Ether	0.116	2.60	0.11
1,1-Dichloroethene*	0.380	0.999*	0.13
Acetone*	0.045	1.000*	0.08
Iodomethane*	0.163	0.995*	0.06
Carbon Disulfide	0.563	15.84	0.07
Allyl Chloride	0.325	4.30	0.02
Methylene Chloride	0.291	9.40	0.13
trans-1,2-Dichloroethene	0.451	12.27	0.11
MTBE	0.372	5.78	0.03
1,1-Dichloroethane	0.514	7.72	0.08
2-Butanone	0.027	10.53	0.12
2,2-Dichloropropane	0.347	10.12	0.03
cis-1,2-dichloroethene	0.487	8.01	0.06
Bromochloromethane	0.148	5.84	0.06
Chloroform	0.488	7.09	0.05
1,1,1-Trichloroethane	0.369	12.79	0.09
Carbon Tetrachloride	0.286	15.31	0.02
1-Chlorobutane	0.540	10.89	0.05
1,1-Dichloropropene	0.402	13.42	0.08
Benzene	1.478	4.75	0.08
1,2-Dichloroethane	0.274	7.27	0.07
Trichloroethene	0.309	8.22	0.10
1,2-Dichloropropane	0.434	5.76	0.09
Dibromomethane	0.090	8.17	0.14
Bromodichloromethane	0.252	9.31	0.06
cis-1,3-Dichloropropene	0.277	11.00	0.10
4-Methyl-2-Pentanone	0.082	6.84	0.17
Toluene	1.370	6.43	0.07
trans-1,3-Dichloropropene	0.208	10.24	0.09
1,1,2-Trichloroethane	0.156	10.92	0.12
Tetrachloroethene	0.474	18.63	0.11
2-Hexanone	0.046	13.88	0.13
1,3-Dichloropropane	0.267	6.67	0.07
Dibromochloromethane	0.127	8.33	0.07
1,2-Dibromoethane	0.116	8.63	0.06

Compound Name	Avg RRF	% RSD	MDL
Chlorobenzene	0.796	4.95	0.08
1,1,1,2-Tetrachloroethane	0.189	10.64	0.03
Ethylbenzene	1.443	7.95	0.06
m,p-Xylene	1.116	9.55	0.12
o-Xylene	1.147	5.29	0.05
Styrene	1.218	6.51	0.05
Bromoform	0.061	12.20	0.17
Isopropylbenzene	1.368	8.32	0.04
Bromobenzene	0.457	5.09	0.06
1,1,2,2-Tetrachloroethane	0.118	8.04	0.11
1,2,3-Trichloropropane	0.040	15.56	0.15
n-Propylbenzene	1.626	9.17	0.04
2-Chlorotoluene	1.016	5.20	0.05
4-Chlorotoluene	1.085	7.32	0.04
1,3,5-Trimethylbenzene	1.164	5.73	0.04
tert-Butylbenzene	0.953	7.10	0.06
1,2,4-Trimethylbenzene	1.163	4.86	0.03
sec-Butylbenzene	1.415	11.54	0.06
1,3-Dichlorobenzene	0.549	4.52	0.08
p-Isopropyltoluene	1.200	9.60	0.04
1,4-Dichlorobenzene	0.528	3.40	0.12
1,2-Dichlorobenzene	0.234	7.82	0.08
n-Butylbenzene	1.196	10.25	0.06
Hexachloroethane	0.146	11.20	0.02
1,2,4-Trichlorobenzene	0.322	13.40	0.09
Hexachlorobutadiene*	0.162	1.000*	0.12
Naphthalene	0.485	13.32	0.07
1,2,3-Trichlorobenzene	0.257	10.23	0.11

Table 4: 524.2 Calibration Data (denotes linear regression,* ^{1} *denotes quadratic regression)*

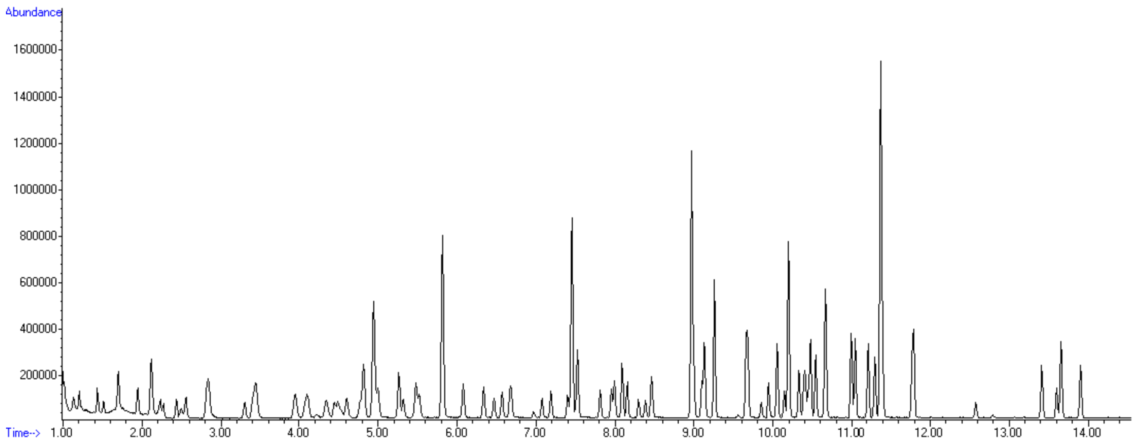


Figure 3: 10 ppb Standard using Hydrogen Carrier Gas for Method 8260C

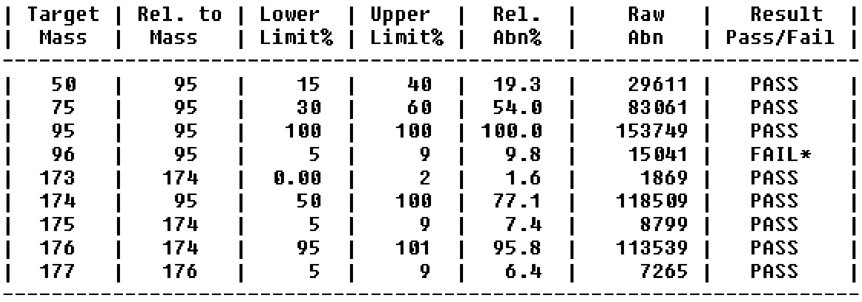
Compound Name	Avg RRF	% RSD	MDL
Dichlorodifluoromethane*	0.481	0.999*	0.08
Chloromethane	0.525	13.3	0.12
Vinyl Chloride	0.803	12.65	0.08
Bromomethane*	0.863	0.996[1]	0.10
Chloromethane	0.538	11.57	0.12
Trichlorofluoromethane	0.800	3.49	0.17
Diethyl Ether	0.358	6.36	0.17
1,1-Dichloroethene	0.747	5.68	0.17
Carbon Disulfide	1.123	9.97	0.19
1,1,2-Trichlorofluoromethane	0.508	4.07	0.32
Iodomethane*	0.336	0.999[1]	0.28
Allyl Chloride	0.697	10.06	0.09
Methylene Chloride	0.592	4.50	0.19
Acetone*	0.134	0.998*	0.18
Trans-1,2-Dichloroethene	0.765	5.33	0.16
Methyl Acetate	0.375	5.59	0.09
Methyl-tert-butyl-ether	1.657	7.03	0.14
Tert-butyl Alcohol	0.027	11.54	2.31
Chloroprene	0.807	5.36	0.11
1,1-Dichloroethane	1.035	6.12	0.10
Acetonitrile	0.355	7.59	0.13
Acrylonitrile	0.228	7.39	0.13
Ethyl Acetate	0.498	9.06	0.10
Vinyl Acetate	1.686	7.83	0.15
Ethyl-tert-butyl Ether	1.682	5.19	0.19
Cis-1,2-Dichloroethene	0.693	4.81	0.10
2,2-Dichloropropane	0.718	6.04	0.07
Bromochloromethane	0.465	4.40	0.26
Chloroform	1.097	6.04	0.07
Carbon Tetrachloride	0.617	8.76	0.07
1,1,1-Trichloroethane	0.830	8.15	0.13
Tetrahydrofuran	0.186	4.86	0.14
Methyl Acrylate	0.501	9.31	0.07
1,1-Dichloropropene	0.855	5.93	0.16
2-Butanone (MEK)	0.171	6.82	0.16
Benzene	2.600	3.94	0.10
Methacrylonitrile	0.416	5.39	0.08
Tert-amyl-methyl Ether	1.577	7.27	0.12
1,2-Dichloroethane	0.938	4.14	0.12
Isopropyl Acetate	1.051	10.25	0.11
Trichloroethene	0.405	4.17	0.11

Compound Name	Avg RRF	% RSD	MDL
Dibromomethane	0.258	5.73	0.09
1,2-Dichloropropane	0.379	4.36	0.08
Bromodichloromethane	0.403	11.54	0.13
Methyl Methacrylate	0.262	8.95	0.22
n-Propyl Acetate	0.419	9.40	0.09
2-Chloroethyl Vinyl Ether	0.236	6.91	0.10
cis-1,3-Dichloropropene	0.476	12.13	0.11
Toluene	0.954	3.90	0.05
2-Nitropropane	0.068	9.97	0.23
Tetrachloroethene	0.423	7.63	0.17
4-methyl-2-pentanone	0.261	8.82	0.16
1,1,2-Trichloroethane	0.309	7.15	0.11
Ethyl Methacrylate*	0.431	0.997*	0.11
Dibromochloromethane	0.288	9.12	0.13
Trans-1,3-Dichloropropene	0.462	10.66	0.10
1,3-Dichloropropane	0.637	4.05	0.19
1,2,3-Trichloropropane	0.870	6.27	0.07
1,2-Dibromoethane	0.376	11.76	0.17
n-butyl acetate	0.247	12.04	0.10
2-Hexanone	0.112	13.96	0.24
Chlorobenzene	1.209	4.54	0.10
Ethylbenzene	2.133	4.71	0.08
1,1,1,2-Tetrachloroethane	0.319	10.03	0.29
m,p-Xylene	0.805	6.94	0.25
O-Xylene	1.740	3.85	0.11
Styrene	1.299	7.61	0.10
Bromoform	0.214	10.95	0.14
Isopropylbenzene	2.010	5.79	0.11
n-Amyl Acetate*	0.548	0.998*	0.16
n-Propylbenzene	2.458	4.01	0.14
trans-1,4-Dichloro-2-Butene	0.271	4.07	0.12
Bromobenzene	0.810	5.20	0.10
1,1,2,2-Tetrachloroethane	0.954	7.54	0.15
1,3,5-Trimethylbenzene	3.262	4.87	0.03
2-Chlorotoluene	2.722	4.38	0.04
Cis-1,4-Dichloro-2-Butene	0.132	12.67	0.18
4-Chlorotoluene	3.238	5.19	0.13
tert-Butylbenzene	2.856	3.33	0.16
1,2,4-Trimethylbenzene	3.288	4.87	0.07
sec-Butylbenzene	4.016	3.59	0.13
p-Isopropyltoluene	3.448	5.15	0.14
1,3-Dichlorobenzene	1.757	5.73	0.14

Compound Name	Avg RRF	% RSD	MDL
1,4-Dichlorobenzene	1.807	7.74	0.10
n-Butylbenzene	3.292	4.90	0.10
1,2-Dichlorobenzene	1.696	5.31	0.13
1,2-dibromo-3-Chloropropane	0.144	11.50	0.12
Hexachlorobutadiene*	0.426	0.997*	0.28
1,2,4-Trichlorobenzene	1.156	14.04	0.19
Naphthalene*	3.097	0.998*	0.10
1,2,3-Trichlorobenzene	1.095	14.48	0.21

Table 5: 8260C Calibration Data (denotes linear regression, ^{1} denotes quadratic regression)*

Tuning for these methods was the greatest area of difference, versus utilizing helium as the carrier gas. Meeting the tuning criteria, especially the 95/96 ion ratio, proved to be, and continues to be a challenge. Screenshots of passing and failing BFB tunes can be found in Figures 4 and 5.



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| Target | Rel. to | Lower  | Upper  |  Rel.  |     Raw    |   Result  |
|  Mass  |  Mass   | Limit% | Limit% |  Abn%  |     Abn    | Pass/Fail |
-----------------------------------------------------------------------
|   50   |   95    |    15  |    40  |  19.3  |     29611  |  PASS     |
|   75   |   95    |    30  |    60  |  54.0  |     83061  |  PASS     |
|   95   |   95    |   100  |   100  | 100.0  |    153749  |  PASS     |
|   96   |   95    |     5  |     9  |   9.8  |     15041  |  FAIL*    |
|  173   |  174    |  0.00  |     2  |   1.6  |      1869  |  PASS     |
|  174   |   95    |    50  |   100  |  77.1  |    118509  |  PASS     |
|  175   |  174    |     5  |     9  |   7.4  |      8799  |  PASS     |
|  176   |  174    |    95  |   101  |  95.8  |    113539  |  PASS     |
|  177   |  176    |     5  |     9  |   6.4  |      7265  |  PASS     |
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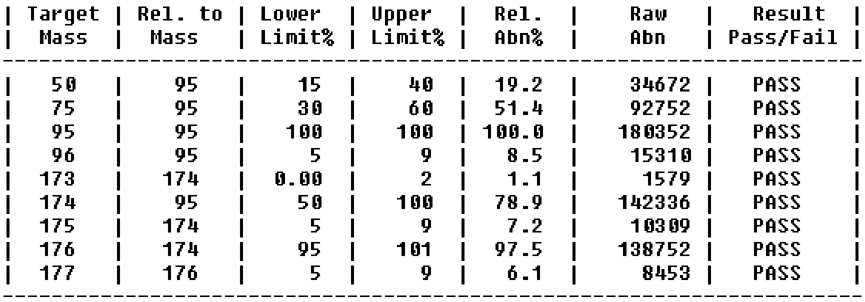
Figure 4: Failing BFB Tune Criteria using Hydrogen Carrier Gas – Blank Sample



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| Target | Rel. to | Lower  | Upper  |  Rel.  |     Raw    |   Result  |
|  Mass  |  Mass   | Limit% | Limit% |  Abn%  |     Abn    | Pass/Fail |
-----------------------------------------------------------------------
|   50   |   95    |    15  |    40  |  19.2  |     34672  |  PASS     |
|   75   |   95    |    30  |    60  |  51.4  |     92752  |  PASS     |
|   95   |   95    |   100  |   100  | 100.0  |    180352  |  PASS     |
|   96   |   95    |     5  |     9  |   8.5  |     15310  |  PASS     |
|  173   |  174    |  0.00  |     2  |   1.1  |      1579  |  PASS     |
|  174   |   95    |    50  |   100  |  78.9  |    142336  |  PASS     |
|  175   |  174    |     5  |     9  |   7.2  |     10309  |  PASS     |
|  176   |  174    |    95  |   101  |  97.5  |    138752  |  PASS     |
|  177   |  176    |     5  |     9  |   6.1  |      8453  |  PASS     |
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Figure 5: Passing Tune Criteria using Hydrogen Carrier Gas – Calibration Standard

Lowering the column flow showed the most promising results, but the criteria are still only met intermittently. Lowering the flow too much had a negative effect on the total chromatography, but helped the consistency of passing the BFB tune. The amount of methanol in the system also seems to have an effect, as higher level standards pass frequently. If hydrogen is to be used in these EPA methods, then the tuning criteria will need to be addressed and investigated further to set optimal parameters for passing the tune or adjusting the ion ratios accordingly.

Conclusions

With the increased costs and limited supplies associated with using helium as a carrier for gas chromatography, the demand for alternatives has also grown. Nitrogen and hydrogen are desirable choices due to their relatively low costs and the ability to generate them onsite as needed. Unfortunately, many of the normal GC and GC/MS methods have not been validated using such alternative gases, so there is little information available on their applicability.

This application note presents data for two VOC purge and trap methods, EPA 524.2 and 8260C, using hydrogen carrier gas and nitrogen purge gas. By completely eliminating the need for helium, costs and availability are no longer issues. Aside from issues with the tuning criteria, similar performance to helium methods was achieved using hydrogen and nitrogen. As this application note demonstrates, these readily available gases are viable alternatives for these analyses, although the methods themselves must be further evaluated and updated to allow for their use.

Acknowledgement

Teledyne Tekmar would like to thank Dale Walker of Agilent Technologies for his assistance with this application.

References

1. USEPA Method 524.2, “Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS),” Revision 4.1, 1995.
2. USEPA Method 8260C, “Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS),” Revision 3, August 2006.