Exploration of Suitable Alternatives for GC-MS He Carrier Gas Conservation

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Overview

Purpose: The following methodology explores the use of alternative carrier gasses as well as a system configuration for purge and trap analysis of volatiles optimized for carrier gas conservation.

Methods: Purge and trap GC-MS using a helium conservation device was used to develop a method for the analysis of Volatile organic content. Use of nitrogen as a purging gas for sample introduction was also explored.

Results: Use of nitrogen as a purging gas produced similar results to those found when using traditional helium gas. When used in combination with the helium conservation device the potential for dramatic reductions in helium usage was presented.

Introduction

The impact of increased price and decreased availability of helium continues to drive the need for alternative carrier gases or system adjustments to conserve helium for GC-MS. During sample introduction for volatile organic compound analysis via purge and trap apparatus large amounts of helium are consumed. Various solutions have been attempted to ease the burden of helium shortage including the use of alternate carrier gasses. Observations of hydrogen carrier gas limitations are discussed. Additionally a method was developed for volatile analysis using a innovative He conservation device that limits the flow of helium during sample vaporization in the inlet. The use of nitrogen as a purge gas was employed to decrease helium usage associated with sample preparation.

The following methodology demonstrates the effectiveness of the Atomx automated sample preparation system's nitrogen purge feature in conjunction with Thermo Scientific™ TRACE™ 1300 Gas Chromatograph series Helium Saver inlet at producing quality data while also reducing helium consumption.

Methods

A Tekmar Atomx Automated Sample Preparation System autosampler coupled to a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph, equipped with a instant connect helium saver split/splitless injection module provided 1.0 µL sample introduction into the mass spectrometer. Chromatographic separation was achieved using a Thermo Scientific™ **TraceGOLD** TG-VMS, column with 0.18 mm internal diameter, 20 meter length and 1 µm film thickness. The detection of the volatile compounds was performed using the Thermo Scientific™ ISQ™ LT Single Quadrupole GC-MS system operated in full scan mode. Thermo Scientific™ TraceFinder™ 3.2 software provided automated acquisition and processing of all data, including quantitation and response factor calculations. Extended operating parameters are available in Figure 1.

Sample and Standard Preparations

A nine-point calibration curve was prepared in deionized water, ranging from 0.5–200 ppb. A mixed internal standard and surrogate standard solution was prepared in methanol and injected to a concentration of 25 ppb via the Atomx standard addition system. The preparation of standards was done according to the procedure detailed in U.S. EPA Method 8260C[2].

FIGURE 1. Additional operating parameters for the Purge and Trap GC/MS analysis.

Trace 1310 GC Parameters	
Inlet Module and Mode:	iC He Saver S/SL, Split
Inlet Liner:	Splitless w/glass wool (P/N 453A1925)
Inlet Temperature (°C):	200
Injection Volume (mL):	1.0
Carrier Gas, (mL/min):	He, 1.5
Split flow, (mL/min):	N_2, 12.0
Helium Delay (min.):	0.1
GC Oven Temperature Program	
Initial Temperature:	1min delay, 35°C Hold for 3.0 min
Ramp 1 (°C):	35°C to 300°C @ 14°C/min
Ramp 2 (°C):	300°C to 210°C @ 25 °C/min, Hold for .2 min
Runtime (min.):	14.7
ISQ LT Mass Spectrometer Parameters	
Acquisition Mode, Mass range(m/z):	Full Scan, 35-260
Transfer line (°C):	230
Ionization type:	EI
Ion source (°C):	325

Atomx Purge and Trap Parameters			
Trap:	K Trap	Dry Purge (min):	2
Sample Volume (mL):	5	Dry Purge Flow (mL/min):	100
Sparge Vessel Temp. (°C):	40	Desorb Time (min):	0.5
Purge Gas:	Nitrogen	Desorb Temp. (°C):	250
Purge Time (min):	11	Transfer Line(°C):	140
Purge Flow (mL/min):	40		

Results

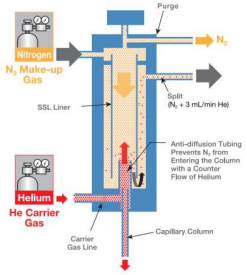
Hydrogen carrier gas migration limitations

- Safety concerns[1]
- Method translation/optimization
- Reduced sensitivity

When used as a purge gas for sample purging unforeseen reactions within the purge and trap apparatus has been reported.

Method Development Using He

FIGURE 2. He saver device layout.



All calibrations are average response factor (Avg RF), unless otherwise noted. Those that did not meet the minimum requirements for Avg RF utilized a 1/X weighted quadratic calibration. The relative standard deviation (%RSD) and Avg RF is reported for each target compound, internal standard, and surrogate standard in Table 1.

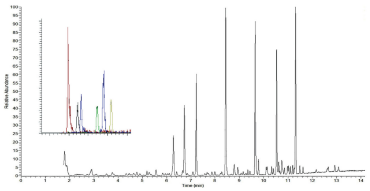
Method detection limits (MDL) were determined for all 91 target compounds. Seven replicates spiked to a concentration of 0.5 ppb were used to determine the MDL of each target compound. One exception was the handling of the para and meta isomers of xylene, which were combined, and therefore analyzed at a concentration of 1 ppb. The MDLs, and their associated %RSDs are also presented in Table 1.

TABLE 1. Calibration and MDL results.

*Denotes r2 value of weighted quadratic calibration
**Denotes MDL calculated at 1 ppb.

Compound	Calibration		MDL		Compound	Calibration		MDL	
	%RSD	Avg RF	(ppb)	%RSD		%RSD	Avg RF	(ppb)	%RSD
Carbon Disulfide	11.44	1.37	0.13	7.58	1,1,2-Trichloroethane	5.85	0.26	0.1	7.62
1,1,2-Trichlorotrifluoroethane	11.62	0.3	0.12	8.43	Dibromofluoromethane (Surr)	7.87	0.63	0.07	4.96
Iodomethane	*0.99		0.18	5.47	Dibromochloromethane	10.02	0.32	0.06	4.62
Allyl Chloride	6.67	0.76	0.16	12.55	1,3-Dichloropropane	5.44	0.62	0.07	5.63
Methylene Chloride	4.91	0.63	0.09	6.95	1,2-Dibromoethane (EDB)	5.5	0.36	0.04	2.9
Methyl Acetate	9.29	0.92	0.11	7.54	Butyl Acetate	8.26	0.91	0.06	4.56
trans-1,2-Dichloroethene	8.33	0.64	0.06	4.27	2-Hexanone	4.2	0.67	0.04	2.94
Acetone	13.63	0.36	0.22	15.08	Ethylbenzene	4.99	1.42	0.07	4.26
Methyl-tert-butyl-Ether (MTBE)	7.49	1.82	0.05	3.23	Chlorobenzene	5.09	0.92	0.07	5.06
tert-Butyl Alcohol	9.37	1.09	0.11	8.49	Chlorobenzene-d5 (IS)	3.09			
Acetonitrile	8.79	0.19	0.28	10.66	1,1,1,2-Tetrachloroethane	9.76	0.81	0.06	4.48
Chloroprene	10.77	0.7	0.04	2.9	m,p-Xylene	5.83	1.18	**0.14	4.79
1,1-Dichloroethane	9.96	0.92	0.06	4.77	o-Xylene	4.99	1.24	0.06	4.14
Acrylonitrile	9.48	0.42	0.12	9.48	Styrene	5.79	1.09	0.07	5.14
Ethyl Acetate	14.24	0.84	0.15	12.8	Bromoform	12.88	0.26	0.1	7.58
Ethyl-tert-Butyl-Ether (ETBE)	8.67	1.69	0.06	4.53	Isopropylbenzene	6.72	1.39	0.07	4.75
Isobutanol	6.28	0.74	0.04	5.42	Amyl acetate	10.54	0.81	0.06	4.68
Isopropyl acetate	6.3	0.73	0.03	5.27	4-Bromofluorobenzene (Surr)	2.31	0.53		
cis-1,2-Dichloroethene	7.33	0.69	0.07	5.32	n-Propylbenzene	7.33	1.6	0.1	6.75
2,2-Dichloropropane	6.5	0.69	0.11	9.28	Bromobenzene	6.52	0.86	0.07	4.88
Bromochloromethane	10.29	0.48	0.08	5.75	1,1,2,2-Tetrachloroethane	6.11	0.53	0.05	4.62
Chloroform	6.38	0.82	0.05	3.63	2-Chlorotoluene	6.47	1.19	0.09	6.31
Carbon Tetrachloride	11.44	0.46	0.12	9.66	1,2,3-Trichloropropane	6.31	0.52	0.09	6.39
Tetrahydrofuran	*0.99		0.07	3.12	trans-1,4-Dichloro-2-Butene	9.25	0.93	0.05	3.95
Vinyl Acetate	9.76	1.23	0.08	6.09	4-Chlorotoluene	3.28	3.41	0.26	18.6
1,1,1-Trichloroethane	9.83	0.62	0.09	6.9	tert-Butylbenzene	5.58	3.41	0.1	7.32
Dibromofluoromethane (Surr)	1.82	0.5			Pentachloroethane	*0.98		0.18	-7.93
2-Butanone (MEK)	7.38	0.43	0.07	5.05	1,2,4-Trimethylbenzene	5.67	3.91	0.07	4.36
1,1-Dichloropropene	9.2	0.85	0.14	9.6	sec-Butylbenzene	7.68	4.54	0.08	5.22
Benzene	5.14	1.36	0.07	5.08	p-Isopropyltoluene	7.4	3.84	0.1	6.49
Propanenitrile	13.15	0.2	0.2	16.09	1,3-Dichlorobenzene	2.6	2.26	0.11	6.93
Pentafluorobenzene (IS)	2.66				1,4-Dichlorobenzene	2.59	2.39	0.06	3.68
tert-Amyl Methyl Ether (TAME)	4.91	1.84	0.14	9.2	1,4-Dichlorobenzene-d4 (IS)	4.48			
1,2-Dichloroethane	8.44	0.41	0.03	2.36	n-Butylbenzene	9.74	3.3	0.1	5.9
Propyl acetate	8.95	0.94	0.04	3.29	Nitrobenzene	*0.98		0.82	-6.92
Trichloroethene	6.98	0.33	0.09	5.79	1,2-Dibromo-3-chloropropane (DBCP)	6.17	0.7	0.22	13.73
1,4-Difluorobenzene (IS)	3.35				1,2-Dichlorobenzene	3.89	2.21	0.08	5.16
Dibromomethane	6.85	0.19	0.07	5.9	Hexachlorobutadiene	8.87	0.24	0.1	6.87
1,2-Dichloropropane	5.46	0.35	0.12	9.22	1,2,4-Trichlorobenzene	7.35	1.46	0.16	9.31
Bromochloromethane	8.24	0.37	0.08	6.47	Naphthalene	9.38	5.33	0.1	7.23
Methyl Methacrylate	11	0.74	0.06	4.44	1,2,3-Trichlorobenzene	6.92	1.45	0.08	4.78

FIGURE 3. Chromatogram with VOC standard at 2 ppb in full scan mode. The inset depicts the extracted ions chromatograms for the first six gases.



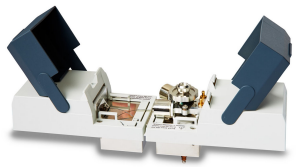
Calibrations meeting the criteria of U.S. EPA method 8260C were achieved in all but two compounds tested, representing a failure rate of 0.02%, well below the limit of 10% for method validation.

Conclusion

Methodology developed using the helium conservation device produced equivalent results to those typically observed when using traditional split/splitless GC inlet and He carrier gas.

- Using nitrogen to replace helium in the inlet during sample introduction with the helium saver drastically reduces the amount of helium consumed during sample analysis.
- Using nitrogen as a purge gas for sample introduction via Purge and trap provides another potential avenue for helium conservation.
- The use of nitrogen mitigates risk associated with migration to hydrogen carrier gas.

The ISQ LT system and Helium Saver inlet combined with the Atomx system nitrogen purge gas provides a solution for reducing the costly burden of high volume helium consumption and reduces the cost of VOC sample analysis.



References

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2. US EPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3, August 2006.

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