Using Hydrogen as the GC Carrier Gas in Combination with the CDS 7550S Pro Automated Thermal Desorber

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Application Note
General

Abstract
With increasing concern about helium availability and continually rising costs, there is a need to find alternatives to helium as an alternative carrier for gas chromatography applications. Hydrogen is the primary candidate as a replacement to helium because of its availability and low cost. This is application note demonstrates that hydrogen can be safely and quantitatively used with the CDS Analytical 7550S Pro Automated Thermal Desorber while reproducibly meeting the US EPA criteria for mass spectrometer performance as demonstrated by the ion ratios of 1-bromo-4-fluorobenzene.

Introduction
Helium has long been the standard as a carrier gas for gas chromatography (GC) due to it's ability to serve as an easy-to-use and efficient mobile phase for gas chromatography. However, due to limited availability and the cost of helium, alternatives for a GC carrier are needed. Nitrogen and hydrogen are commonly used as carrier gas alternatives to helium. Hydrogen is especially attractive not only due to the low cost but also because of increased separation efficiency leads to shorter GC runs and higher sample throughput. The only drawback to using hydrogen as a carrier gas; however, it's high flammability requires heightened safety precautions when in use.

For GC sample introduction techniques, such as thermal desorption, there is a need for demonstrating that hydrogen can also be safely and reliably used in combination with sample introduction instrumentation. The application note demonstrates that the 7550S Pro automated thermal desorber can reproducibly and quantitatively deliver volatile organic compounds to the GC injection port when hydrogen is used as the carrier gas. Additionally, 1-bromo-4-fluorobenzene (BFB), which is a key standard for establishing mass spectrometer performance, is an assessed for it's ion ratios and their stability as it pertains to passing the tuning specifications.

Experimental Setup
A CDS 7550S Pro automated thermal desorber with the automated sample split / sample saver, automated internal standard addition, and cold trapping capability (Peltier) was used for testing. A standard solution of 2000 ppm of benzene, toluene, ethylbenzene, and m-, o-, and p-xylene (BTEX) standard was purchased from Restek. From the stock solution, a 200 ppm BTEX solution was prepared. 1 µL of the 200 ppm BTEX solution was injected onto a pre-conditioned thermal desorption sample tube and purged with nitrogen at 100 mL/min for 1 min. This thermal desorption tube was then loaded into the autosampler rack of the 7550S for analysis. The sample tubes were manufactured by Camsco and packed with Carbograph 1/Carbograph 2/Carboxen 1000 (P/N SU644-4). Once the sample tube was loaded into the tube heater, a 5mL portion gaseous internal standard was automatically added to the sample tube. The internal standard mixture contains benzene-d6, toluene-d8, and 1-bromo-4-fluorobenzene all with a concentration of 2ppmv.

Table 1:

7550S Pro Thermal Desorber:

Valve oven:	250 °C
Tube purge flow:	40 mL/min
Tube Rest temp.:	40 °C
Tube Desorb temp.:	300 °C
Tube Desorb time:	2 min
Sample and Sample Saver Tube:	carbograph 2/carbograph 1/ carboxen 1000
Trap Rest temp.:	-5 °C with Peltier
Trap Desorb temp.:	300 °C
Trap Desorb time:	2 min
Trap Type:	Vocarb 3000
Peltier transfer line:	250 °C
GC transfer line:	250 °C

GCMS QP-2010

GC conditions:

Column:	Restek RTX VMS
Oven temp.:	35.0 °C
Injection temp.:	240 °C
Injection mode:	Split
Pressure:	3.0 psi
Column Flow:	1.44 ml/min
Split Ratio:	2.0 : 1
Temp. program:	35.0 °C hold 4 min 10.0 °C/min to 150.0 °C 50.0 °C/min to 220.0 °C Hold 3.10 min

MS conditions:

Ion Source:	200.00 °C
Interface Temp.:	220.00 °C
Start m/z:	35.00
End m/z:	260.00

The volatile organics desorbed from the thermal desorption sample tube were first split at a user-selected split percent, which was electronically controlled by a mass flow controller. The split percents that were used were 50, 75, 90, and 97.5%. Using 97.5% as an example, split percents are interpreted as 2.5% goes to the focusing trap, and 97.5% is vented. The volatile organics adsorbed by the secondary focusing trap was electronically cooled by a Peltier module. Sample adsorbed inside the focusing trap was then transferred to the GC injection port. Although the 7550S Pro comes equipped with automated sample saver capabilities, it was not utilized as part of the work that is described here. The 7550S Pro and GC-MS parameters are listed in Table 1.

For the components of the BTEX standard, a 5-point calibration curve was constructed from the 4 split percents described in the previous paragraph and from the non-split 200 ppm standard. Therefore, the calibration curve ranges from approximately 5 to 200 ng. The internal standard reproducibility was also assessed. The calibration curve and reproducibility data were established from the integrated peak areas of the extracted ion chromatograms of each target or internal standard.

Finally, the BFB tuning results were also analyzed from the ion ratios in the mass spectra. The mass spectrum was extracted from the apex of the BFB peak in each chromatogram. US EPA Method 524.4 was referred to for the acceptance criteria to establish successful tuning and mass spectrometer performance. The GC conditions shown in Table 1 were selected to ensure that the BFB acceptance criteria were met, in particular for m/z 96. Hydrogenation of some ions is known to occur when hydrogen is used as the carrier gas, and this leads to m/z 96 having a greater relative abundance in the mass spectrum in the case of BFB. This is acknowledged in US EPA Method 524.4, therefore, the acceptance criteria for m/z 96 is different when using hydrogen compared to using helium as a carrier gas.[1]

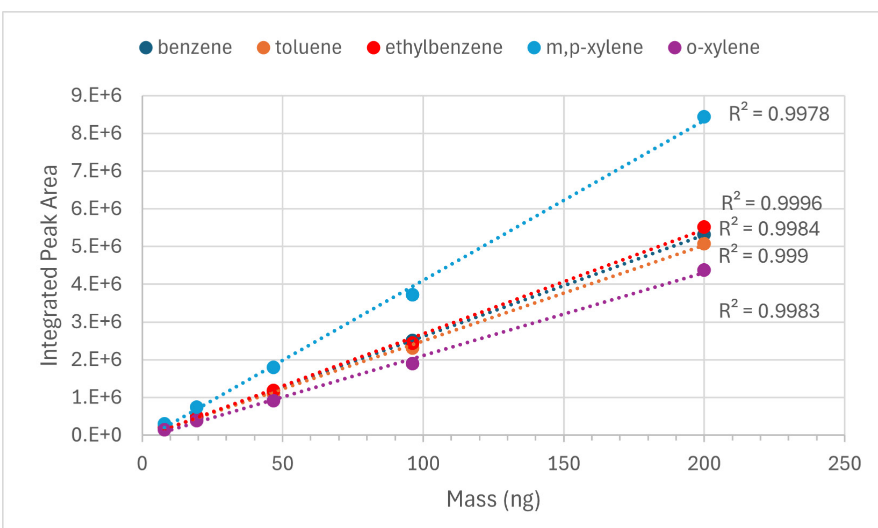

Figure 1. Integrated peak areas vs mass benzene (green), toluene (orange), ethylbenzene (red), m,p-xylene (blue), and o-xylene (purple). Each data point is the average of 4 replicate measurements.

Results and Discussions

Figure 1 shows the 5-point calibration curve for benzene, toluene, ethylbenzene, m-,p-xylene, and o-xylene fit with a linear regression. Each of the linear fits has a $R^2 \geq 0.997$. This indicates quantitative calibration curves can be produced with the use of the 7550S Pro sample splitting capabilities and also by using hydrogen carrier gas in combination with the 7550S Pro. The reproducibility was also analyzed. Table 2 shows the precision as %RSD for each of the BTEX and internal standard components for 12 replicate measurements for 200 ppm BTEX. The %RSD for each of the BTEX components was found to be between approximately 3 and 6% while the internal standard was between approximately 4 and 8%. This indicates that targets can be reproducibly transferred from the thermal desorber to the GC and that the automated internal standard addition of the 7550S Pro is reproducibly added to each thermal desorption tube and transferred to the GC. Figure 2 shows a representative chromatogram for BTEX and internal standard.

From Figure 2, BFB is the last eluting component at 15.4 minutes. A mass spectrum was extracted from the apex point of the BFB peak in each chromatogram. The ion ratios of 7 ions from each spectrum were analyzed based on the criteria outlined in US EPA Method 524.4. Figure 3 shows a representative mass spectrum of BFB while Table 4 shows the ions, the average experimental relative abundance, and whether or not the criteria of method 524.4 are met. Ion 96 particularly presents a challenge for meeting the criteria when hydrogen is used as the carrier gas. This is due to hydrogenation that occurs as a byproduct of using hydrogen. For that reason, the acceptable upper limit of m/z 96 increases from 9% with helium to 15% with hydrogen.[1] In the case of each ion, the criteria were successfully met to demonstrate the mass spectrometer is tuned to the proper criteria. Figure 4 shows each ion over the 10 measurements and how the relative abundance compares to the upper limit (orange) and the lower limit (gray). Each ion in all 10 measurements meets the criteria every time, again demonstrating that the criteria are reproducibly met from run to run.

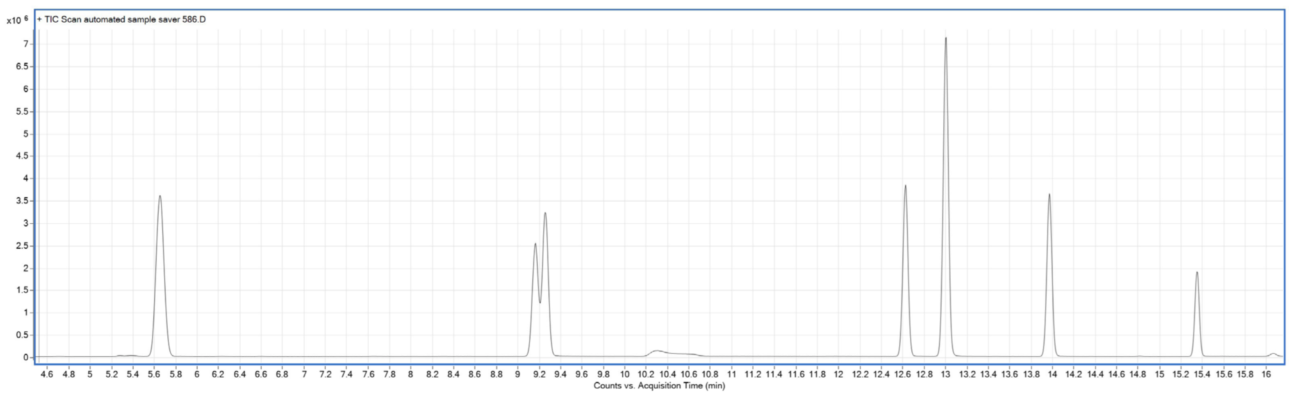

Figure 2. Chromatogram of BTEX standard (200 ppm) and gaseous internal standard (2ppmv).

Table 2. Reproducibility of BTEX standard (200 ppm) and gaseous internal standard (n=12).

Target	%RSD
benzene	6.7
benzene-d6 (IS)	8.2
toluene	5.3
toluene-d8 (IS)	5.9
ethylbenzene	4.2
m,p-xylene	3.4
o-xylene	2.9
1-bromo-4-fluorobenzene (IS)	3.6

Table 3. Average relative abundance of ions for BFB (n=10) and status of pass or fail compared to the criteria of US EPA Method 524.4.

m/z	Relative Abundance	Pass or Fail
95	100%	Pass
96	11.8%	Pass
173	0.6% (relative to 174)	Pass
174	79.6%	Pass
175	7.1% (relative to 174)	Pass
176	95.7% (relative to 174)	Pass
177	6.5% (relative to 176)	Pass

Conclusions

The results here demonstrate that quantitative calibration curves can be produced and internal standard reproducibly added all while using hydrogen as the GC carrier gas in combination with the 7550S Pro thermal desorber. Additionally, the 7550S Pro comes equipped with sample splitting capability that can assist in the production of linear calibration curves. A BTEX standard was used to demonstrate such capability here. Also, the high precision of the internal standard indicates that the 7550S Pro reproducibly adds gaseous standard to the thermal desorption tube each time. Finally, the BFB was used to demonstrate that the mass spectrometer meets the performance requirements outlined in US EPA Method 524.4. The ion ratios all successfully met the criteria and also were to continue to meet those criteria over a series of replicate measurements.

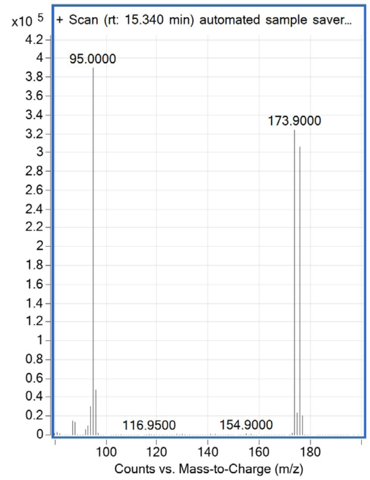

Figure 3. Electron ionization mass spectrum of BFB.

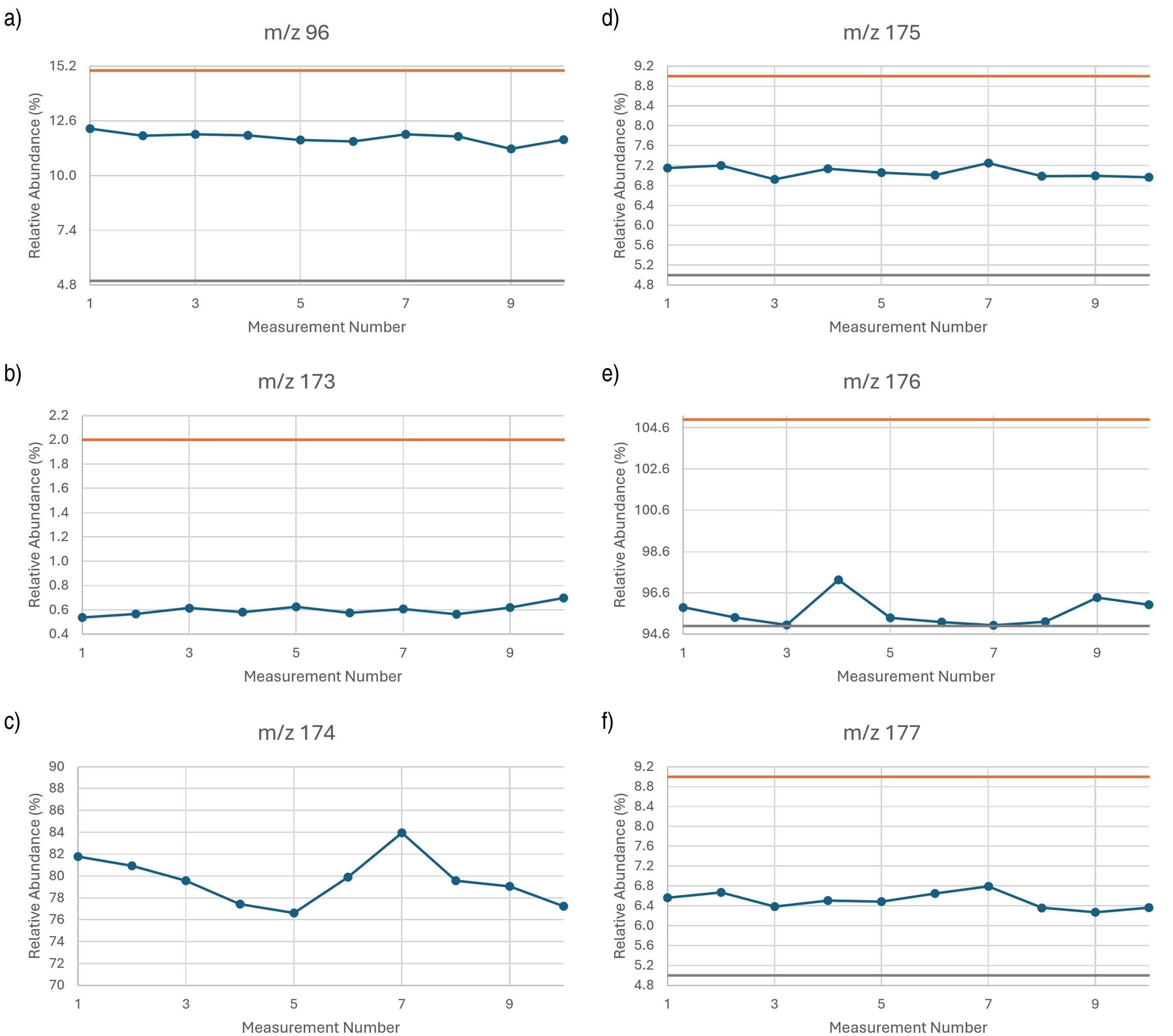

Figure 4. Percent relative abundance for ions, in blue a) m/z 96 b) m/z 173 c) m/z 174 d) m/z 175 e) m/z 176 and f) m/z 177 over 10 replicate measurements. The upper limit for acceptance criteria are in orange, and the lower limit of the acceptance criteria are in gray.

References

1. Environmental Protection Agency. Method 524.4. Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas, 2013.