

Fast GC-MS Analysis of Semi-Volatile Organic Compounds: Migrating from Helium to Hydrogen as a Carrier Gas in US EPA Method 8270

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Overview

Purpose: Optimize US EPA Method 8270 with hydrogen carrier gas

Methods: Configure hydrogen carrier with smaller id column and installation of hydrogen kit on mass spectrometer

Results: Improved peak shape, resolution, and run time

Introduction

The global helium shortage and price increase of this non-renewable noble gas cause more and more laboratories to migrate to hydrogen as a carrier gas. This transition is easy for the gas chromatography (GC) methods utilizing FID, TCD, ECD, and other non-mass-selective detectors. However, for the gas chromatography-mass spectrometry (GC-MS) methods, especially complex and regulated ones, migration to hydrogen carrier gas presents significant challenges. In addition to the changes in chromatographic conditions of the run due to the physical property differences of hydrogen, its chemical reactivity brings about chemical reactions in the mass spectrometer's ion source that do not occur with helium.

The analysis of semi-volatile organic compounds (SVOCs) in wastewater by United States Environmental Protection Agency (EPA) Method 8270¹ involves identification and quantitation of more than 120 analytes of varying chemical structure, polarity and volatility. The diversity of the analytes in this method presents particular challenges when migrating from helium to hydrogen carrier.

GC-MS analysis of SVOCs was performed in accordance with EPA Method 8270 on the Thermo Scientific™ TRACE™ 1310 GC coupled to a Thermo Scientific™ ISQ™ single quadrupole mass spectrometer using helium or hydrogen as carrier gases. Key modifications to both GC and MS hardware and methods are necessary for successfully switching to hydrogen. The final, optimized EPA Method 8270 was fully migrated to hydrogen carrier gas with improved peak shape, resolution, and run time.

Methods

Sample Preparation

All standards were prepared in methylene chloride. A performance mix containing pentachlorophenol, DFTPP, benzidine, and p,p'-DDT was made at a concentration of 50 ppm. A calibration curve was prepared from 1 to 200 ppm with internal standards and surrogates at 40 ppm.

Gas Chromatography

An instant connect split/splitless injector module was used in the split mode. The standard Thermo Scientific™ TraceGOLD™ TG-5MS capillary column (30 m x 0.25 mm x 0.5 µm) was replaced with a TraceGOLD TG-5MS column of smaller i.d. (20 m x 0.18 mm x 0.36 µm). A one microliter injection was made.

Mass Spectrometry

The ISQ mass spectrometer was equipped with the new hydrogen kit and preconditioned by baking out with an elevated hydrogen carrier flow rate.

Data Analysis

Data was collected using Thermo Scientific™ Xcalibur™ 2.0 acquisition software, and processing was performed using Thermo Scientific™ Target 4.14 software. Xcalibur software was configured for direct target processing. A typical chromatogram of a 40 ppm standard is shown in Figure 1.

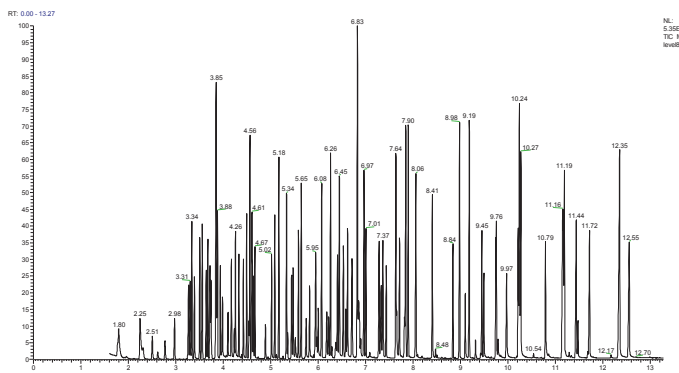


FIGURE 1. TIC of 40 ppm standard with hydrogen carrier gas

Results

Stabilization Bake Out for Hydrogen Carrier Gas

When switching from helium to hydrogen as a carrier gas, a brief stabilization period is required. If using a hydrogen generator, no gas filters are necessary. Gas lines should be plumbed with pre-cleaned 1/8" stainless steel tubing. If a cylinder of hydrogen is used, grade UHP 5.0 or better is required with inline gas purifiers. The hydrogen kit is installed in the mass spectrometer. The source temperature is set to 350 °C for bake out. The hydrogen carrier is set to 4 mL/min. The filament is turned on for one hour during the bake out period. After bake out, the hydrogen flow is reduced to 1 mL/min, and the source temperature was set to 325 °C. Figures 2–5 show the effect of bake out. The hydrogen gas strips the contamination off the entire flow path. If water is present in the gas lines, a m/z of 19 is seen. This is due to protonation of water ($M+1$). Other ions typical of chemical ionization and protonation are also seen, m/z 29 and m/z 41 (Figure 2). Elevated levels of low mass hydrocarbons are observed in the calibration gas spectrum (Figure 4). These all are reduced after the one hour bake out.

FIGURE 2. Air/water spectrum before bake out

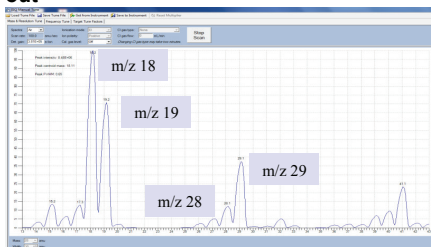


FIGURE 3. Air/water spectrum after bake out

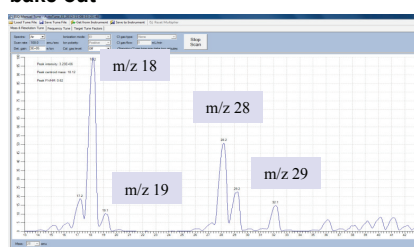


FIGURE 4. Cal gas (FC-43) spectrum before bake out

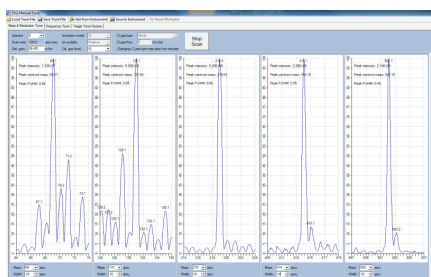
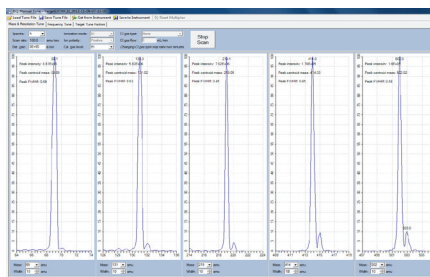


FIGURE 5. Cal gas (FC-43) spectrum after bake out



Selecting the Appropriate Column Dimensions and Inlet Pressure

Due to the lower viscosity of hydrogen carrier gas as compared to helium, a lower head pressure is required to obtain 1 mL/min of column flow rate. By reducing the i.d. of the column, the pressure may be set to usable level (Figure 6). Also note the reduction in the vapor volume of methylene chloride at higher pressures (Figure 7).

FIGURE 6. Comparison of inlet pressure for helium and hydrogen for a 0.25 mm and 0.18 mm i.d. column

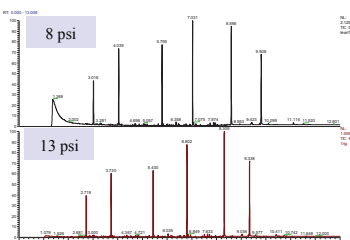
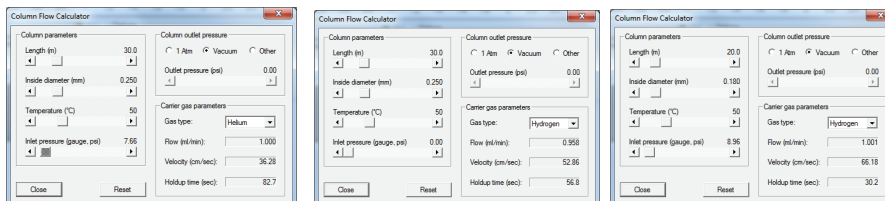


FIGURE 7. Methylene chloride solvent tailing at low vs. high inlet pressures

Peak Shape and Resolution

The advantage of hydrogen carrier is that higher than helium linear velocities can be used without sacrificing resolution. With less residence time in the stationary phase, the late eluting polynuclear aromatic hydrocarbons (PNAs) come out with a narrower peak width (Figure 8). The critical separation of benzo[g,h]flouranthene was easily achieved (Figure 9).

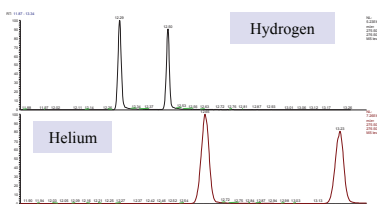


FIGURE 8. Improvement of Peak Shape for Indeno[1,2,3-cd]pyrene (peak 1) & benzo[g,h,i]perylene (peak 2)

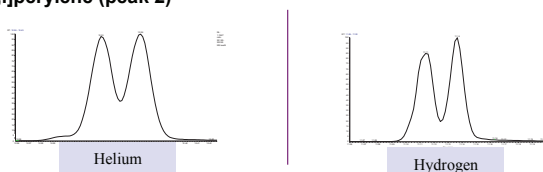


FIGURE 9. Critical Separation of benzo[g,h]flouranthene

Linearity

A linearity study was performed in the range of concentration from 1 to 200 ppm in CH_2Cl_2 . The results are shown in Figures 10 and 11 below. Helium carrier gave lower relative percent standard deviations (%RSD) than hydrogen but still met the criteria for the method. A few compounds required the fit of least squares ($R^2 > 0.99$).

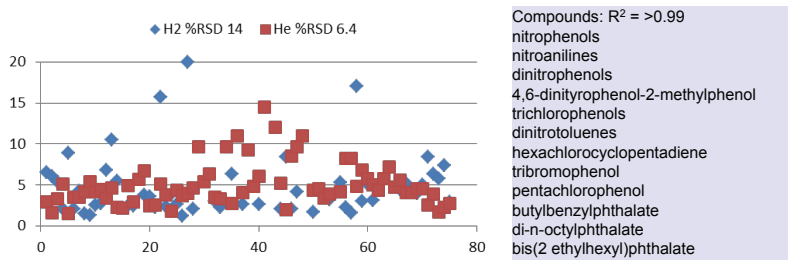


FIGURE 10. Comparison of linearity with helium and hydrogen carrier (the compounds on the insert required R^2 fit with hydrogen)

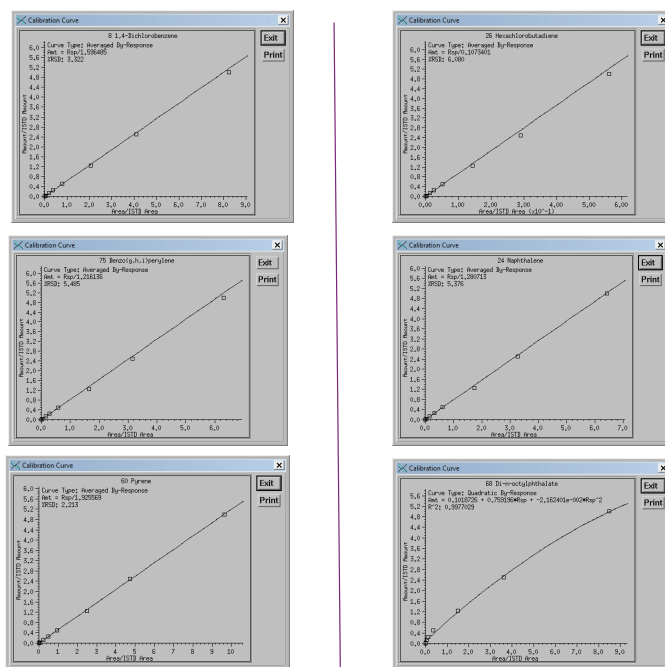


FIGURE 11. Typical linearity plots with hydrogen carrier

Sensitivity

The sensitivity of the method using hydrogen carrier was within a factor of two to that achieved with helium. The average Instrument Detection Limit (IDL) with helium was 0.082 ppm and 0.15 ppm with hydrogen. The chart in Figure 12 shows most of the IDLs at around 0.1 ppm. Replicate injections of the standard were made at 1 ppm.

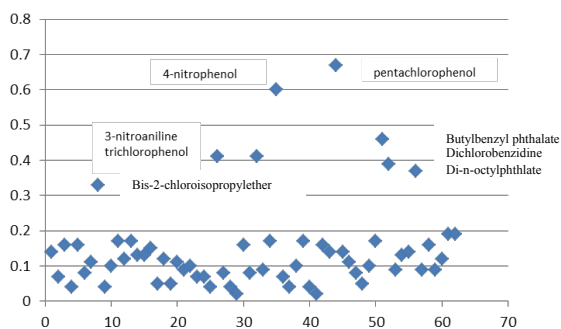


FIGURE 12. Instrument Detection Limits (ppm) Average = 0.15 ppm

Robustness and Ion Ratio Stability

The stability of ion ratios for DFTPP was studied. The values were very stable. The performance is shown in Figure 13. Next, a robustness study was run by injecting 30 of 5 % diesel samples in methylene chloride. The samples also contained 40 ppm of the internal standards. The diesel sample TIC is shown in Figure 14. A chart was plotted of the internal standards in Figure 15. A check standard was run after each set of 10 diesel samples. All check standards met the QC criteria for the method.

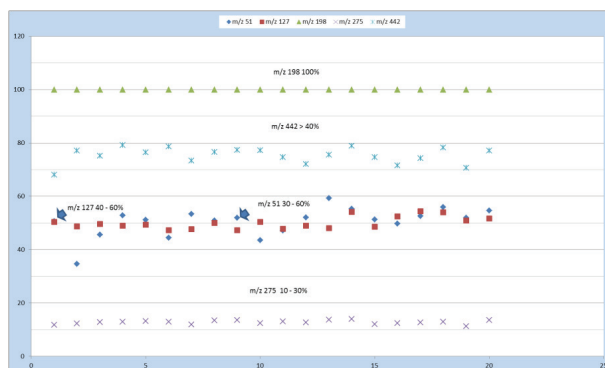


FIGURE 13. Ion Ratios for DFTPP

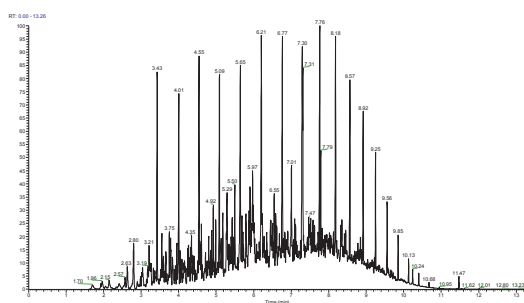


FIGURE 14. TIC 5 % diesel sample

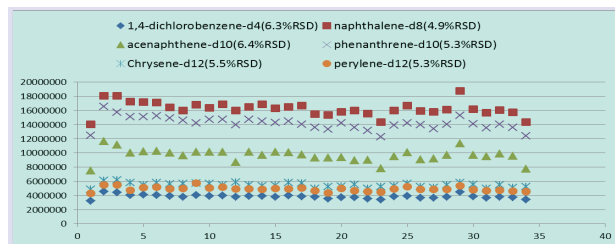


FIGURE 15. Stability of internal standard areas during injection of 5% diesel

Run Time

The run time was reduced by using a smaller i.d. column (TG-5MS 20 m x 0.18 mm x 0.36 μm) and hydrogen carrier gas. The more commonly used column with helium is the TG-5MS 30 m x 0.25 mm x 0.5 μm (Figure 16).

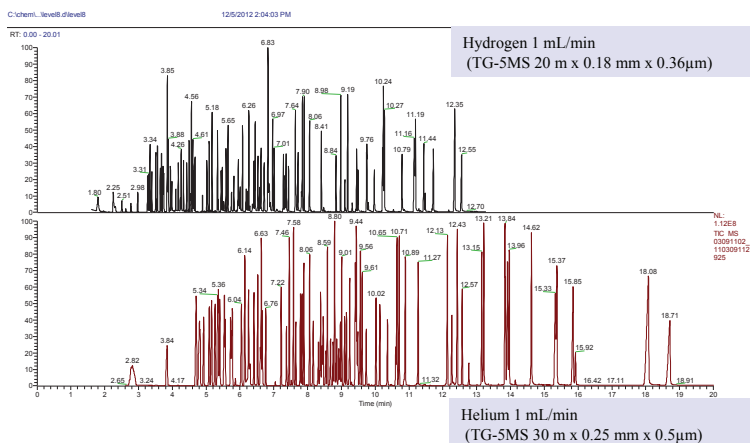


FIGURE 16. Comparison of run time with hydrogen and helium at 1 mL/min

Conclusion

GC-MS analysis of SVOCs was performed in accordance with US EPA Method 8270 on a TRACE 1310 GC coupled with an ISQ single quadrupole mass spectrometer utilizing hydrogen as a carrier gas. Key modifications to both GC and MS hardware and methods necessary for successful migration to hydrogen carrier were performed. The final, optimized EPA Method 8270 fully was migrated to hydrogen carrier gas with improved peak shape, resolution, and run time. The ISQ GC-MS was stable and maintained good ion ratio stability after injecting 5% diesel samples.

- Resolution was good and peak shape was improved
- Linearity met the criteria of the method
- Sensitivity was within a factor of 2 of that obtained with helium carrier gas
- Ion ratio stability and robustness were good
- Run time was shortened

References

1. EPA Method 8270D, Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Rev. 4, 2007, Environmental Protection Agency.

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