

From Helium to Hydrogen: Case Study in the GC-MS Analysis of VOCs and SVOCs

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Overview

Purpose: EPA Methods 8270, 524, and 525 were optimized with hydrogen carrier gas

Methods: Hydrogen carrier gas was configured by using a smaller ID column and adding a hydrogen kit to a mass spectrometer

Results: Peak shape, resolution, and run time improved

Introduction

The global helium shortage and price increase of this non-renewable noble gas cause more and more laboratories to migrate to the use of hydrogen as a carrier gas. This transition is easy for the GC methods utilizing FID, TCD, ECD, and other non-mass-selective detectors. However, for the 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 reactivity brings about chemical reactions in the mass spectrometer's ion source that do not occur with the use of helium.

The analyses of semi-volatile organic compounds (SVOCs) in wastewater by EPA Method 8270¹ and volatile organic compounds (VOCs) in drinking water by EPA Methods 524² and 525³ involve identification and quantitation of well over a hundred 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 on a Thermo Scientific™ TRACE™ 1310 GC coupled to a Thermo Scientific™ ISQ™ Series single quadrupole mass spectrometer utilizing helium and hydrogen carrier gases. Key modifications to both GC and MS hardware and methods are necessary for successful migration to hydrogen carrier gas. The final, optimized EPA methods were migrated to hydrogen carrier gas with improved peak shape, resolution, and run time.

Methods

Sample Preparation

For EPA Method 8270, 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. For EPA Method 524, a 5 mL volume of water was used in a purge and trap concentrator (Eclipse 4660 Purge-and-Trap Sample Concentrator, OI Analytical), and a calibration curve from 0.4 to 200 ppb was run. For EPA Method 525, a 1 L volume of water was extracted with ethyl acetate. A calibration curve was run from 0.1 to 10 ppm.

Gas Chromatography

For EPA Methods 525 and 8270, an Instant Connect split/splitless injector module was used in the split mode. A one microliter injection was made. The standard Thermo Scientific™ TraceGOLD TG-5MS capillary column (30 m × 0.25 mm × 0.5 μm film) was replaced with a TraceGOLD TG-5MS column of smaller ID (20 m × 0.18 mm × 0.36 μm film). For EPA Method 524, a purge and trap (P&T) adapter was used to make the injection of gases purged from water sample of 5 mL volume onto a TraceGOLD TG-VMS column of smaller ID (20 m × 0.18 mm × 1.0 μm film).

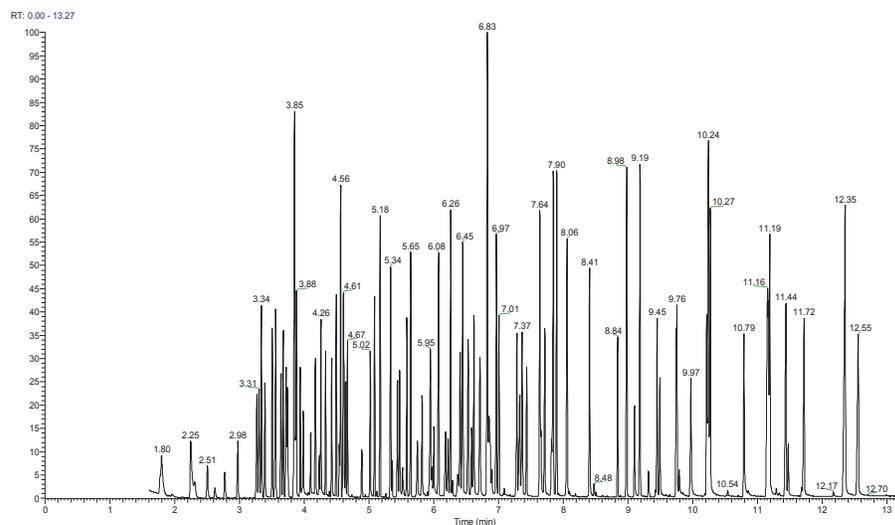
Mass Spectrometry

The ISQ Series mass spectrometer was equipped with a hydrogen kit. The instrument was preconditioned by baking it out with an elevated hydrogen carrier flow rate with the EI ion source filament turned on for one hour.

Data Analysis

Data was acquired using Thermo Scientific™ Xcalibur™ 2.0 software and processed using either Thermo Scientific™ Target 4.14 or Thermo Scientific™ TraceFinder™ 3.0 software. The 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 EPA Method 8270 standard with hydrogen carrier gas.



Results

Stabilization Bake out for Hydrogen Carrier Gas

When switching from helium to hydrogen carrier gas, a brief stabilization period is required. If using a hydrogen generator, no gas filters are necessary. Gas lines should be plumbed with new, pre-cleaned 1/8 in. stainless steel tubing. If a cylinder of hydrogen is used, grade UHP 5.0 or better is required with in-line 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 desorbs the contamination off the entire flow path, and the reactive hydrogen species formed in the ion source clean it out. 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.

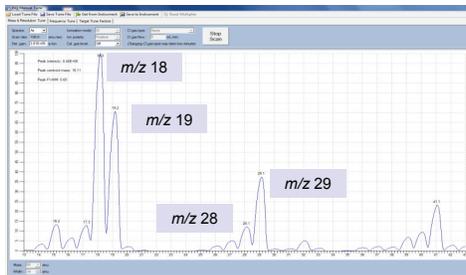


FIGURE 3. Air/water spectrum after bake out.

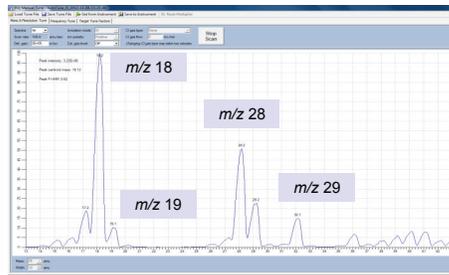


FIGURE 4. Cal Gas (FC-43) spectrum before bake out.

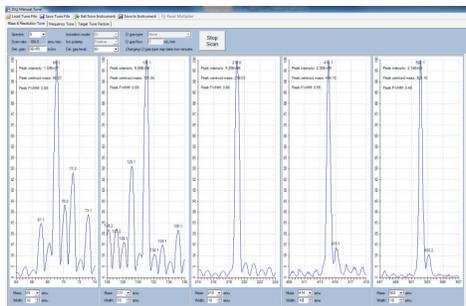
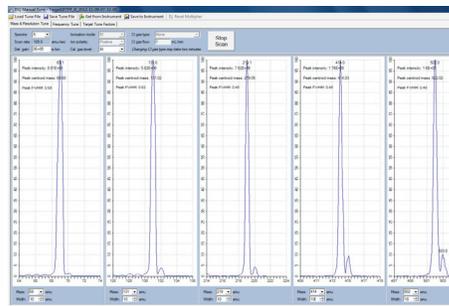


FIGURE 5. Cal Gas (FC-43) spectrum after bake out.



Selecting the Appropriate Column Dimensions and Inlet Pressure

Due to the lower viscosity of hydrogen carrier gas compared to helium, a lower head pressure is required to obtain 1 mL/min of column flow rate. By reducing the ID of the column, the pressure may be set to a 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 ID column.

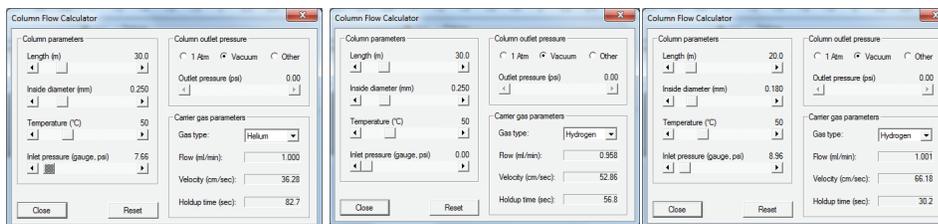
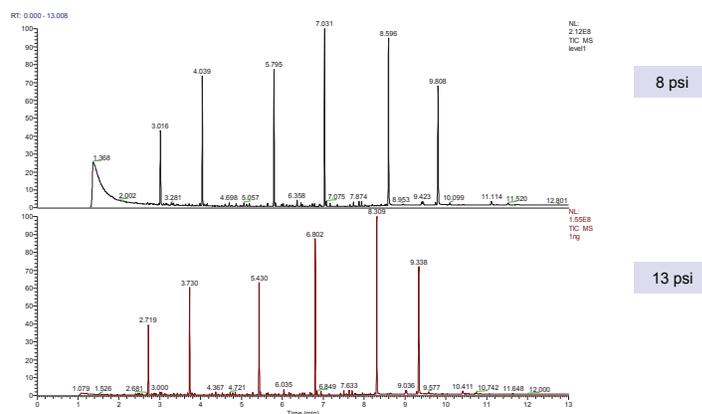


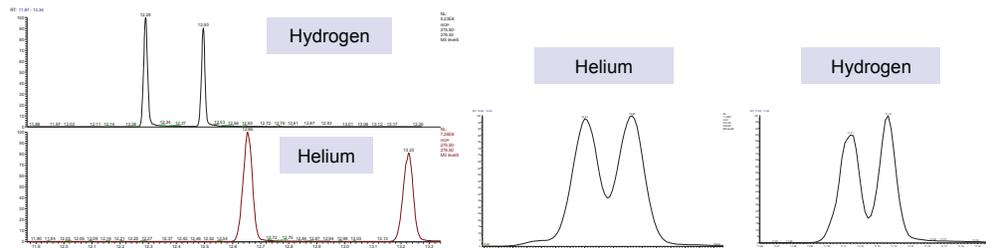
FIGURE 7. Methylene Chloride solvent tailing at low vs. high inlet pressures.



Peak Shape and Resolution

The advantage of hydrogen carrier gas is that higher than helium linear velocities can be used without sacrificing resolution. By spending less time in the stationary phase, the late eluting polynuclear aromatic hydrocarbons (PAHs) come out with a narrower peak width, and the critical pair of benzo[*g,h*]fluoranthenes was easily separated (Figure 8).

FIGURE 8. Improvement of Peak Shape for Indeno[1,2,3-*cd*]pyrene & benzo[*g,h,i*]perylene and separation of the critical pair of benzo[*g,h*]fluoranthenes.



Linearity

A linearity study was performed in the range of concentration from 1 to 200 ppm in CH₂Cl₂ for EPA Method 8270. The results are shown in Figures 9 and 10 below. Helium carrier gas 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 9. Comparison of linearity with helium and hydrogen carrier (the compounds on the insert required R² fit with hydrogen).

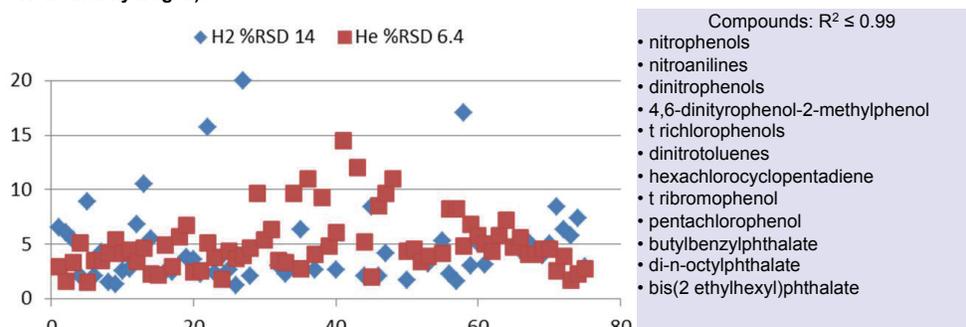
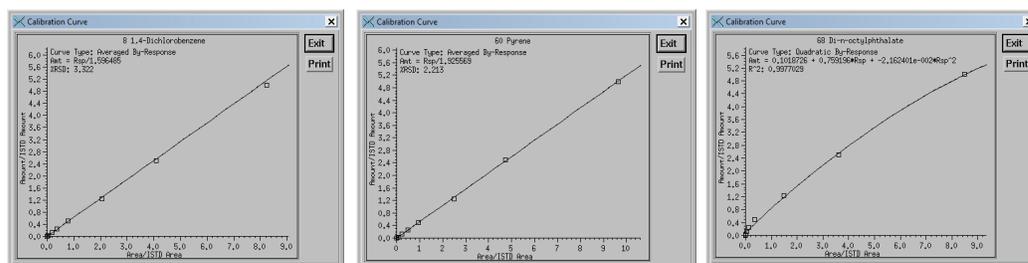


FIGURE 10. Typical linearity plots with hydrogen carrier gas.



A linearity study was performed in the range of concentration from 0.05 to 10 ppm for EPA Method 525. An excerpt of results for the PAHs is shown in Figure 11. Similarly, for EPA Method 524, a linearity study was performed in the range of concentration from 0.4 to 200 ppb.

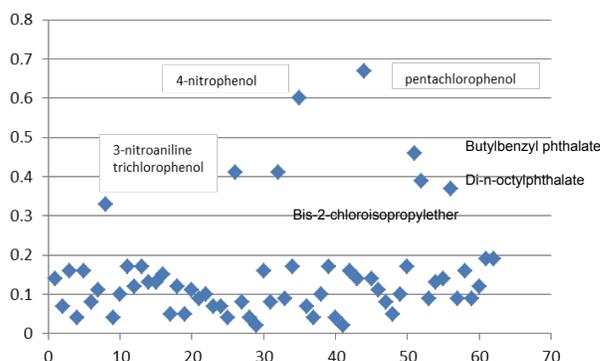
FIGURE 11. Typical linearity of PAHs in EPA Method 525 with hydrogen carrier gas.

Compound	%RSD	Compound	%RSD
naphthalene	6.1	flouranthene	6.7
2-methylnaphthalene	8.7	benzo(a)anthracene	8.2
1-methylnaphthalene	7.7	chrysene	5.9
acenaphthylene	8.5	benzo(b)fluoranthene	8.6
acenaphthene	8.5	benzo(k)fluoranthene	9.2
flourene	8.5	benzo(a)pyrene	7.8
phenanthene	3.8	indeno(1,2,3,c,d)pyrene	5.1
anthracene	7.0	dibenz(a,h)anthracene	5.4
pyrene	3.6	benzo(g,h,i)perylene	6.0
acenaphthene-d10	4.6	phenanthene-d10	4.5
chrysene-d12	9.7	perylene-d12	7.4

Sensitivity

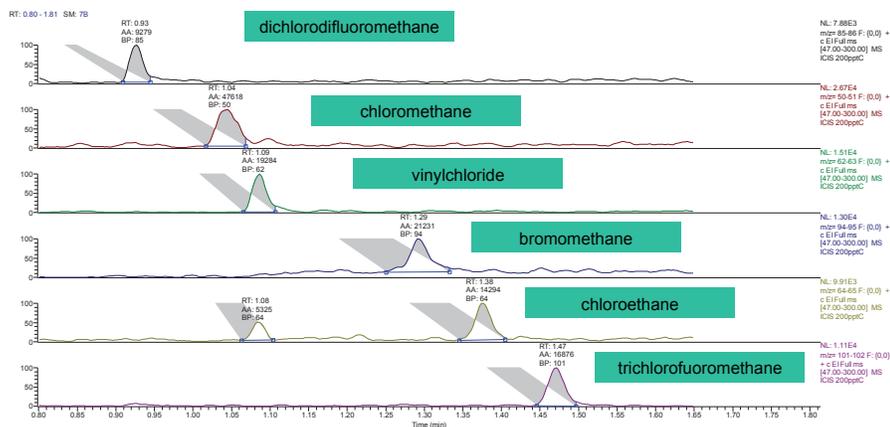
The sensitivity of the EPA Method 8270 using hydrogen carrier was within a factor of two to that achieved with helium. The average Instrument Detection Limit (IDL) with helium was 0.08 ppm and 0.15 ppm with hydrogen. The chart in Figure 12 shows most of the IDLs are around 0.1 ppm. Replicate injections of the standard were made at 1 ppm.

FIGURE 12. EPA Method 8270 Instrument Detection Limits (ppm) Average = 0.15 ppm.



Instrument detection limits for EPA Method 524 were determined by running replicate injections at 0.4 ppb. The average IDL was 0.074 ppb (74 ppt) vs. 0.048 ppb (48 ppt) with helium. Excellent sensitivity for the first six gases, even at as low level as 200 ppt, was obtained (Figure 13).

FIGURE 13. EPA Method 524 first six gases at 200 ppt with hydrogen carrier gas.



Robustness and Ion Ratio Stability

The stability of ion ratios for DFTPP and BFB was studied. The values were very stable (Figure 14). Next, a robustness study was run for EPA Method 8270 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 15. A chart with the internal standards plotted is shown in Figure 16. A check standard was run after each set of 10 diesel samples. All check standards met the QC criteria for the method.

FIGURE 14. Ion ratio stability for DFTPP (left) and BFB (right).

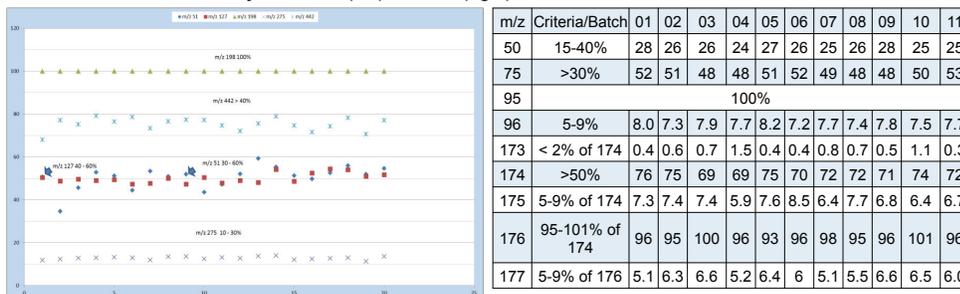


FIGURE 15. TIC 5% diesel sample.

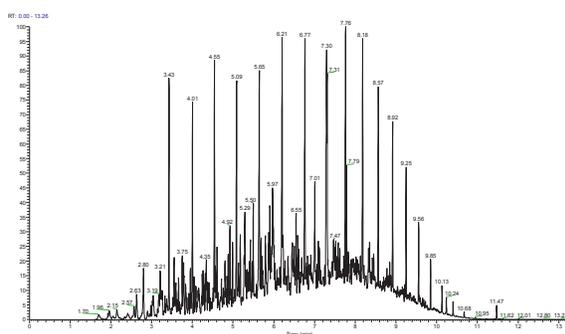
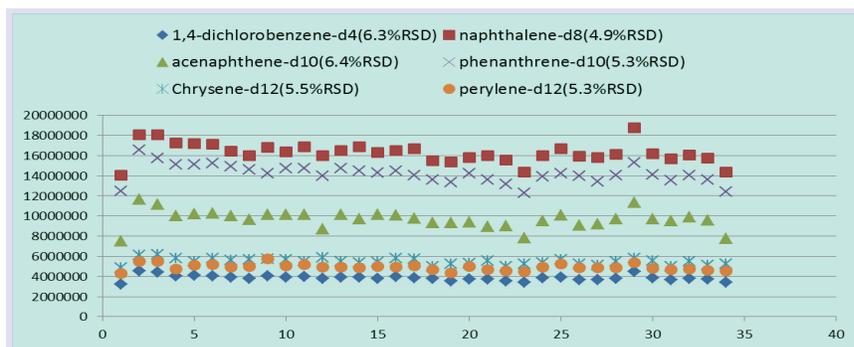


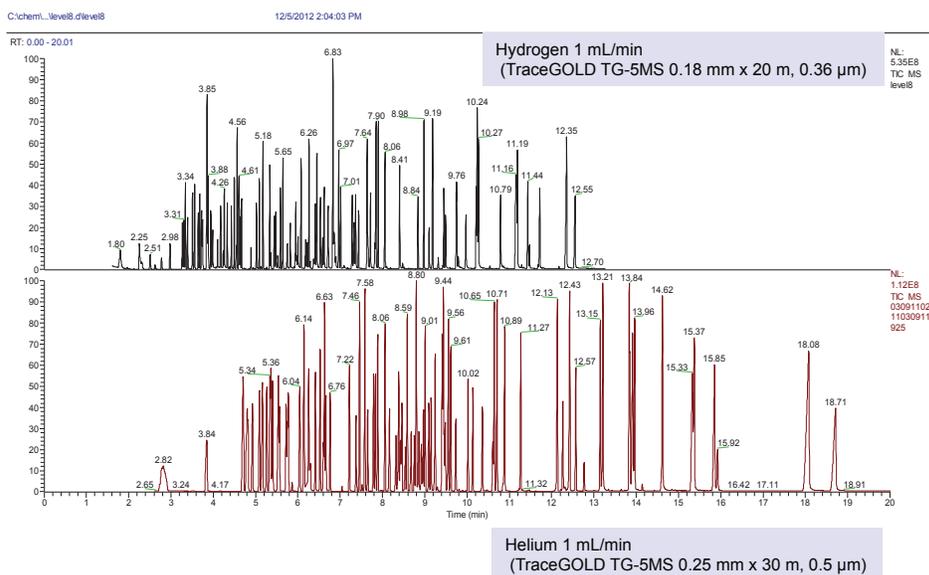
FIGURE 16. Stability of internal standard areas during injection of 5% diesel.



Run Time

The run time for EPA Method 8270 was reduced by using a smaller ID column (TraceGOLD TG-5MS 0.18 mm x 20 m x 0.36 μ m) and hydrogen carrier gas. The more commonly used column with helium is the TraceGOLD TG-5MS 0.25 mm x 30 m x 0.5 μ m. (Figure 16).

FIGURE 17. Comparison of run time with hydrogen and helium at 1 mL/min.



Conclusion

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

- Good resolution and improved peak shape
- Linearity met the criteria of the method
- Sensitivity was within a factor of 2 of that obtained with helium carrier gas
- Good ion ratio stability and robustness
- Shorter run time

References

1. EPA Method 8270D, Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) REV. 4, 2007, Environmental Protection Agency.
2. EPA Method 524.2, Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry. Rev. 4.1, 1995.
3. EPA Method 525.2, Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/mass spectrometry. Rev.2, 1995.

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