

Unintended Consequences with Conversion to Hydrogen Carrier in Gas Chromatography

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INTRODUCTION

Carrier gas is an important component in generating a gas chromatogram. The analytes must be transported through the column by the carrier for them to fully interact with the stationary phase to achieve a separation of the different target species. The choice of carrier gas is limited by demands of the measurement. These requirements include:

- Inert, to avoid any chemical interaction with sample analytes and column degradation.
- Appropriate for detector used.
- Optimum flow rate achievable to minimize peak width while shortening run time.
- Readily available.
- Pure.
- Inexpensive.

In the early days of gas chromatography, helium and nitrogen were commonly deployed as carrier gas, as they met all of the requirements when used with packed columns and worked quite well, and were interchangeable for most applications. Advent of capillary columns in the late 1970's generated a mass conversion to helium to take advantage of the improved analyte transfer between the capillary stationary phase and the carrier gas with the narrower columns. Now with supplies of helium dwindling and helium price soaring, hydrogen is being considered often as a direct replacement as a carrier gas.

Hydrogen is obviously very reactive. When used as carrier gas, it can alter the structure of analytes in the chromatographic process, impact column performance and change the dynamics in detectors. When mixed with air, hydrogen can form explosive mixtures over a wide range of concentrations. At atmospheric pressure, hydrogen is combustible at concentrations from 4% to 74% by volume,¹ has the highest burning velocity of any gas and very low ignition energy, and can self-ignite if allowed to expand rapidly. Despite these concerns, hydrogen has been in common use in many parts of the world where helium has already been difficult to procure.

Much of the on-going discussions in various forums involving the conversion from helium to hydrogen has centered on impacts with enhancements of hydrogen in faster and sharper peaks from its lower viscosity. Not much is presented on the impacts on the whole chromatographic process, especially regarding detectors.

The following discussions provide important considerations in the transition over to hydrogen carrier involving all aspects of the chromatographic process. Many impacts may not be expected and can have major unintended consequences on operations of the gas chromatographic system.

DISCUSSION

Standard Operating Procedures

Conversion to hydrogen can have extraordinary effects on overall performance of a gas chromatographic method, and can dramatically alter injection, column chromatography and detector operations. Some standard methods, especially ones involving FDA and EPA procedures, do not allow any deviations until the complete protocol is revalidated. This new effort to fully document a change to hydrogen carrier gas can require substantial efforts.

Pneumatic Components

Flow controllers are usually calibrated to a specific gas, but often can be reset to other gases. Changing the gas without specifying the gas type, for example, from helium to hydrogen, can dramatically alter the actual flows from the specified set points. Flows should be reverified with a calibrated flowmeter. Pneumatic component calibration can be adjusted with K-factors related to the physical characteristics of the gas. Some electronic controllers have user entries to automatically perform this correction.

Hydrogen being the smallest gas is more prone to leaks than the others. Careful reassessment that all pneumatic fittings remain intact is important to ensure that the change to hydrogen did not provoke unanticipated leaks. The best tool for locating these leaks is a high performance leak detector, based on a thermal conductivity detector, with sensitivity to 0.0005 ml/min.

The inherent reactivity of hydrogen often cleanses pneumatic pathways and can generate unexpected backgrounds at the detector. An overnight purge of the system, especially at elevated temperatures, can help stabilize the detector signal.

Filters can be set up in the incoming gas lines to reduce contamination from hydrocarbons, oxygen and moisture. Normally these filters come prepacked in nitrogen or helium, and will need to be fully purged with hydrogen before use. Purifiers with heat-activated gettering-alloys cannot be used with hydrogen.

Injectors

The reactivity of hydrogen and the presence of reactive surfaces in injectors can alter the chemical make-up of many analytes, especially olefinic species, such as styrene and ethene. The reducing atmosphere with hydrogen can chemically transpose these into their saturated forms prior to separation in the column, and reduce reported concentrations for the original species. An inert pathway must be provided to minimize this effect. Also, a pulsed split injection can move analytes quickly through the injector innards, again to reduce this transformation. Glass wool in the injector liner should be avoided, as this surface provides more sites for reactions to occur.

Another issue is possible formation of acids in hot injectors from solvents used in the injection process, including conversion of dichloromethane to hydrochloric acid and carbon disulfide to hydrogen sulfide. This chemical transformation can have debilitating effects on the entire instrument system and can dramatically impact use of these solvents.

Excess carrier flow from split operations with a split/splitless injector is commonly vented into the laboratory environs. With hydrogen, this vent flow should be appropriately vented into a hood to minimize risks with the potential accumulation of hydrogen around the instrument.

Purge/Trap with Nitrogen Purge

Although many of the EPA methods involving purge and trap operations do not specifically indicate the purge gas choice, most analytical laboratories use helium for both purging and column carrier gas. EPA Methods 524.3² for purgeable organics in drinking water is an exception and specifically lists helium as the purge gas, and a new revision, Method 524.4,³ is set up for nitrogen purge. Comparing performance provided in the methods, and listed for representative analytes in Tables I and II, shows degradation in recoveries and detection limits with nitrogen over helium. These differences can be attributable to the change in the diffusion rate across the water/gas interface, explained by Graham's Law of Diffusion:

$$diffusion\ rate \propto 1/\sqrt{density}$$

with nitrogen having a large detrimental effect over helium, as listed in Table III.

Table I. Comparisons of Percent Recoveries from EPA Methods 524.3 and 524.4 for representative analytes at 0.50 µg/L

Analyte	EPA 524.3 (helium purge)	EPA 524.4 (nitrogen purge)
Dichlorodifluoromethane	115	77.4
Vinyl chloride	108	103
Benzene	100	81.6
Ethylmethacrylate	103	90.9
o-Xylene	92.1	77.3
1,2,4-Trichlorobenzene	85.0	90.7

Table II. Comparisons of Detection Limits from EPA Methods 524.3 and 524.4 for representative analytes

Analyte	EPA 524.3 (helium purge)	EPA 524.4 (nitrogen purge)	Percent Change
Dichlorodifluoromethane	0.016	0.12	+750%
Vinyl chloride	0.029	0.063	+217%
Benzene	0.017	0.058	+341%
Ethylmethacrylate	0.030	0.10	+333%
o-Xylene	0.010	0.11	+250%
1,2,4-Trichlorobenzene	0.013	0.071	+367%

Table III. Comparisons of Densities and Diffusion Rates for common carrier gases⁴

Gas	Density (kg/m ³)	Diffusion Rate relative to He
Hydrogen	0.0899	1.41
Helium	0.1785	1.00
Nitrogen	1.2506	0.38
Argon	1.7837	0.32

Chromatography

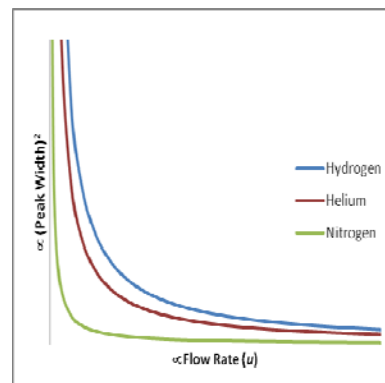
Effects on Peak Sharpness – The interaction of analytes in the chromatographic process is very dependent on their ability to partition in and out of the stationary and mobile phases. J.J. van Deemter, et alii,⁵ related characteristics of the process to a simple equation:⁶

$$(\text{peak width})^2 \propto A + B/u + C * u$$

where A, B and C are constants for a given chromatographic condition, and u is linear velocity [related to column flow rate]. “A” represents eddy diffusion from turbulent flow, “B/ u ” term relates the contribution from diffusion along the length of the column, and “C* u ” defines the resistance for analytes to migrate in and out of the stationary and mobile phases.

The eddy diffusion term is negligible with capillary columns for all carrier gases, as flows approach laminar flow over the length of the column and do not exhibit much turbulence except at the injector. Nitrogen, being the least diffusive of the common carrier gases, generates the sharpest peaks at lower flows, whereas hydrogen being the most diffusive is less effective at low flows (Figure 1). However, the lower viscosity of hydrogen makes its contribution to “resistance to mass transfer” between the mobile and stationary phases smaller and over a longer flow span (Figure 2). After combining all factors together (Figure 3), hydrogen is clearly the better choice to achieve

Figure 1. Plots of Longitudinal Diffusion for common carrier gases



faster run times and still accomplish adequate separations. However, some published reports have shown peak distortions occurring with hydrogen carrier that was attributed to decomposition of analytes with reactive hydrogen during the chromatographic process.⁷

Packed columns, with compatible detectors, can use alternatively hydrogen, nitrogen or argon with little chromatographic changes, as eddy diffusion dominates the van Deetmer plots for packed columns and is nearly independent of carrier selection.

Conversion of Carbon Monoxide and Carbon Dioxide to Methane – Detection of carbon monoxide and carbon dioxide can be enhanced by catalytically converting them post-column to methane with a reduction catalyst packed with nickel with added hydrogen flow. With hydrogen carrier, this reaction can occur when these analytes pass by active metal surfaces earlier in the chromatographic process, such as valves and associated interconnecting tubing. Now the chromatography becomes a separation of transformed methane from these compounds. The final results are dramatically distorted, and the true concentrations for carbon monoxide and carbon dioxide are underreported.

Detectors

Many gas chromatographic detectors use hydrogen as a fuel gas to generate the chemical species to detect. Their performance is usually dependent on the optimization of the fuel flow. Hydrogen coming from the carrier gas must then be consistent across the chromatogram to maintain performance, especially with column temperature programming. True flow controllers set a flow rate and then allow the column backpressure to adjust to maintain this mandated steady flow. These devices can inherently keep hydrogen flow constant and independent of column temperature. Split/splitless injections mandate a pressure controller to allow flexibility in maintaining carrier though the column with various settings on split operations. With constant pressure maintained over the

Figure 2. Plots of Resistance to Mass Transfer for common carrier gases.

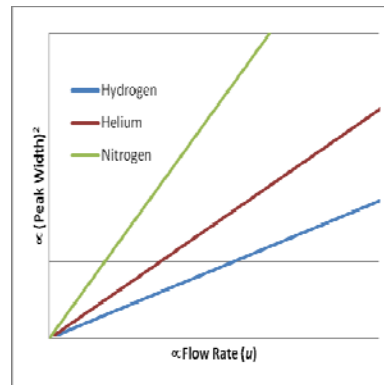


Figure 3. van Deetmer plots for common carrier gases.

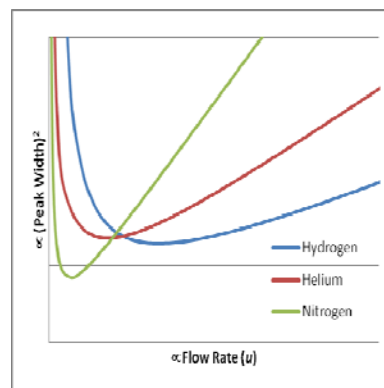
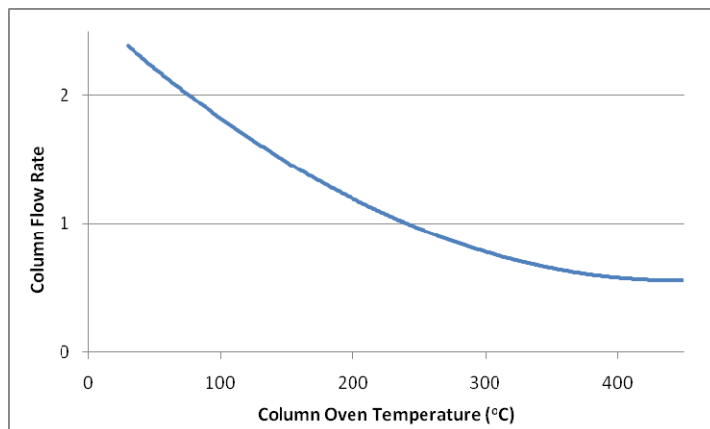


Figure 4. Change in flow rate with constant column head pressure versus column oven temperature.



temperature program of the column, hydrogen carrier becomes more viscous due to Gay-Lussac's Law and gives lower flows at higher temperatures, as shown in Figure 4.

Some chromatographs can specify operation of the pneumatic flow in "constant flow". Here pressures are set up in time-program ramps based on the calculation from Hagen-Poiseuille equation to match the column temperature ramps and provide a constant calculated flow. As many chromatographic detectors are impacted by changes in hydrogen fuel settings, this mode is preferred to maintain optimum performance for these detectors. Detector hydrogen fuel flows need to be adjusted for the added hydrogen from carrier, especially detectors with low hydrogen flow settings.

Thermal Conductivity Detector (TCD) – This detector's sensitivity is largely due to the difference in conductivity between the analyte and the carrier gas; a larger difference will enhance peak size for analytes by typically 25% for hydrogen over helium. Table IV illustrates the effects of a change in detector gas for common carrier gases. If a protocol is established with helium as carrier, conversion to hydrogen will boost analyte responses and change the calibration curves, rendering the procedure subject to reevaluation.

Table IV. Comparison of Thermal Conductivities for Common Gases.

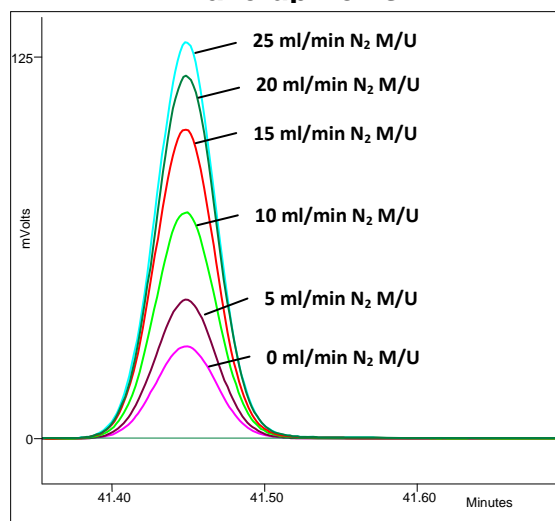
Analyte	Relative Conductivity to Hydrogen	Relative Conductivity to Helium	Relative Conductivity to Nitrogen	Relative Conductivity to Argon
Hydrogen	1.00	1.25	7.17	10.36
Helium	0.80	1.00	5.72	8.27
Neon	0.26	0.32	1.84	2.66
Methane	0.19	0.24	1.36	1.96
Oxygen	0.14	0.18	1.04	1.50
Nitrogen	0.14	0.17	1.00	1.45

Flame Ionization Detector (FID) – This detector uses a hydrogen diffusion flame to burn organics to generate electrons that are then measured with an electrometer. The resulting signal is then related to standards to yield a concentration for unknowns. A pure hydrogen flame is very diffuse in its flame cone and results in poorer response, compared with using an insert gas, such as helium or nitrogen, as a make-up flow (Figure 5). Since nitrogen is less diffusive than helium, the flame is tighter and hotter, the signal is enhanced by nearly a factor of two,⁸ and helium use is eliminated. Eliminating the inert make-up flow completely yields a drop of 76% from the optimum.

Sulfur Chemiluminescence Detector (SCD) – Some chemiluminescence detectors have a dual burner design with the first one being oxygen-rich to convert sulfur to sulfur monoxide for later reaction with ozone to produce light proportional to the concentration of sulfur. Addition of extra hydrogen from the column effluent could dramatically alter the chemistry at this burner. If hydrogen carrier is less than 5 ml/min, then the hydrogen feed gas to the detector can be reduced appropriately. Higher flows with Megabore columns require a change in the physical setup for this detector to reduce an unintended alteration of the chemistry at the first burner.

Thermionic Specific Detector (TSD) – With this “nitrogen-phosphorus” detector, hydrogen is aimed at a heated rubidium bead to form a “cold plasma” around the bead. When organic analytes possessing nitrogen or phosphorus atoms elute from the column into this detector, they cause a reduction in the work function of the bead and create an increase in release of electrons, which are then detected. The optimum performance of this detector is critically dependent on the flow of hydrogen past the bead, and is typically around 3.8 ml/min. Any additional contribution from hydrogen carrier must be deducted from the flow set through this detector’s pneumatics. As some column flows can surpass this limit, especially for wider bore capillary columns, the total flow generated may exceed the optimum detector flow and can impact detector performance, or could change the chromatography if lower column flows are chosen instead.

Figure 5. Changes in FID response for various nitrogen make-up flows



Electron Capture Detector (ECD) – Electron capture detector uses a ^{63}Ni layer on stainless steel substrate to generate an electron cloud that is reduced when an electrophilic analyte emerges from the column end and grabs onto these electrons. This reduction is what generates a response related to analyte concentrations. Hydrogen in the detector, especially at elevated temperatures, forces ^{63}Ni deeper into the interstitial substrate, leading to moderation of the electron energy by these trapped species, and thus losing the detector’s activity.⁹ Hydrogen should not be utilized with this detector, either as a carrier, or as a cleaning agent, without rendering the detector permanently damaged.

Pulsed Discharge Detector (PDD) – Pulsed discharge detectors utilize a stable, low powered, pulsed DC discharge of helium as an ionization source. Eluents from the column, flowing counter to the flow of helium from the discharge zone, are ionized by photons from the helium discharge. Obviously hydrogen cannot be deployed as a carrier in these applications, as it too would be detected, and would give a dramatically huge background signal, rendering the detector’s purpose ineffectual. Helium carrier is mandated for this detector. Valco Instruments has recently introduced a new version of this detector that requires only 1/5 of the amount of helium as an earlier model.¹⁰

Pulsed Flame Photometric Detector (PFPD) – This detector is critically reliant on establishing a specific mode of pulsations with a sequence of filling with combustible gases, ignition (“tick”) and propagation of the flame (“tock”) and subsequent emission from the excited species. This “tick-tock” operation is very dependent on the ratio of hydrogen to air in the detector reaction chamber, and any change in one can alter performance. With hydrogen as carrier, detector flows must be adjusted based on set column flow, as indicated in Table V.¹¹

Table V. Optimum Flow Settings for Pulsed Flame Photometric Detector.

Carrier Gas	Carrier Gas Flow Rate (mL/min)	H ₂ (mL/min)	Air-1 (mL/min)	Air-2 (mL/min)
Helium	2	13	17	10
	5	13	20	10
	10	20	33	10
Hydrogen	2	11	17	10
	5	9	18	10
	10	15	31	10
Nitrogen	2	14	17	10
	5	16	21	10
	10	24	33	10

Mass Spectrometer (MS) – This technique is based on an ionization process of chemical species in the spectrometer’s source to generate charged molecules and fragments, separating the ions with a mass analyzer and then on to a detector. While helium is not normally ionized in this course, hydrogen is and yields an abundance of protons surrounding all of the analyte ions. This path can alter the character of the species and change their mass spectra,⁷ especially with olefins and aromatics. This possible protonation is very dependent on the source design and the pressure buildup in the source, especially with lower pump capacities. Although many spectra with hydrogen carrier will still generate acceptable matches against the NIST library, their match factors are often lower than those with helium. This issue is likely to be amplified with ion trap technology, as the protons can be held within the trap as the other ions are ejected to the detector, especially when the ion trap is continuously inundated with new protons from the carrier.

Many standard methods mandate a match with specific tune criteria for key ions and their relative ion abundances.¹² Decafluorotriphenylphosphine (DFTPP) for EPA method 8270 appears to easily pass with most high performance quadrupole mass spectrometers.¹³ However, bromofluorobenzene (BFB) for EPA methods 524, 624, 8260B and TO-15 can suffer from degradation of its spectrum with hydrogen, especially in qualifying the relationship between masses 95 and 96. The USEPA and National Environmental Laboratory Accreditation Conference (NELAC) may need to reassess this criterion when hydrogen carrier is more commonly deployed. Even with this tune discrepancy, library searches remain successful. And some workstations allow the operator to generate a custom library, thus providing better correlations with spectra generated from unknown samples with hydrogen carrier. Additionally, when selected ion monitoring (SIM) is used, library matching is usually meaningless, as only a few ions are monitored for each analyte and are not enough to properly match the library.

Another consideration is the inherent difficulty in pulling out hydrogen with a vacuum pump, compared with helium. Compression efficiency of vacuum pumps is related to the square root of the mass. With hydrogen having the lowest mass, higher capacity pumps are needed to allow a wider range of carrier gas flows into the spectrometer.

Safety

Hydrogen is a potentially dangerous gas and must be used with caution. Explosions, although rare, have occurred over the years with excess hydrogen building up in the column oven.¹⁴ The column oven is the most likely culprit in possibly collecting excess hydrogen, and with an exposed ignition source in the oven heater, can detonate violently. Some top performing chromatographs and mass spectrometers are certified by independent testing agencies in accordance with the ATAX Directive 94/9/EC, using harmonized standards from MIL-STD-810 G-Method 511.5, ANSI NCSL Z 540-1 and ISO 17025:2005. In the event of an internal explosion, this testing verifies that no instrument cover can come disengaged from the instrument and pose potential danger to the user.

These high performance gas chromatographs and spectrometers can have built in safety monitoring. When an excess amount of hydrogen is consumed and sensors are tripped, the system controller will shutdown all hydrogen flows, all thermal zones and detector electronics, and then open the column oven vent door to allow the excess hydrogen build up to escape. However, a broken column with enough column segment remaining in the injector can still provide sufficient backpressure to satisfy the flow sensors, but emit ample hydrogen to get into the explosive range inside an enclosed chamber. A hydrogen sensor mounted inside the oven will detect this leak, shutdown the system, and generate an alarm and error message. Also, to prevent accumulation of hydrogen in the mass spectrometer manifold with a turbo pump failure, some systems have an interconnection between the spectrometer and chromatograph to trigger a fault and turn off all hydrogen flows.

Since an appropriate hydrogen generator creates hydrogen on demand, it will limit the amount of hydrogen available to the instrument and will shut down automatically with significant pressure loss from a pneumatic failure, and enhance the safety factor.

SUMMARY

Conversion over to hydrogen carrier can provide relief from the persistent reduction in helium market supplies and from the dramatic increases in cost, but protections must be undertaken to ensure that operations are safe and do not alter overall chromatographic operations, especially unexpected effects.

Precautions must be undertaken when switching from helium to hydrogen with operations with pneumatic components, injectors and chromatography due to the inherent reactivity of hydrogen. Flows through the column can be different, if not appropriately adjusted. The reactivity of hydrogen can induce changes to analytes in the injector and column. And the change in physical properties with hydrogen can alter the possible chromatographic separations. Also, changeover to hydrogen from helium can have unintended impacts on nearly every chromatographic detector, including mass spectrometers. Adjustments to detector gas flows with the added fuel from the carrier are necessary to maintain optimum performance. And to prevent changes to performance for most detectors during a column temperature program, column carrier flows must be controlled either with true flow controllers or with a constant flow mode for pressure systems. Constant pressure settings for the carrier can result in considerable changes to the fuel composition in the detector and push performance dramatically away from best operations. Moreover, some detectors can only operate with helium carrier due to their intrinsic detection principles involved.

Recommendations to consider for a safer switch to hydrogen as a carrier include:

- Check and double check for leaks everywhere between hydrogen source and detector, especially around column connections.
- Use an appropriate hydrogen generator.
- Operate an independently certified explosion-proof gas chromatograph.
- Install hydrogen sensor in column oven.
- Utilize built-in safety monitoring and automatic shutdown of operations with MS turbo pump failure, gross hydrogen leaks, and unexpected column pressure drops.

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