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Application Note for Specialty Gases.

Hydrogen as an alternative to Helium for gas chromatography.

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- Key Words: hydrogen, helium, carrier gas, GC, HiQ® Specialty Gas

Abstract

The choice of carrier gas depends on the type of gas chromatography (GC) detector that is used and the components that are to be determined. In general carrier gases for gas chromatographs must be of high purity and chemically inert towards the sample.

Many gas chromatographers are considering hydrogen carrier gas instead of helium or nitrogen, but they might hesitate to do so because they have questions about performance, safety and cost.

This guide presents the basic steps to safely convert from helium to hydrogen as a carrier gas for gas chromatography. It presents useful data to estimate costs and demonstrates the excellent separation performance of hydrogen.

1. Introduction

The carrier gas has an important role transporting the sample through the column and into the detector. The carrier gas must be inert or at least must not react with the stationary phase in the column. Helium, nitrogen, and hydrogen are commonly used as carrier gases. The choice depends on the type of detector, column, application and safety requirements (Hydrogen is explosive). But the choice of the carrier gas is also dependent on requirements in terms of separation efficiency and speed. Hydrogen has the lowest viscosity of all gases, thereby provides the highest mobile phase velocity and therefore the shortest analysis time. Helium, on the other hand, gives the best overall performance and peak resolutions for many applications, making it an optimum choice of carrier gas in those cases.

The purity of the carrier gas is another important factor. Impurities, especially hydrocarbons, cause base line noise and reduced sensitivity and might increase detection limits. Traces of water and oxygen may also decompose the stationary phase, which leads to premature destruction of the column.

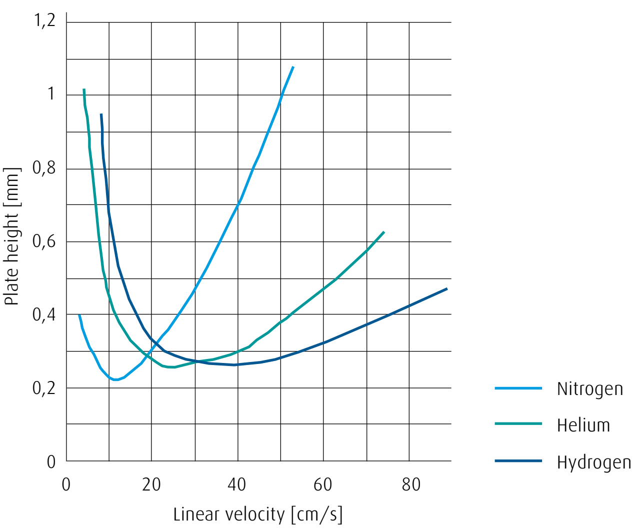
Gas chromatographs are widely used for quantitative and qualitative analysis in laboratories and processes. In view of the large quantity of different detectors, separation columns and applications this guide can only make general recommendations.

2. Separation performance of carrier gases – Helium, Nitrogen and Hydrogen

Van Deemter profiles

The linear velocity of a carrier gas has a similar influence on the separation of the compounds to the column temperature: higher linear velocity accelerates the analysis but it reduces the separation of the analytes. The linear velocity is influenced by column dimensions, pressure drop and viscosity of the carrier gas.

Figure 1: Van Deemter profiles for Helium, Nitrogen and Hydrogen



Due to its high diffusivity and high optimal linear velocity, hydrogen is the best choice to reduce GC run time. A higher flow rate can be used for hydrogen than for helium or nitrogen, while maintaining the same plate height (separation performance).

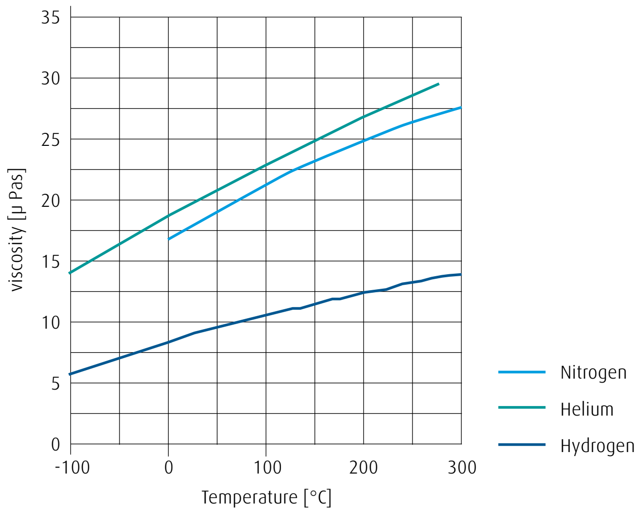
Viscosity, influence of temperature and carrier gas

Viscosity is the resistance of a liquid or gas to flow. The viscosity of a gas is determined by two factors: the molecular weight of the gas and its temperature. For all gases, as temperature increases, viscosity increases. The viscosity of hydrogen is influenced less by temperature than the viscosity of helium and nitrogen. Therefore it is easier to maintain higher linear velocities with hydrogen.

Helium vs. Hydrogen

The difference in the efficiency between hydrogen and helium increases with increasing temperature. This phenomenon is attributed to the fact that the viscosity of helium increases more rapidly with temperature than the viscosity of hydrogen. This results in faster analysis times, particularly at high temperatures.

Figure 2[1]: Influence of carrier gas and temperature on viscosity



Typical separation example

Also the diffusion speed of the solute in the carrier gas determines the speed of chromatography – higher diffusion increases the optimum velocity. For example, the gas-gas diffusion rate of n-octane in helium at 130 °C is 0.38 cm^2/s, while in hydrogen it increases to 0.47 cm^2/s, therefore the optimum velocity increases with hydrogen carrier gas compared to helium.

The effect of switching from helium to hydrogen on retention time will be to cut retention times roughly by 50 % to 70 % if the inlet pressure is unchanged.

Figure 3[2]: Carrier gas separation example

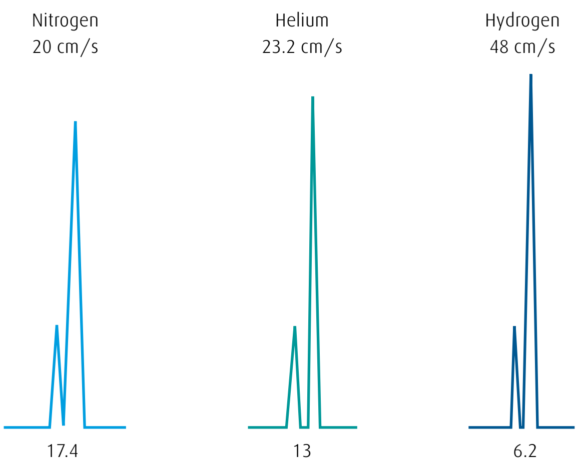
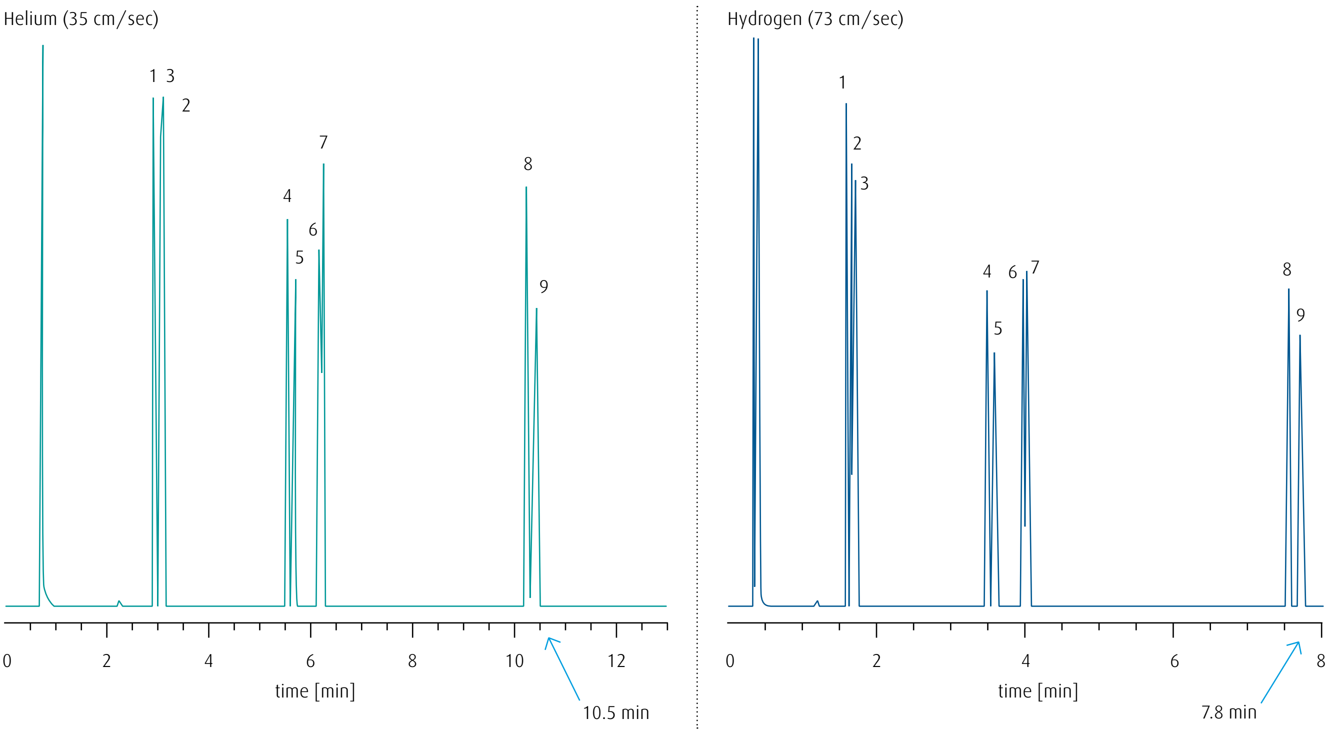


Figure 4[2]



3. Properties of Hydrogen and Helium, material compatibility

Table 1

Properties	Helium	Hydrogen
Molecular weight [g/mol]	4.0026	2.016
Thermal conductivity [W/m K]	0.146	0.161
Viscosity [μPa s]	18.6	8.4
Density [kg/m^3] (15 °C, 1.013 bar)	0.169	0.0852
Flammability range in air [% volume]	Non combustible	4.0 – 74.5
Material compatibility	**Helium**	**Hydrogen**
Metals		
Aluminium	appropriate	appropriate
Brass	appropriate	appropriate
Copper	appropriate	appropriate
Stainless steel	appropriate	appropriate
Plastics		
PA	appropriate	appropriate
PCTFE	appropriate	appropriate
PVDF	appropriate	appropriate
PTFE	appropriate	appropriate
PFA	appropriate	appropriate

PA: Polyamide (eg. Nylon®)
PCTFE: Polychlorotrifluoroethylene (eg. Kel-F®)
PVDF: Polyvinylidene fluoride
PTFE*: Polytetrafluoroethylene (eg. Teflon®)
PFA*: Perfluoroalkoxy (eg. Teflon® PFA)

*The use of PFA and PTFE are not recommended, because the hydrogen and oxygen diffusion through the walls could change the quality of the hydrogen.

4. Carrier gases for various detectors

Table 2

	Detector					
Carrier gas	DID	MSD	TCD	FID	FPD	PID
Helium	Yes	Yes	Yes	Yes	Yes	Yes
Hydrogen	No	Yes	Yes	Yes	Yes	Yes

DID: Discharge Ionisation Detector (requires helium as the carrier gas)
MSD: Mass Selective Detector
TCD: Thermo Conductivity Detector
FID: Flame Ionisation Detector
FPD: Flame Photometric Detector
PID: Photo Ionisation Detector

Contact your GC supplier if you are not sure about the hydrogen compatibility of your instrument or application.

5. Typical gas chromatography carrier gas set up

Figure 5: Helium supplied by cylinder

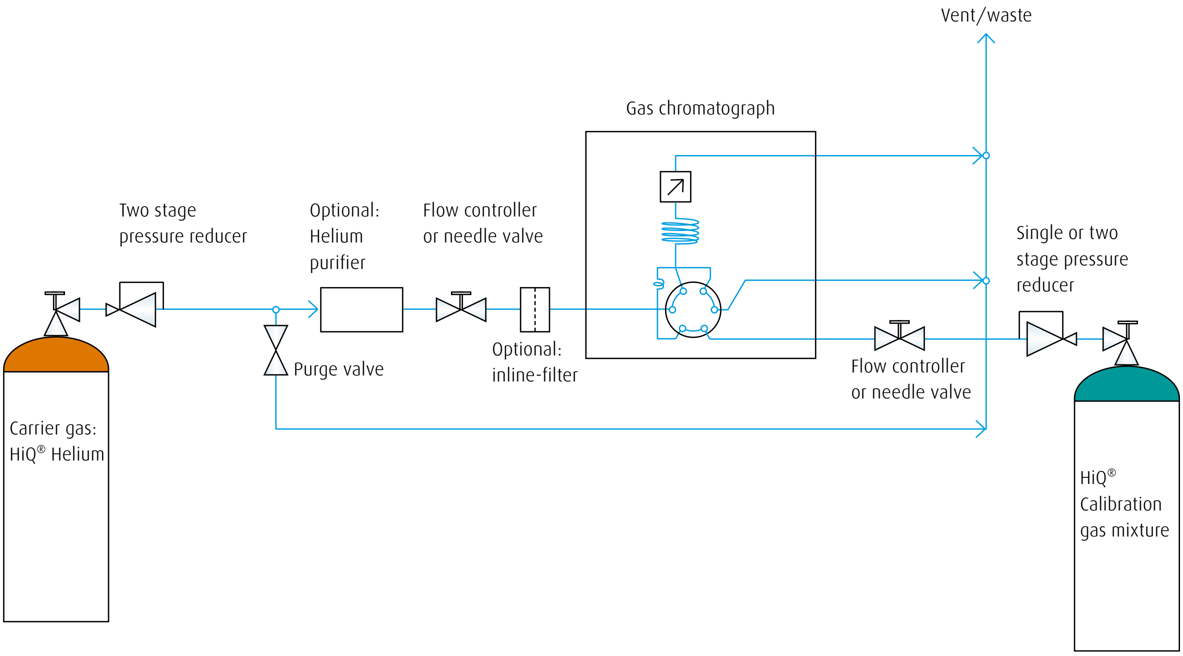
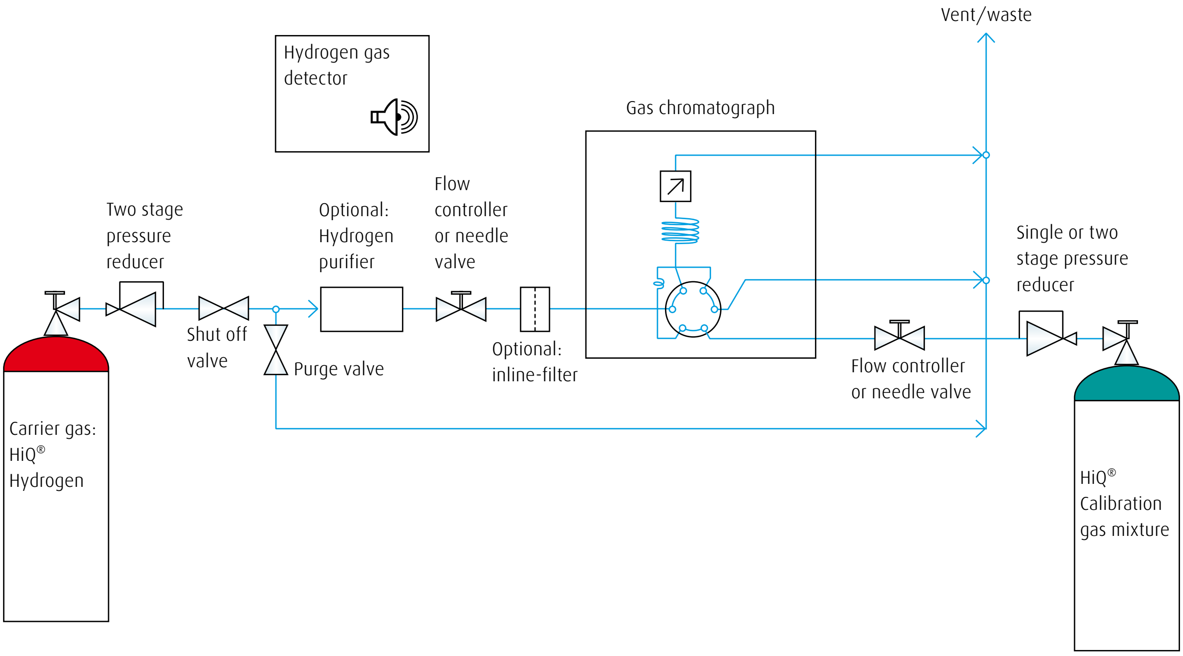


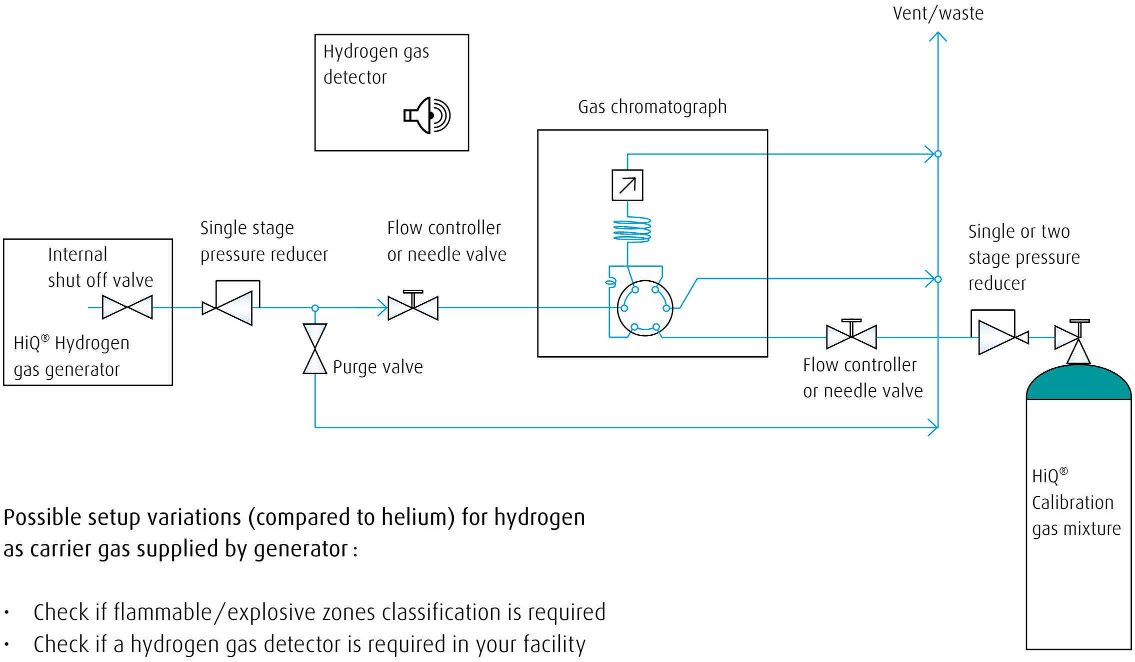
Figure 6: Hydrogen supplied by cylinder



Possible setup variations (compared to helium) for hydrogen as carrier gas supplied by cylinder:

- Hydrogen has a different cylinder connection than helium
- Check if flammable/explosive zones classification is required
- Check if a combination of gas detection system and hydrogen shut off valve is required in your facility
- Check if hydrogen cylinder can be installed outside (recommended option)
- Check if purifier is compatible to hydrogen (eg.: Getter purifiers for helium are not suitable for hydrogen)
- Check if in-line filter is qualified for hydrogen
- Check if flow regulator is suitable for hydrogen
- Check if exhaust lines are properly installed
- Check if the vent point is to a safe place

Figure 7: Hydrogen supplied by generator



Possible setup variations (compared to helium) for hydrogen as carrier gas supplied by generator:

- Check if flammable/explosive zones classification is required
- Check if a hydrogen gas detector is required in your facility
- Check if flow regulator is suitable for hydrogen
- Check if exhaust lines are properly installed
- Check if the vent point is to a safe place

6. Hydrogen correction factor for thermal mass flow meters

Most modern GCs control the flow rates electronically using thermal mass flow controllers. When these controllers are used with different carrier gases than the originally calibrated one, a conversion factor must be used to calculate the correct flow. If the GC is controlled by a computer, then the gas being measured can usually be selected in the gas chromatography software (see figure 7). The conversion factor of the gas is then used to determine the accurate flow setting.

If you need to calculate the gas conversion factor manually, the following approximation can be used:

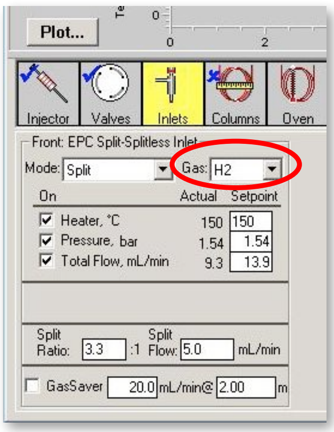
$$c_f = \frac{\rho_{n_1} \cdot c_{p_1}}{\rho_{n_2} \cdot c_{p_2}}$$

C_f: conversion factor, $\rho_{n1,2}$: density of gas, $C_{p1,2}$: heat capacity at constant pressure, indices 1 and 2 are for gas 1 and 2, index 1 is the calibrated gas type

Table 3

Gas	p	c_p
Helium	0.178	5.196
Hydrogen	0.0899	14.27
Nitrogen	1.250	1.041

Figure 8



7. Safety

Potential safety hazards of hydrogen

If appropriate safety measures are taken, hydrogen hazards can be kept to a minimum. Prior to implementing hydrogen systems and equipment in a laboratory, some planning activities should be performed to ensure that the hazards of hydrogen systems and equipment are managed.

In particular, hydrogen has the following properties that relate to potential hazards:

- Colourless and odourless gas. Thus, a hydrogen detector may be required to locate leaks
- Very light element (1/15th the density of air), consequently, rises when released

- Broad flammability range of 4–74.5 % hydrogen in air
- Low ignition energy, even static electricity can ignite hydrogen
- An almost invisible flame when ignited, and does not smoke or radiate heat like a normal flame
- Non-toxic
- Asphyxiant in high concentrations

For more information please refer to the relevant Safety Data Sheet (SDS).

The most common hydrogen hazard is the possibility of fire when leaking hydrogen is ignited, therefore:
- Install hydrogen leak detection, alarm system and shut off valve
- If a leak is detected increase the ventilation rate to dilute any leaked hydrogen to well below its flammable limit

Minimise safety hazards:
- A hydrogen generator is considerably safer than a hydrogen cylinder supply

Risk assessment and safety considerations of hydrogen supply

In order to safely switch from helium to hydrogen:
- Discuss your project with your responsible safety officer
- Prior to implementing a hydrogen supply in your laboratory, initiate a hazard analysis to identify hazards, consider electrical system upgrades according to a flammable/explosive zones classification
- Document hazards and required safeguards
- Provide the operator with an understanding of the hazards associated with hydrogen
- Arrange operator safety training
- Add facility signs to remind personnel of restrictions on open flames, smoking, cell phone use and other ignition sources

A special hazard to consider when using hydrogen as a carrier gas are explosions in GC ovens. Due to high carrier gas pressure hydrogen may leak into the oven, heating filaments may ignite the explosive mixture of hydrogen in air.
To mitigate this risk, turn off the hydrogen gas supply at its source when changing columns or servicing the gas chromatograph.
For any specific precautions for your GC instrument and the use of hydrogen as carrier gas, consult the supplier's safety and operating instructions.

Safety features of the HiQ® hydrogen generators:
- Internal leak tests carried out during start-up and operation
- Generator produces hydrogen at low pressures of 10 bar compared to cylinders at 200 bar this means much smaller volumes
- Generator will shut down immediately in the event of a leak (line pressure) down stream
- Generator can also distinguish a small, slow constant leak and will shut down
- Total stored volume of hydrogen in a generator is < 40 ml

8. Necessary steps to convert from Helium to Hydrogen

General guidance

To switch from helium to hydrogen use the following general guidance:
- Discuss your project together with your responsible safety officer
- Leak check the system
- Purge the system to ensure there is no air in the system before supplying hydrogen
- Review and document all existing run conditions
  - Measure and record all flow rates
  - Document temperature programs used
  - Obtain a good sample chromatogram for comparison
- Shut down system
- Install new lines (and purifiers)
- Establish flows for hydrogen
  - Turn hydrogen carrier on and establish column flow with oven and detector off
  - Check for leaks using a hydrogen gas detector
  - If necessary, change the carrier gas type in your GC software to indicate that you are using hydrogen
  - Purge system for about one hour (best to purge the system overnight)
  - Turn on detector and any needed detector electronics, give the system time to stabilise
- Inject sample and compare run to previous helium
  - Consider if you want to speed up run or if you just want to duplicate the helium analysis times and separation
  - Re-establish peak identification

Case study

Using the procedure described above, we switched from helium to hydrogen for the following application: 2.0 % (mol/mol) nitrogen in balance hydrogen. Figure 9 shows a sample chromatogram which was obtained using helium as carrier gas.

We shut down the system and purged with hydrogen. Three hours later we started up again and obtained a sample chromatogram of the test gas. We supplied the same carrier gas pressure as with helium (2.5 bar). We did not change any flow settings. Figure 10 shows the sample chromatogram which was obtained using hydrogen. The retention time for nitrogen is shortened from 2.08 (Helium) to 0.95 (Hydrogen) minutes. The hydrogen balance gas peak disappeared from the chromatogram. This application can easily be done using hydrogen as carrier gas.

GC parameters
- Detector: TCD
- System: Shimadzu GC 14B
- Column: 2.6 metre packed MS4A
- Temperature: 160 °C
- Helium carrier gas flow @ 2.5 bar: 13 ml/min
- Hydrogen carrier gas flow @ 2.5 bar: 28 ml/min

Figure 9

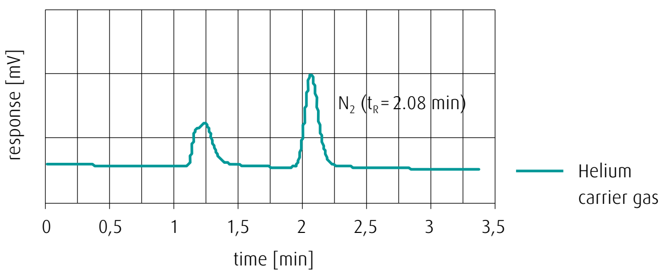
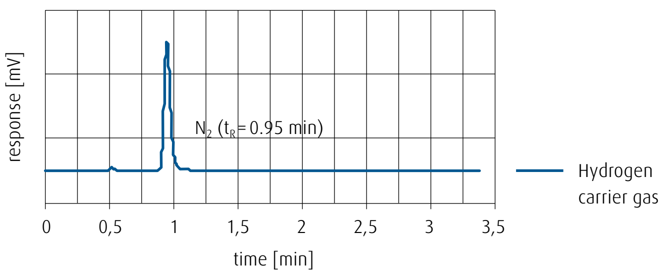


Figure 10



9. Questions and answers

Does hydrogen carrier gas affect retention times?
If the same carrier gas pressure is applied with hydrogen as with helium, then retention times are reduced.

Does hydrogen react with unsaturated hydrocarbons?
Depending on column material, temperature and carrier gas pressure, hydrogen might hydrogenate unsaturated hydrocarbons and aromatics.

What are the necessary safety precautions to use hydrogen as carrier gas?
Discuss your project with your responsible safety officer. Safety precautions depend much on the type of hydrogen supply: gas cylinders or gas generation. Safety precautions should be the outcomes of a proper risk assessment.

Can I use my helium purifier for hydrogen?
Heated helium Getter purifier can not be used with hydrogen. Contact your purifier suppler if you are not confident regarding the hydrogen compatibility.

What is the explosive level of hydrogen in air?
Hydrogen has a broad flammability range of 4.0 – 74.5 % hydrogen in air.

10. HiQ® Specialty Gases and Specialty Equipment

HiQ® specialty gases and specialty equipment have an important role in many areas of research and development. Instrument grade pure gases such as synthetic air, helium, hydrogen or nitrogen are used to zero and purge analytical equipment and as carrier gases. All of the pure HiQ® specialty gases are named HiQ + Gas type + purity. So, HiQ® Hydrogen 5.0 supplied in a cylinder is hydrogen at purity 99.999 % and not more than 10 part per million (ppm) total reported impurity level. HiQ Hydrogen 6.0 is hydrogen at purity 99.9999 % and not more than 1 ppm total reported impurity level.

Specialty equipment such as BASELINE® cylinder regulators are suitable up to purity 5.0 (99.999%). Supplied in one-stage, or two-stage configurations BASELINE® regulators are designed to offer a more stable operation than "industrial" or "technical" quality equipment can provide. Typical applications include gas chromatography, carrier gases, zero and span calibration gases.

Linde's REDLINE® represents premium Specialty Equipment including cylinder regulators and the full range of equipment required for fixed gas distribution systems installations. REDLINE® stretches from wall mounted automatic switch-over gas panels to shut off valves and furniture mounted point of use regulators. All REDLINE® components are designed for use with high purity specialty gases up to 6.0 grade (99.9999%).

A wide range of gas mixtures are used to calibrate analytical equipment and to ensure its correct operation. Normally, these mixtures are supplied in high-pressure or disposable gas cylinders. Depending on the consumption and the required mobility, the size of the cylinders varies from 1 to up to 50 litres. Linde has developed the portable ECOCYL® specialty gas packages that represents innovative, refillable, sustainable packaging for specialty gases. All ECOCYL® models are equipped with an integral valve and flow regulation device to avoid the need to purchase and fit separate valves and pressure regulators. The HiQ® MINICAN and HiQ® MAXICAN are disposable cylinders favoured for their ultra light weight and their commercial and operational simplicity. The HiQ® MICROCAN is a high pressure cylinder of truly micro proportions … however, because it is a high pressure cylinder it contains a surprisingly large amount of gas.

While specialty gases are an integral part of today's laboratory, there are situations when the use of a cylinder may not be practical due to transportation, safety or other concerns. Where the use of cylinder hydrogen is restricted, the HiQ® hydrogen generator is safe to operate, due to its small contained volume (< 40 ml). These units are highly reliable and include a range of features to ensure continuous operation, for example selectable, multiple alarms alert to unwanted shifts in operating conditions such as low water level, poor water quality, low pressure (leak) and power supply conditions. HiQ® offers a broad range of high purity gas generators for in-house production of Hydrogen, Nitrogen, and Zero Air.

Gas detectors differ from gas analysers in that where analysers are used to analyse a sample for a variety of specific compounds, a gas detector is used to monitor for, and warn of the existence of specific toxic or combustible gases and oxygen deficiency hazards. Typical measurement levels will be in the low parts per million level for toxic gas, while combustible gases are measured in percent LEL (Lower Explosive Limit). The Linde G-TECTA™ portable gas detection range has been designed to be easy to use, offering simple one button operation, capable of being used and tested by field engineers through to manufacturing operatives.

11. References

1. J.V. Hinshaw, Chromatography Online, "Frequently asked questions about hydrogen carrier gas", 2008
2. "Carrier Gases in Capillary GC Analysis", Agilent J&W Scientific Technical Support

Imprint

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