Together, we can safely improve the efficiency of Gas Chromatography

Helium supplies are diminishing and prices are rising

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Helium supplies are diminishing and prices are rising

Helium is running out and worldwide demand is exceeding current production levels. This global shortage means that not only are prices going through the roof, rationing is taking place to ensure that areas such as healthcare take priority.

Thankfully there is an alternative that can both save you money and protect you from future disruption caused by helium shortages.

The new generation of in-house hydrogen gas generators from Parker domnick hunter offers a safe, affordable and virtually limitless supply of carrier gas for Gas Chromatography.

Time for change

Practical alternatives to using helium need to be implemented before costs escalate and supplies run out

The global helium shortage and why it's so important for your industry

The world is facing a critical helium shortage and it's not one with a known solution. Despite being the second most abundant element in the universe after hydrogen, helium is difficult to find or store in practical quantities. Most supplies are extracted from underground gas reserves, and most stocks are held in one area of the USA.

Factors for the shortage include the declining natural resources of helium, the planned and unplanned closures of helium refineries in the U.S.A and Algeria, new helium using applications, and increasing global demand from countries such as China. In addition to this, the U.S.A is to sell off its helium reserves to private refiners by 2015, as part of the 1996 Helium Privatisation Act.

What effect is this having on your industry?

First and foremost, as the supplies of helium reduce, the cost of helium is steadily and irreversibly rising.

Supplies are also being disrupted by rationing. For example, the availability for minor applications such as gas chromatography is being rationed as priority is given to other sectors such as healthcare.

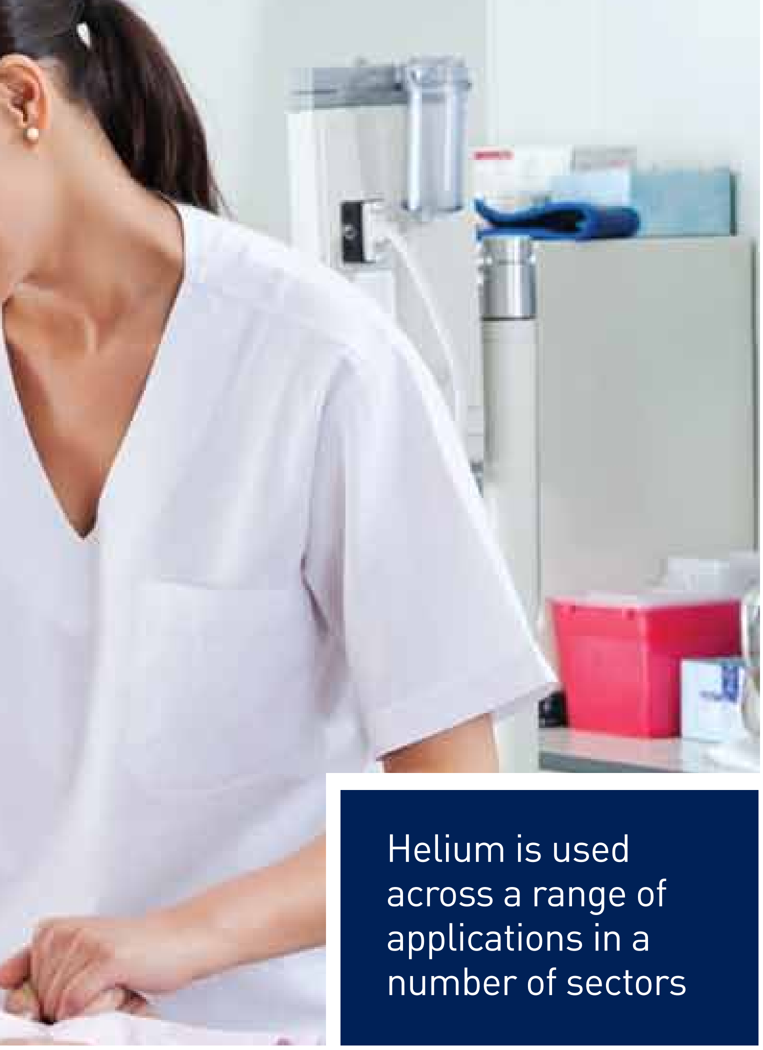
Helium has the lowest boiling and melting points of all the chemical elements and liquid helium is the only liquid that cannot be solidified by the lowering of its temperature. It's these properties that make helium so irreplaceable in cryogenics and many industries.

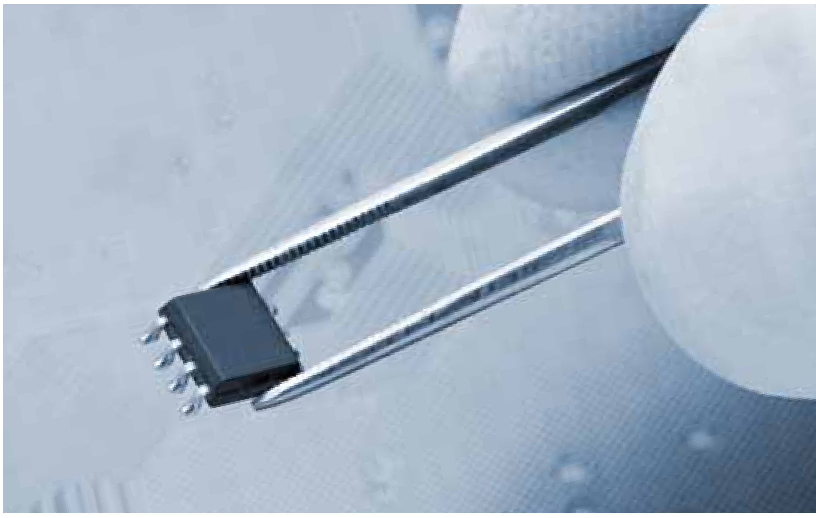
Thinking beyond party balloons, helium is essential for air-to-air missile guidance, computer chips, optical fibre and medical lasers, rocket-engine testing, arc welding, and numerous other civilian and military uses. It goes to show how big the demand is for this finite resource.

Unfortunately, chromatography is way down the priority list as critical applications such as hospital MRI scanners will remain at the top.

Rationing

Helium is being rationed and applications such as gas chromatography will lose out to sectors such as healthcare





Helium is used across a range of applications in a number of sectors

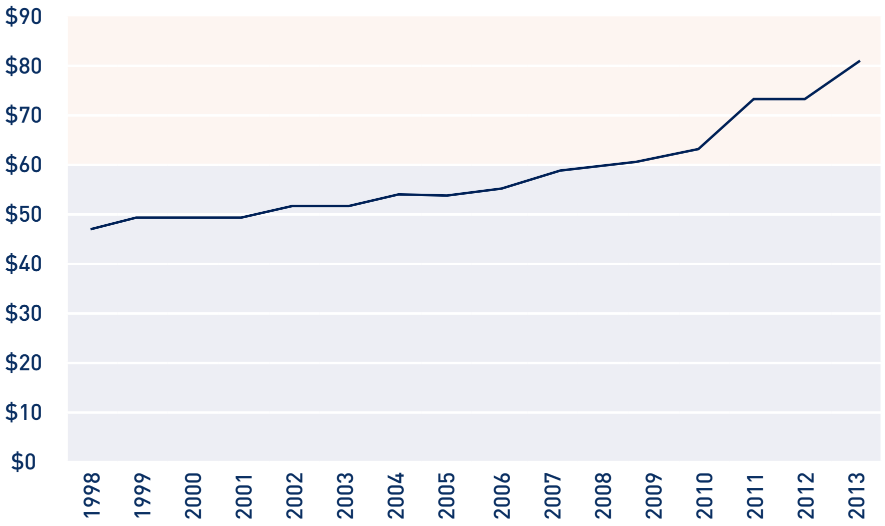
Rising costs

The current 2013 crude helium price per thousand cubic feet (Mcf) is approx $84 up from the 2012 price of $75 and $49 per mcf in 2000. According to the US Bureau of Land Management (BLM) the estimated price for crude helium on the open market will be $95/mcf by 2015.

It's worth noting that a typical standard helium cylinder in Europe (for an analytical laboratory using GC grade helium), the cost is currently approximately Ð450 (excluding rental and delivery), so the price rises will be considerable.

With rationing, it will also become increasingly difficult to guarantee regular deliveries of supplies, causing disruption to the laboratory through put and efficiency.

BLM open market price of crude Helium table



What are the viable alternatives?

The most widely used gases for chromatography today are nitrogen, hydrogen, and helium.

Whilst each has unique benefits, there are also drawbacks - for example, nitrogen displays the best efficiency but does so over a low and narrow linear velocity range. It's therefore very slow as a carrier gas, and certainly not the best choice for temperature-programmed use.

Helium is a compromise between nitrogen and hydrogen in relation to analysis and efficiency, however as we've seen, it's now ruling itself out of contention due to both cost and availability.

Hydrogen on the other hand, provides the fastest analysis time over a broad linear velocity range and is the most practical alternative to helium.

Here we can see and compare the advantages of using hydrogen over helium.

Practical alternatives

Hydrogen is the cost-effective and practical solution to helium for labs


Helium


Nitrogen


Hydrogen

Hydrogen

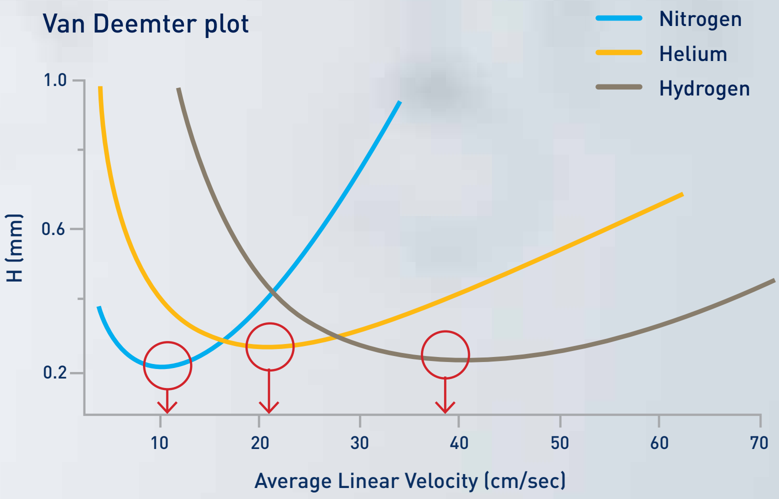
Hydrogen is the earth's lightest element and can be manufactured easily and inexpensively.

The performance of hydrogen at higher carrier gas velocities provides distinct advantages for laboratories to decrease run times and therefore increase sample through-put but without compromising on sample quality. The Van Deemter curves, which show the relative carrier efficiencies of nitrogen, hydrogen and helium, indicate that helium and hydrogen perform similarly at medium gas velocities with hydrogen outperforming helium at high velocities.

In addition, hydrogen frequently allows for the use of a lower oven temperature for separation, thereby increasing column longevity.

However, since the 1950's, helium's inert nature has made it the carrier gas of choice for the majority of gas chromatography (GC) applications. This is largely due to the perceived safety concerns with hydrogen, despite all GC-FID instruments using hydrogen (typically from a cylinder), as the flame gas for the FID (flame ionisation detector).

Hydrogen can be used as an effective replacement for helium in most GC and GCMS applications. It has a wide range of applicability, provides good efficiency, and, for the most part, separations are faster than with helium carrier gas.



Van Deemter plot

Safety is not compromised with hydrogen

Most concerns about hydrogen are about the perceived danger of flammability. If hydrogen reaches 4%-75% volume in air it will burn, but a risk of explosion only occurs between 18% and 59%. It should be noted however, that because hydrogen is less viscous than helium, it escapes far more easily - so unless a large quantity is suddenly released into the environment, the danger of reaching the LEL (lower explosive limit) is very low. Hydrogen also rises twice as fast as helium, at a speed of 20 m/s (45mph). In a laboratory with regular air turnover, it would be very difficult to achieve the explosive limits.

GC instrument manufacturers have recommended hydrogen as a carrier gas for several years and there are multiple safeguards in place to ensure all equipment is safe.

Multiple Safeguards

Numerous safety measures ensure that using hydrogen as a carrier gas is not a danger in lab use

Are GC and GC/MS systems safe to use with hydrogen carrier gas?

A common concern when considering using hydrogen as a carrier gas is the potential for explosion if there is a leak inside the GC oven.

Most modern GC's manufactured in the last 10 years use PPC (Pneumatic Pressure Control) or EPC (Electronic Pressure Control) to control the gas flow (generally, the older instruments use a pressure regulator located upstream of the injection port and are head pressure regulated). PPC and EPCs are designed to limit the total flow into the instrument and in many cases put the GC into standby mode – the gases will be turned off and all heated zones will be cooled, if a down-stream leak, detected as low pressure, is seen.

It's possible to insert flow controllers or limiters to the carrier gas supply line to limit the maximum flow rate into the GC. If a leak occurs inside the oven, the flow rate will be limited to that needed for the chromatography.

Other safety measures include the use of automatic leak-testing which is available on many GC's with PPC or EPC. The total flow into the GC injector will be measured at the start of each analysis and used to calculate an effective leak flow rate. If this exceeds the value entered, then the GC will enter a shutdown process – i.e. the gases will be turned off and all heated zones will be cooled.

If we consider the worst case scenario of a column breaking and leaking 20 ml/min of hydrogen directly into the oven, it would require 2.5 litres to reach the LEL (lower explosive limit) in an oven with a typical 14 litre capacity. It would take over 2 hours to reach the explosive level. Most analyses would be shorter than that, so the oven contents would be purged each time the oven is cooled. Furthermore, modern GC instruments have spring-loaded, explosion-ready oven doors.

With the helium crisis there has been a huge increase in the number of online articles and documents (and many webinars) by the instrument manufactures which cover in great detail, both the practical and safety considerations when converting to hydrogen carrier gas. The very latest instruments to be launched - such as the Agilent 5977A GC/MS and Bruker Scion, have been specifically designed to run on hydrogen. Conversion software to change methods from helium to hydrogen are also included as standard.

There are also other approaches to guard against leakage that use hydrogen sensors. These are integral to the oven and alert the user via LED lights and acoustic signals should there be a leak. If the leak goes to 25% of the LEL, the carrier gas will automatically switch to an inert gas. Similar sensors can also monitor the levels in the laboratory room also.

Benefits of in-house gas generators

As we've seen, the benefits of using hydrogen as a GC carrier gas are proven. Hydrogen is now the cost-effective option with no problems with current or future supply, but other benefits include the faster analysis, greater resolution and longer column life.

Here we can see the benefits of using in-house hydrogen gas generators and why they are safer and more convenient. This option is also far cheaper than using hydrogen cylinder gas and a fraction of the cost of using helium cylinders.

Clear advantages

Using in-house gas generators is the smart solution for cost and convenience, without compromising safety.

Maximising safety

An in-house generator is considerably safer than cylinder gas as only a small amount of generated gas is present at low pressure at any given time and the gas is ported directly to the instrument. If a leak occurs, only a small amount of quantity of gas is dissipated into the laboratory. In contrast, serious hazards exist if gas is supplied using a high-pressure gas cylinder.

Safety can be compromised by accidental venting, injury or damage from transportation and installation of the heavy canisters, and most importantly a leaking hydrogen cylinder can cause an explosion.

Increasing convenience

An in-house gas generator can supply gas on a 24/7 basis with no requirement for user interaction (barring annual routine maintenance). If cylinders are used, the user needs to monitor gas levels and adjust for the desired analyses – they also require a qualified individual to be present to install replacement cylinders when they run out. As they are usually stored outside in remote areas for safety, this can also be inconvenient and time consuming.

Reducing costs

One of the main benefits of in-house gas generators is the dramatic economic benefit when compared to gas cylinders. The running cost is extremely low as the gas is obtained from water and the maintenance costs amount to only a few hundred euros per year for periodic filter replacement.

In comparison, gas cylinders' cost goes beyond unit sale as factors such as transportation, installation, returning of used cylinders and time for the system to equilibrate need to be taken into account.

Precise cost comparisons for a given user depend on a broad range of local parameters and the amount of gas used, but what is certain is that the cost savings will be significant.

A comparison table displaying annual costs for in-house hydrogen gas generators versus gas cylinders is shown here.

Annual cost: In-house generation vs. high-pressure cylinders

	In-house Generator (€)	Hydrogen Cylinders (€)	Helium Cylinders (€)
Maintenance	600	0	0
Cylinders	0	2340	26,000
Cylinders rental	0	252	252
Labour (changing cylinders)	0	781	781
Order processing	23	270	270
Shipping	38	2792	2792
Invoice processing	8	90	90
Inventory control	0	54	54
Total	**668**	**6581**	**36,820**

Why Parker domnick hunter hydrogen generators are the intelligent choice

We have seen the benefits of using hydrogen as a GC carrier gas – which include cost, faster analysis, greater resolution and longer column life – and we've seen why the alternative of using helium or canisters is expensive and has supply issues. However we understand that safety concerns are paramount and this is why the Parker domnick hunter H-MD hydrogen gas generator is the obvious choice.

With minimal maintenance, it is simple to install to and operate. It eliminates the requirement for dangerous hydrogen cylinders in the work setting as well as the expense and inconvenience of changing and storing cylinders.

The Parker domnick hunter H-MD hydrogen gas generator offers intelligent control and safety alarms to counter such risks whilst facilitating optimum GC instrument performance, and reduced bottom-life gas costs. With a two-year standard cell warranty and minimal maintenance costs, it's the cheaper and safer alternative.

The Parker Solution

Parker's gas generators reduce hydrogen gas costs, eliminate the need for dangerous cylinders, and decrease maintenance times

Hydrogen generators

The Parker domnick hunter H-MD ultra high purity hydrogen gas generators offer the optimum combination of safe operation, reliability, performance and low cost of ownership.

Utilising field proven PEM cell technology, hydrogen is produced on demand from deionised water and electricity, at low pressure and with minimal stored volume. Innovative control software allows unrivalled operational safety and reliability.

The H-MD generators ideally supply GC and GC/MS carrier gas, in addition to all known combustion detectors that are routinely used in today's laboratory workflows. Four models operate at flow rates; 160 ml/min, 250 ml/min, 500 ml/min and 1100 ml/min.

Hydrogen generators are available with Remote Networking software. Remote Networking software allows up to 27 hydrogen generators to be actively controlled from one central PC, and facilitates true cascading capabilities.

Product features:

- Eliminate dangerous hydrogen cylinders from the work place
- Simple to install and operate
- Compact, reliable with minimal maintenance
- Produces a continuous supply of 99.99995% pure hydrogen up to 1,100ml/min and 6.9 bar
- 2 year standard cell warranty
- Optional automatic water fill and remote
- networking capability

Parker domnick hunter H-MD

Product selection

Model	Flow Rate	Purity*	Water Consumption (24/7, full flow)	Delivery Pressure		Optional Auto Water Fill (AWF)
	ml/min	%	L/week	bar g	psi g	
20H-MD	160	>99.99995	1.69	0.69-6.89	10-100	YES
40H-MD	250	>99.99995	2.41	0.69-6.89	10-100	YES
60H-MD	500	>99.99995	4.82	0.69-6.89	10-100	YES
110H-MD	1100	>99.99995	10.60	0.69-6.89	10-100	Standard

*With respect to oxygen

Note: For auto water fill option add suffix AWF ie 20H-MD-AWF

Technical data

Ambient Temperature Range		5 - 40°C 41 - 104°F
Water Supply Pressure*		0.1 bar g 1.45 psi g
Water Supply Flow Rate*		1 L/min
Water Quality		Deionised. ASTM II, >1MΩ, <1µs, filtered to <100µm
Supply Voltage Range		90V - 264V 50/60Hz
Port Connections	**Hydrogen Outlet** **Water Drain** **Water Fill***	1/8” Compression Fitting Quick Release Push in Fitting Quick Release Push in Fitting

*With optional AWF

Weights and dimensions

Model	Height (H)		Width (W)		Depth (D)		Weight (Empty)		Weight (Full of Water)	
	mm	in	mm	in	mm	in	kg	lb	kg	lb
20H-MD	456	17.9	342	13.5	470	18.5	20.5	45.2	25	55.1
40H-MD	456	17.9	342	13.5	470	18.5	20.5	45.2	25	55.1
60H-MD	456	17.9	342	13.5	470	18.5	20.5	45.2	25	55.1
110H-MD	456	17.9	342	13.5	470	18.5	23.6	51.8	28	61.7

Preventative maintenance

Preventative Maintenance Kit	Part Number	Change Frequency
6 Month Kit	604971500	6 Months
24 Month Kit	604970720	24 Months

Optional extra’s

Description	Part Number	Required for
Remote Networking User Software	604971530	Allows cascading of two generators or more
Remote User Expansion Module	604971540	Each additional generator (604971530 required)
Installation kit	IK7532	Suitable for all hydrogen generators

How to convert from helium to hydrogen as a carrier gas in gas chromatography

This 'how to' guide will take you though the steps necessary to convert from helium to hydrogen as a carrier gas for Gas Chromatography. The use of hydrogen from an in-house generator will lead to considerable benefits in cost, safety and convenience in the laboratory.

The order of the steps is important to the successful conversion to hydrogen. Please follow these steps carefully and you will benefit from a quick and easy conversion to hydrogen as a carrier gas.

An easy process

The conversion from using helium to using hydrogen can be a quick and straightforward process

Step 1

Review and document all existing run conditions

1. Leak check the system; leaks may affect the determination of the actual flows you are using for your analysis.
2. Measure and record the existing dead volume time and calculate the Linear Gas Rate (LGR).
3. Measure and record the Septum flow at the initial run temperature.
4. Measure and record the Make-up Gas rate.
5. Measure and record Vent flow at initial run temperature.
6. Measure and record the Fuel gas (hydrogen) flow rate.
7. Measure and record the Air gas flow rate.
8. Document any flow changes that take place during the run.
9. Document any temperature program rates used.
10. Obtain a good sample chromatogram for comparison with the chromatogram obtained after conversion.

Step 2

Perform all routine maintenance before switching to hydrogen

1. Change purifiers - Add purifiers to lines as needed to obtain at least 99.9999% pure gas.
2. Change septa - Use a good low bleed septum.
3. Change Injection Port Liners/Inserts and Seals - Clean as needed and avoid contamination with oils. Clean parts with acetone before installation.

   ⚠ **Caution: Acetone is flammable and can cause health issues.**
   Avoid open flames in the laboratory.
4. Clean Detector/Detector inserts/Jets.

Step 3

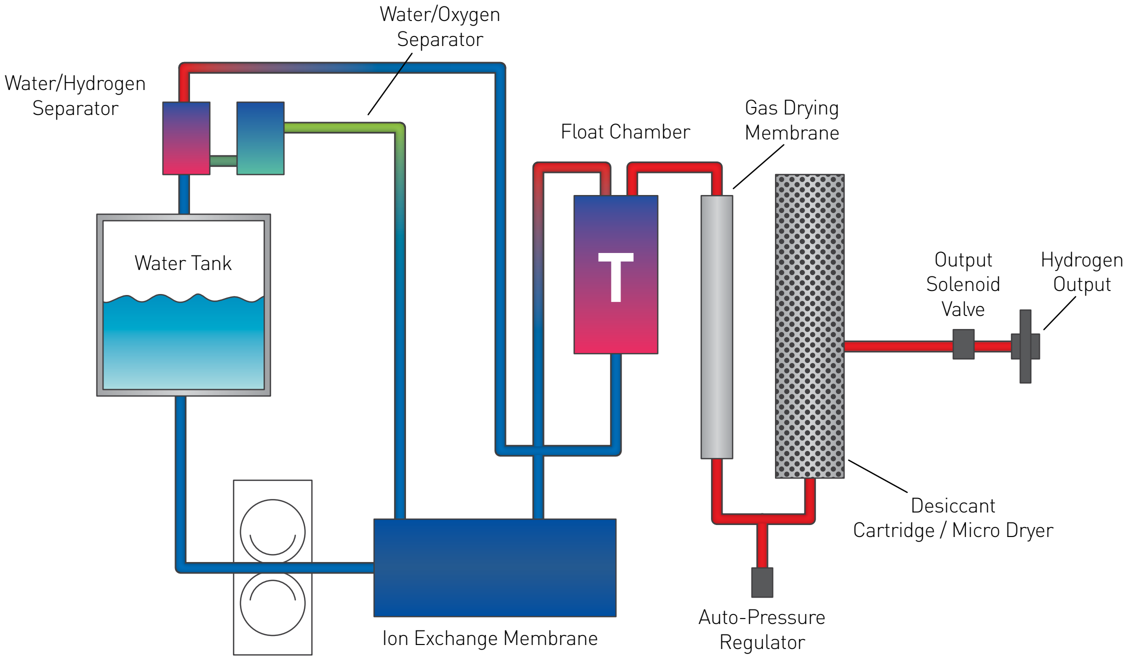
Installation of new lines and purifiers

1. Carrier gas lines – Depressurise and vent the Hydrogen line. Then cut the fuel gas line (hydrogen) and add a tee. Extend a line into the Carrier Gas in-port behind the GC from the other side of the tee.
2. Add purifiers to this line if gas purity does not meet at least 99.9999% purity. Use hydrocarbon, oxygen and moisture removing purifiers or a combination purifier to obtain the required gas purity.

   Hint: Add purifiers that have indicators to show the percentage of usage of the purifier so that you know when to change the purifiers.
3. Add new make-up gas line preferably for use with nitrogen.

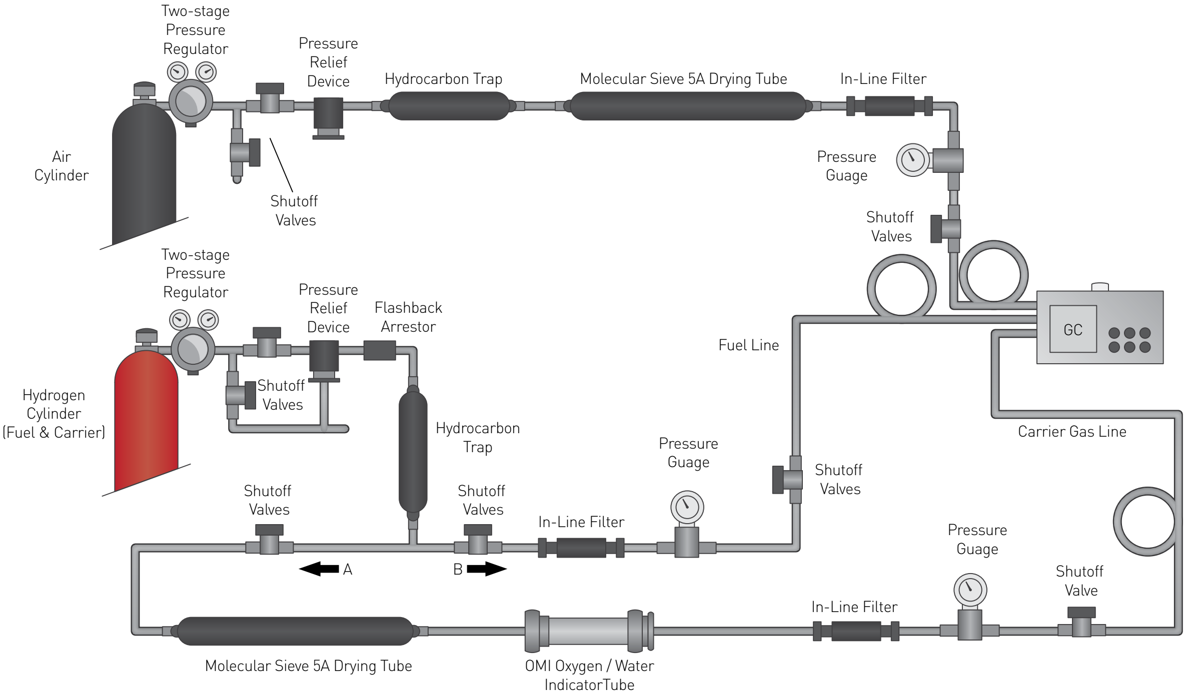
How the generator works

Figure 1: Hydrogen Technology



Optimum Single-GC System Configuration

Figure 2: Ideal configuration for a Single-GC System: Hydrogen used as carrier and fuel gas



Step 4

Establish flows for hydrogen and nitrogen (make-up gas)

Carrier Gas

1. Turn gas on and establish column flow with the oven off. With some computer controlled systems, it may be necessary to change the carrier gas input to indicate you are using hydrogen so that the system makes them correct flow adjustments based on the density of hydrogen.
2. Turn Oven, Injection port, and Detector on after one hour of flow. (It is important to purge all lines and purifiers before establishing temperatures in the various zones of the GC. It takes a considerable amount of time to purge lines and purifiers.

   Hint: If time permits, it would be best to purge the system overnight.
3. Establish Split Vent flow and measure Septum Vent flow.
4. Bring the column/oven up to run temperature and again measure the column flow.

Detector Flows

1. Establish the correct flow of hydrogen to the detector (this includes the sum of all sources of hydrogen going into the detector).
2. Establish the correct Make-up gas flow.
3. Establish the correct Air flow.

System Adjustments

1. Ignite the detector and turn on any needed detector electronics. Give the system one hour to stabilise.

   Hint: A longer warm up period (e.g. overnight) may lead to a more stable response.
2. Recheck the system to make sure that all run conditions and temperatures are correct.
3. Inject and measure the dead volume time using methane and calculate the Linear Gas Rate (LGR). Make corrections to the LGR as needed.

First Run

- **Inject sample and compare run to previous helium run.**
- **Consider if you want to speed run up by doubling LGR or if your goal is just to duplicate the helium analysis times and separation.**

Calibration

- **Re-establish peak identification – there should be no changes unless you are using very polar columns.**
- **If the run is as you desire, proceed to run your Calibration Standards.**

Flow = π r2 L / tm
Where: π = 3.1416
r =radius of the column in cm (convert from mm)
L = Length of the column in cm (convert from meters)
TR = Retention time of a non retained peak typically methane
Where: LGR = L / tm = L / μ
Simplified: Flow = π r2 μ (Remember to use units in cm.)

Step 5

Changing from cylinders to gas generators

1. Install gas generators on bench following instructions provided in the installation manuals.
2. Reduce tubing line lengths as much as possible. (See Figure 3).
3. Use high quality GC grade copper or stainless steel tubing or clean new lines with solvents and bake dry under nitrogen flow.
4. Add gas purifiers as needed. Different makes and models of gas generators provide different purities of hydrogen. You will need to add purifiers if the delivered gas is not at least 99.9999% pure.
5. Consider adding nitrogen generators and high quality air generators to eliminate cylinders and the use of high-pressure gases in the laboratory. A schematic diagram for a typical system using an in-house generator is shown in Figure 4.

Figure 3: Standard Configuration for Single GC System: Gas Delivered from Cylinders

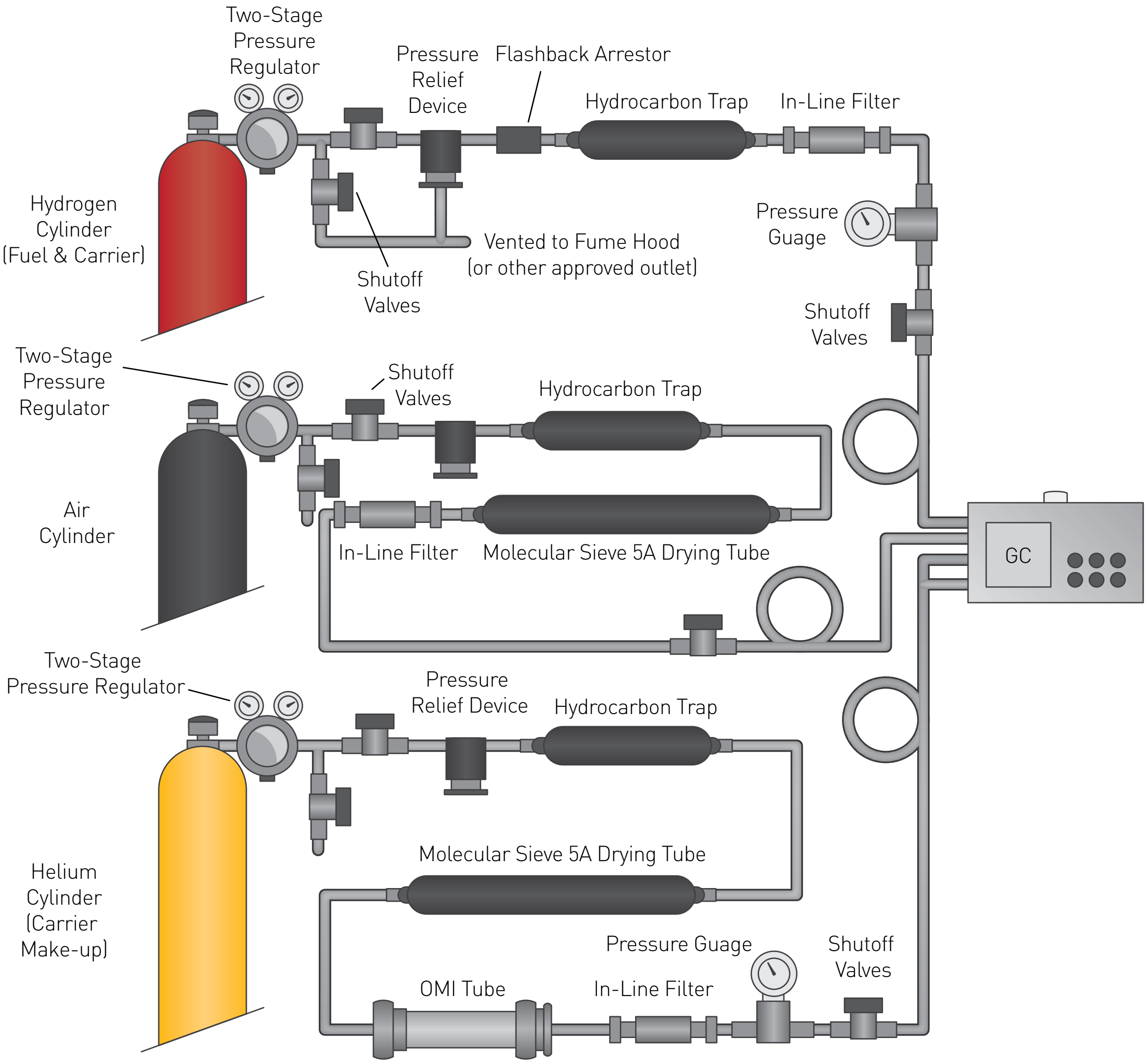
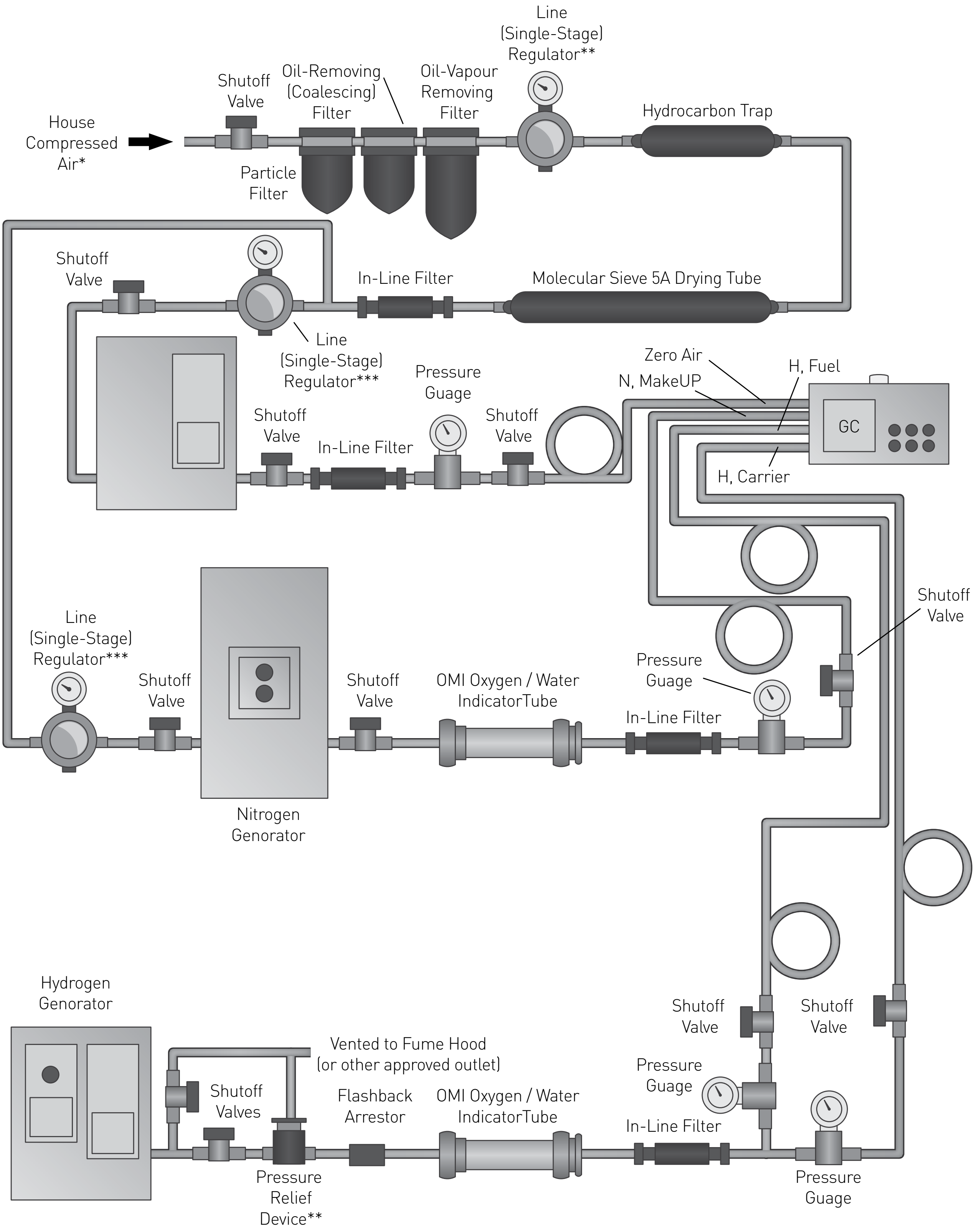


Figure 4: Ideal Configurations for a Single-GC System: All generator System



* Replace an oil-sealed compressor with an oilless unit to eliminate the need for the particle filter, oil-removing / coalescing filter, and oil vapou-removing filter.

** Not needed if the hydrogen generator has a built in relief device.

*** Consult generator manual for correct inject pressure.

Figures 5 to 7 demonstrate the equivalence of helium and hydrogen in typical separations.

Figure 5:

Equity 1 Isothermal
50 cm/sec helium carrier

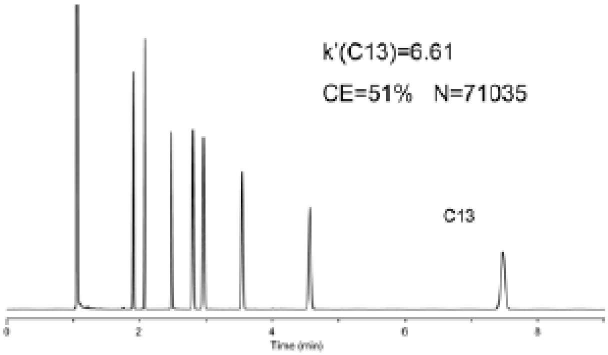


Figure 6:

Bacterial acid methyl
Esters 25 cm/sec LGR equity

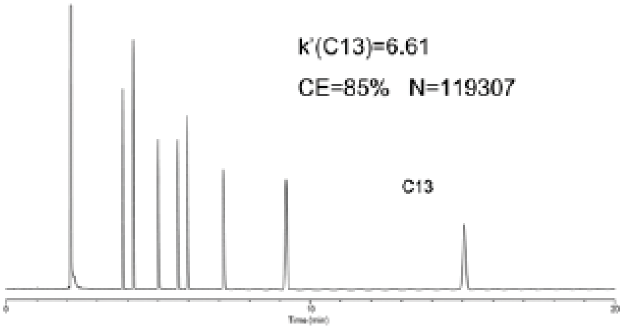
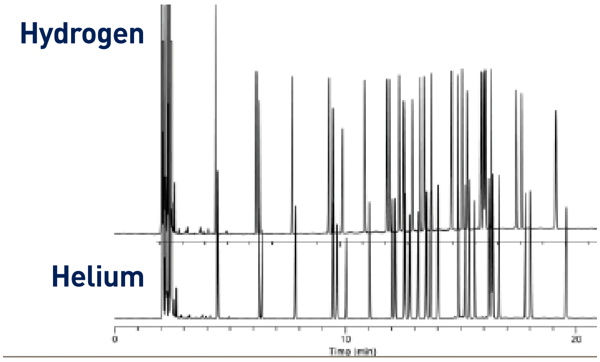


Figure 7:

Equity 1 Isothermal
25 cm/sec helium carrier



The Analysis of 12 EPA Phenols by GC/MS using Hydrogen Carrier Gas

Introduction

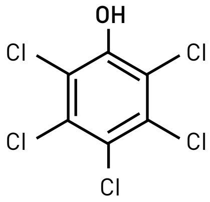
For many GC applications, hydrogen is the carrier gas of choice, due to its superior qualities in terms of analysis speed and increased response. However, its use in GC/MS has widely been avoided due to concerns over safety, high background noise, and potential reactions in the ion source.

Modern technology has allayed these fears to some extent, but routine analysis using hydrogen as a carrier for GC/MS is uncommon, and has not been exploited to its full potential. As helium prices continue to rise, there is no reason why, with safety precautions, hydrogen should not be considered as a viable alternative

Parker domnick hunter manufacture a range of hydrogen generators providing ultra high purity hydrogen gas without the safety hazards associated with high pressure cylinders. These generators improve analytical performance, whilst shortening runtimes.

Phenols, the most common of which is Phenol (C6H5OH) is a series of compounds where a hydroxyl group (-OH) is attached to a benzene ring. The Environmental Protection Agency has designated 12 of these compounds of importance in drinking water, due to their potential adverse effects in humans.

Pentachlorophenol



Analytical considerations

Phenols analysis can be carried out by a variety of methods, such as GC-FID and HPLC. However, the analytical method of choice is GC/MS. Not only does it have superior detection limits, it can also confirm the presence of any phenolic compounds detected something that other analytical methods cannot do.

Samples are first extracted using Solid Phase Extraction, and then, if needed, a clean-up step employed. The final extract is concentrated, and then analysed by GC/MS, either in SCAN mode, or more commonly SIM (Single Ion Monitoring) mode to increase sensitivity and eliminate background interferences. This is of particular importance in complex matrices, where interfering peaks could lead to a false positive.

Typical GC/MS analysis uses helium as the carrier gas, which, as well as having vagaries in supply and an elevated cost due to ongoing depletion of stocks, involves the use of cumbersome, high pressure cylinders of up to 200 bar, which must be changed on a regular basis.

A Parker domnick hunter generator provides ultra high purity hydrogen gas at a constant flow and pressure, with a minimal amount of stored gas, removing hazards common to cylinders.

Experimental

Analysis was performed on a Shimadzu QP2010S GC/MS in SIM mode and splitless injection (www.shimadzu.com)

Hydrogen was supplied from a Parker domnick hunter 110H-MD generator (www.parker.com/dhfns)

Column - J&W HP5-MS
Injector - 260°C
Interface - 280°C
Ion Source - 250°C
Flow rate - 1.5mls/minute (H2)
Injection volume - 1µl

Oven Programme:
40°C (hold 1 minute) to 220°C @ 12°C/minute to 300°C @ 30°C/minute (hold 0.10 minutes) Run time = 18.77 minutes

Sampling time - 0.30 minutes
Control mode - Pressure

Results

8 Standards were prepared in Dichloromethane, and ran over the range of 0.1 ng/µl– 40ng/µl. Excellent calibration curves were obtained, with all compounds having a calibration coefficient of →0.990. This included 3 surrogate standards used to monitor method performance.

Typically, some phenols tend to tail quite badly, including 2-methyl-4,6-dinitrophenol, 2,4,6- tribromophenol and pentachlorophenol. Minimal tailing was observed at both ends of the calibration range with hydrogen carrier gas, and peak tailing factors for these compounds were well within acceptable limits.

As you can see from comparing the two chromatograms, hydrogen has several chromatographic advantages over helium

- **Shorter run time – over 1.5 minutes**
- **Minimal peak tailing of late eluting compounds**
- **Similar response**

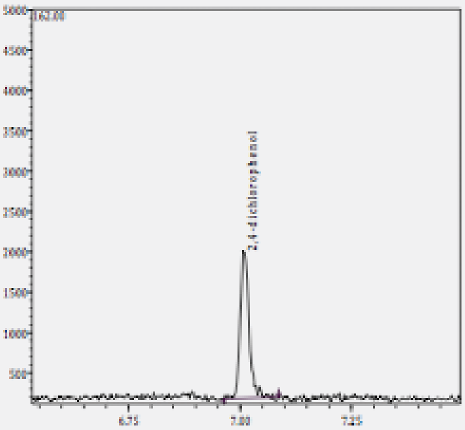
Conclusion

In conclusion, there is no reason why hydrogen, supplied from a 110H-MD generator, cannot be used for the analysis of EPA Phenols by GC/MS. It has been shown to easily get down to the lowest level of the calibration range, has a similar response to helium, but has the major advantage that it has a shorter run time.

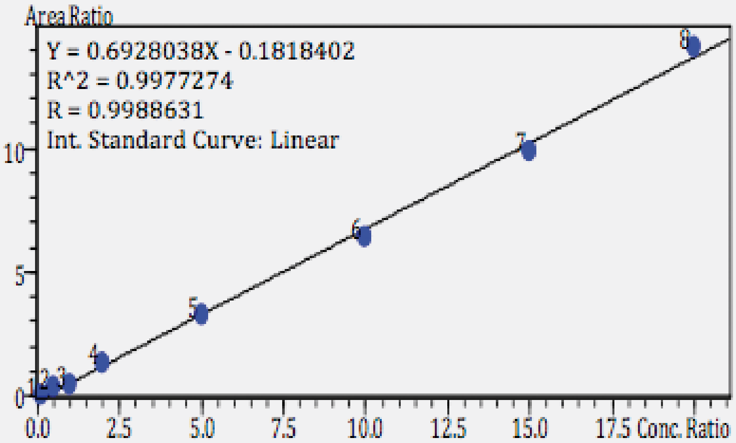
As well as the analytical advantages, there are also safety aspects that are addressed when comparing hydrogen to helium. The amount of stored gas in a generator is very small, compared to the high pressure (up to 200 bar) heavy, cumbersome cylinders that helium is supplied in. A Pdh generator will shut down in the event of a leak, therefore removing the danger of the lower explosive limit being reached.

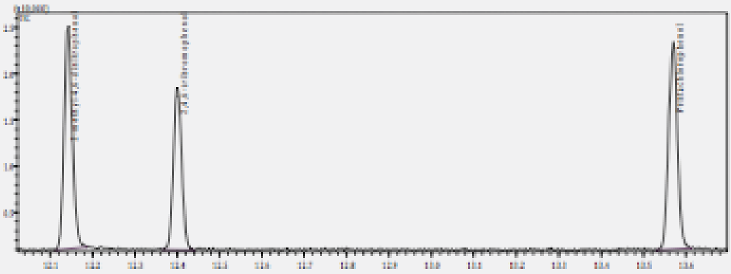
With the price of helium constantly increasing, and vagaries in supply, there is no reason why hydrogen should not be considered as an alternative to helium for carrier gas in GC/MS applications.

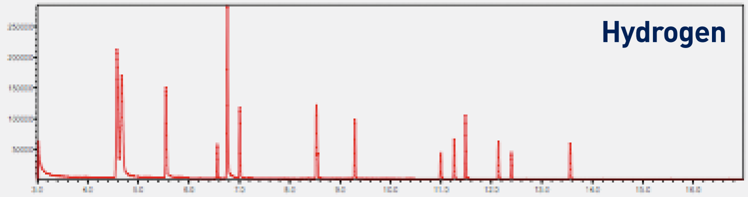
0.1 ng/µl 2,4-dichlorophenol

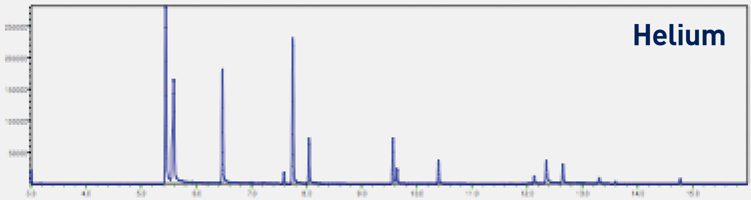


2,4 – Dichlorophenol









The Analysis of 19 EPA Polychlorinated Biphenyls by GC/MS using Hydrogen Carrier Gas

Introduction

For many GC applications, hydrogen is the carrier gas of choice, due to its superior qualities in terms of analysis speed and increased response. However, its use in GC/ MS has widely been avoided due to concerns over safety, high background noise, and potential reactions in the ion source.

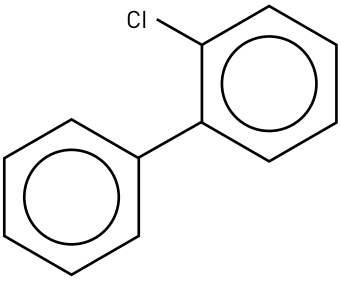
Modern technology has allayed these fears to some extent, but routine analysis using hydrogen as a carrier for GC/ MS is uncommon, and has not been exploited to its full potential. As helium prices continue to rise, there is no reason why, with safety precautions, hydrogen should not be considered as a viable alternative.

Parker domnick hunter manufacture a range of hydrogen generators providing ultra high purity hydrogen gas without the safety hazards associated with high pressure cylinders. These generators improve analytical performance, whilst shortening runtimes.

Polychlorinated Biphenyls (PCB's), are a group of manmade compounds (of which there are 209 in total), which consist of 2-10 chlorine atoms attached to a biphenyl ring. Individual PCB's are known as congeners, where mixes of various PCB's are known more by the trade name of Aroclor's.

PCB's were used extensively in a wide variety of industries, especially electrics, being good insulators, chemically stable, and having a high boiling point. They are now banned, but still may be present in various products and materials manufactured prior to the ban being introduced. They do not decompose readily, and are insoluble in water, and so are of primary importance for the EPA, who has designated 19 PCB's of importance in method 8082

Analytical considerations



PCB detection is normally carried out by either GC-ECD (Electron Capture Detector), or GC-ELCD (Electrolytic Conductivity Detector), both of which are designed for the detection of chlorinated compounds. Whilst both are more than capable techniques, the fact that they rely on retention time alone for identification purposes can have potential problems with false positives. These problems are eliminated with the use of a GCMS system, which can confirm the presence of suspect PCB's in a matrix, something the other detectors can't do

Typical GC/MS analysis uses helium as the carrier gas, which, as well as having vagaries in supply and an elevated cost due to ongoing depletion of stocks, involves the use of cumbersome, high pressure cylinders of up to 200 bar, which must be changed on a regular basis.

A Parker domnick hunter generator provides ultra high purity hydrogen gas at a constant flow and pressure, with a minimal amount of stored gas, removing hazards common to cylinders.

Experimental

Analysis was performed on a Shimadzu QP2010S GC/MS in SIM mode with splitless injection (www.shimadzu.com)

Hydrogen was supplied from a Parker domnick hunter 110H-MD generator (www.parker.com/dhfns)

Column – Restek Rtx-5 20m
 * 0.18mm *0.20µm
Injector - 226°C
Interface - 280°C
Ion Source - 250°C
Flow rate – 0.65mls/minute (H2)
Injection volume - 1µl
Linear Velocity – 54.1cm/sec

Oven Programme:
80°C to 270°C @ 7.5°C/minute
(hold 5.0 minutes)
Run time = 30.33 minutes
Sampling time - 0.75 minutes
Control mode – Linear Velocity

Results

5 Standards were prepared in Hexane, and ran over the range of 0.2 ng/µl– 1ng/µl. Excellent calibration curves were obtained, using 2 internal standards, with all compounds having a calibration coefficient of →0.990. 7 replicates we ran at 0.1 ng/µl to monitor performance. Excellent reproducibility was seen, with all s/n ratios ←10

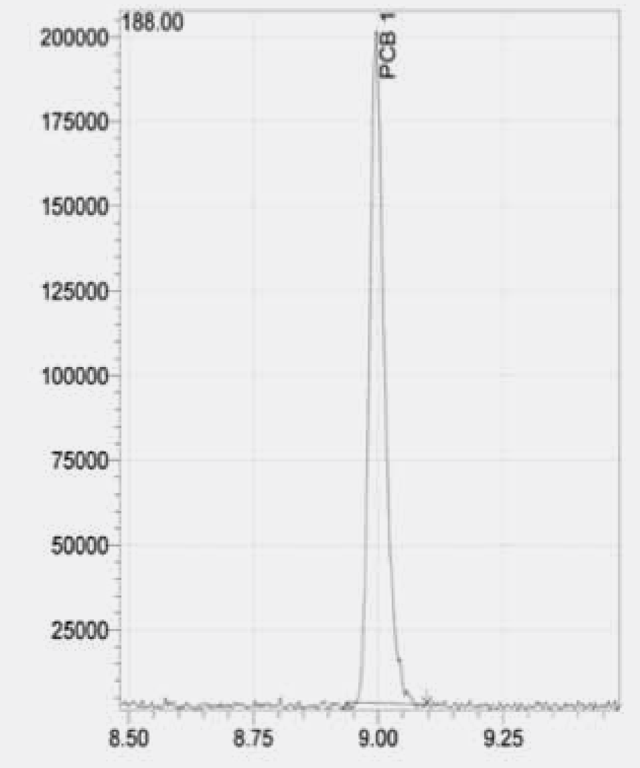
Conclusion

In conclusion, there is no reason why hydrogen, supplied from a 110H-MD generator, cannot be used for the analysis of EPA PCB's by GC/MS. Levels of 0.1ng/µl can easily be achieved in SIM mode, with calibration curves shown to be comparable to that of helium. On average, a saving of 3 minutes can also be achieved by using hydrogen.

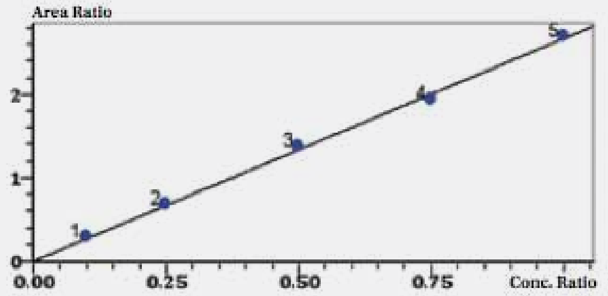
As well as the analytical advantages, there are also safety aspects that are addressed when comparing hydrogen to helium. The amount of stored gas in a generator is very 0.1ng/µl PCB 1 small, compared to the high pressure (up to 200 bacatchpolr) heavy, cumbersome cylinders that helium is supplied in. A Pdh generator will shut down in the event of a leak, therefore removing the danger of the lower explosive limit being reached.

With the price of helium constantly increasing, and vagaries in supply, there is no reason why hydrogen should not be considered as an alternative to helium for carrier gas in GC/ MS applications.

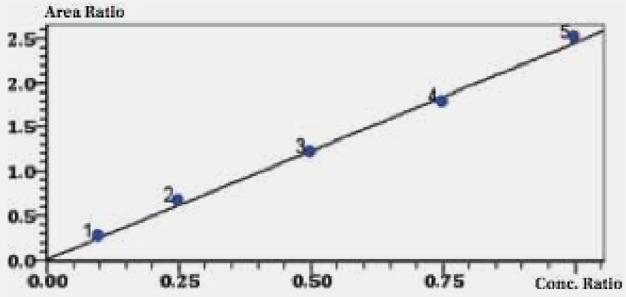
0.1ng/µl PCB 1



PCB 101 Calibration Curve - Helium



PCB 101 Calibration Curve - Hydrogen



The Analysis of 16 EPA PAHs by GC/MS using Hydrogen Carrier Gas.

Introduction

Hydrogen is the choice of carrier gas for many applications, due to faster analysis times (compared with nitrogen and helium) with no reduction in resolution. In fact resolution is normally improved. However hydrogen's use as a GC/MS carrier gas has long been avoided. Reactions in the ion source, lack of pumping ability, and high background noise have all been cited as reasons not to use hydrogen as a carrier gas. Modern technology has to some extent allayed these concerns, but still helium continues to be used for many established methods. Generated hydrogen offers an analytically superior, cost effective and safe solution over and above cylinder fed helium.

One of the most common analytical studies performed in many environmental laboratories is the analysis of Polynuclear Aromatic Hydrocarbons (PAHs). PAHs are a group of compounds consisting of more than one benzene ring, found in fossil fuels, tar and various oils, as well as being formed by the incomplete combustion of carbon containing compounds, such as wood, coal and diesel, to name but a few.

The Environment Protection Agency (EPA) has designated 16 PAHs as primary pollutants. The detection and quantification of these compounds, especially in water and soils, is of paramount importance for human health and the environment, due to their toxic and carcinogenic nature.

Parker domnick hunter manufacture a range of hydrogen generators providing ultra high purity hydrogen gas without the safety concerns associated with high pressure cylinders. These generators improve analytical performance, shorten run times and maximise productivity.

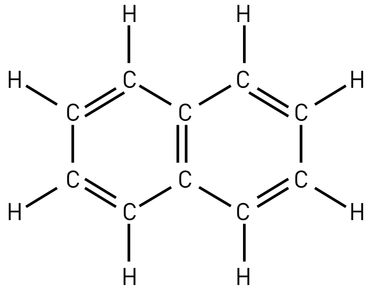
Analytical considerations

Analysis of the 16 EPA PAHs is normally carried out using GC-FID or GC/MS, with varying detection limits depending upon the medium in question and the analytical technique employed. GC/MS is favourable as it can eliminate non-required peaks, leaving only analytical information of interest, utilizing Single Ion Monitoring (SIM) mode. This is especially important in complex matrices, where peaks of similar composition may lead to false interpretation.

In any modern analytical laboratory, sample throughput and productivity are of utmost importance, where time is money. Employing hydrogen as a carrier gas is very common in GC-FID workflows, yielding superior chromatography, as well as reduced run times. Whilst it's use within GC/MS workflows is less common, with the correct conditions, it has the potential to deliver superior performance benefits over and above helium, with the added incentive of enhanced safety and cost savings.

Typical GC/MS analyses uses helium which, as well as having vagaries in supply, often at elevated cost, also necessitates the use of cumbersome, heavy, high pressure cylinders (up to 200 bar g) which must be changed on a regular basis.

A Parker domnick hunter hydrogen generator produces ultra high purity carrier gas at a constant pressure and flow rate, with minimal stored volume, eliminating laboratory hazards associated with high pressure storage vessels, such as cylinders.



Experimental

Analysis was performed on a Shimdazu QP2010s using SIM mode and splitless injection (www.shimadzu.com)

Hydrogen was supplied from a Parker domnick hunter 110H-MD generator (www.domnickhunter.com)

Column supplied by Phenomenex - Zebron ZB5MS 0.25mm X 0.25µm (www.phenomemex.com)

Injector - 300°C
Interface - 320°C
Ion Source - 250°C
Flow rate - 3ml/min (H2)
Injection volume - 1µl

Oven Programme:
40°C (hold 1minute)
100 °C @ 15 °C/min (hold 10 minutes)
225 °C @ 5 °C /min (hold 0 minutes)
320 °C @ 15 °C /minute (hold 2 minutes)
Total run time = 48.33 minutes
Sampling time - 1minute
Control mode - Linear velocity

Results

Detection limits of 1ppb were easily achieved, with excellent baseline resolution. 10 replicates were ran at this level, with typical RSDs of ←0.1, and signal/noise (s/n) ratios varying between 5 and 20 (typically ←10).

Standards were prepared in Dichloromethane over a range of 5 to 100ppb. Calibration over this range showed excellent linearity with all compounds being →0.995.

Typically, late eluting PAHs tend to tail, sometimes quite badly, making integration difficult, and peak asymmetry poor. In the above example, you can see clearly that the use of hydrogen carrier gas minimizes tailing, making integration easier to perform.

As you can see from the comparison of the two chromatograms on the left hand side, hydrogen has many advantages over helium when it comes to chromatographic performance:-

- **Shorter run times, in this case, a saving of over 5 minutes**
- **Increase in sensitivity, which is important for trace level analysis**
- **Less peak tailing of later compounds, which is important for peak integration**
- **Near baseline resolution of later co-eluting peaks**

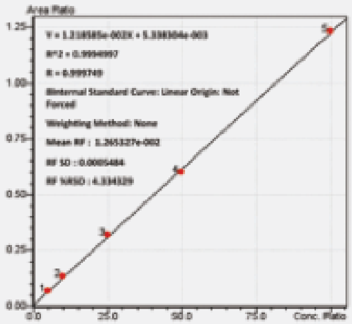
Conclusion

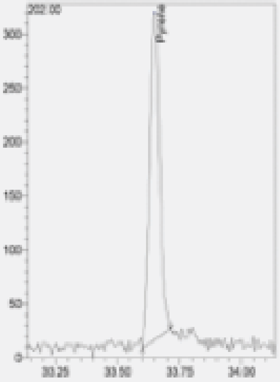
In conclusion, hydrogen carrier gas, supplied by a Parker domnick hunter 110H-MD generator, provides all the necessary requirements needed to perform the analysis of low level Polynuclear Aromatic Hydrocarbons by GC/MS, with many distinct advantages over helium carrier gas.

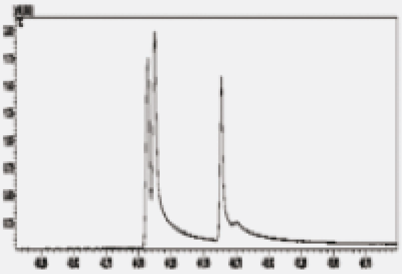
As well as the analytical benefits, safety issues are also addressed through the elimination of the containment and handling of heavy, high pressure storage vessels, not to mention the danger of running out of gas unexpectedly. Instrument downtime through loss of gas and further column damage and loss of vacuum within the GC/MS system are extremely undesirable outcomes. Moreover, the volume of stored gas in a hydrogen generator is very small, and has built in safety features in case of a leak, shutting down the flow of hydrogen, thus removing the danger of the lower explosive limit being reached.

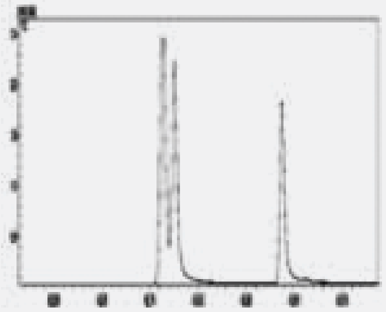
With the price of helium ever increasing, and vagaries in supply, there is a compelling case for ultra high purity generated hydrogen as a GC/MS carrier gas. With maximized instrument uptime of prime importance to many analytical laboratories, the use of hydrogen is a viable and safe alternative over and above helium.

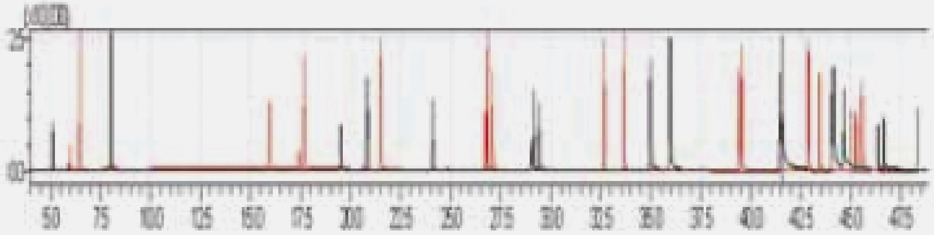
Throughout this paper we have displayed a robust, repeatable and reliable method utilizing hydrogen as a carrier gas to reduce peak tailing, lower limits of detection, provide superior baseline resolution of co-eluting compounds with excellent calibration coefficients, over much reduced analytical run times.











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