

Alternative Carrier Gas for GC and GC-MS Presentation Transcript

Hello and welcome to the Peak scientific webinar which today will concern alternative carrier gas for GC and GC-MS.

My name is Ed Connor, I'm a product manager at Peak Scientific and have a number of years of experience of use of GC and GC-MS in laboratories.

During today's webinar we're going to look at the following topics:

First of all, why look at alternatives to helium, then we'll look at nitrogen and hydrogen carrier gases as alternatives to helium, then gas safety. After this, I'll speak about the process of carrier gas conversion, particularly focusing on GC-MS applications and then after that, I have a small number of application examples which may give you more of an idea of the benefits of changing carrier gas from helium to hydrogen.

So, some people among you may be wondering why would you need to look for an alternative to helium. Well first of all, helium is a finite resource which is normally associated with natural gas deposits and it's refined as a by-product from natural gas. At the end of 2012 and into 2013 there was a worldwide helium shortage which caused supply issues worldwide and this has actually continued for some regions where supply of helium is not as regular as some users might like it to be.

In addition to supply issues the price of helium has risen steadily over the last 15 years and in fact the price has actually increased around 100% percent in that time period.

If you look at the graph on the right-hand side you will see the line is actually the price of helium which, as you can see, has risen quite sharply over the last 10 years or so. From information recently put out by major gas suppliers, prices are set to increase into 2018 and beyond so this is becoming an increasing problem for a number of labs.

The figure here is called the Van Deemter curve and this shows the relative efficiencies of nitrogen, hydrogen and helium across different flow ranges. The vertical axis is theoretical plate height and the horizontal axis is the speed of the carrier gas. Basically, for the best indication of efficiency is where the curve is lowest so that the plate height is reduced.

So if we first of all look at the nitrogen curve, that's the green line, you can see that the optimal velocity or the velocity of gas where we get the lowest plate height is at around 10 to 12 cm per second. This means that if we use nitrogen carrier gas we can get very good separation of our sample but only at lower velocities.

If we then look at the curve for helium which is the red line you can see that by again looking at the lowest point of the curve for the theoretical plate height we're looking at somewhere in the region of 20 to 30cm per second. This is one of the reasons why helium has been one of the preferred carrier gases for a number of years because you get good average speed of analysis, combined with good separation and that's probably why you see many more labs using helium than nitrogen because they can run their samples faster but still achieve good separation.

Now when we look at the curve for hydrogen, the blue line, what you might notice if you compare it with helium is that as we speed up and get up to a velocity of 70, 80 or 90 centimeters per second, the theoretical plate height does not actually increase at the same rate, meaning that if we use hydrogen as an alternative to helium we can actually increase the speed of our analysis without compromising the separation of the products that we're looking at.

So, as I've just discussed, nitrogen has a low optimal velocity meaning that if we run a sample using nitrogen carrier gas, we need to run the gas normally somewhere in the region of 10 to 14 centimetres per second in order to get optimal separation of the product.

Now, it is possible to run samples using nitrogen carrier gas at higher velocities, but what will happen is that the separation between the peaks may not be as good or the separation of products may not be as good and so there's more of a risk of co-elution occurring so that peaks run into one another so it's important if you are considering using nitrogen as an alternative to helium to make sure that you have enough resolution or enough separation between your peaks before you make the change, if you're planning to run it a bit faster.

On the plus side, nitrogen is readily available since it is freely available in air and so it's also cheap and it's inert like helium so it's not going to react with your sample or cause any other issues of that kind. The one note for GC-MS users is that if you are thinking of using nitrogen, then sensitivity can be quite severely reduced compared to helium so typically looking at 20 times reduction in sensitivity.

Now there's been some interesting work done by Restek over the last couple of years looking at nitrogen carrier gas in conjunction with shorter narrower bore columns and I think, if you're not really familiar with nitrogen carrier gases as an alternative that's probably a good place to start looking.

Now, as I discussed in the slide before about the Van Deemter curve, hydrogen offers faster analysis than helium because of its better efficiency at higher velocities. When we look at how our sample will behave when we're running with helium compared to hydrogen the diffusion rate is actually about the same at the same temperature and pressure meaning that our sample will behave fairly similarly. So when we're looking at changing carrier gas

one thing that you can explore is actually keeping the linear velocity of your sample the same when you're running with hydrogen as you did with helium. What you should see is an increase in the efficiency when using hydrogen but the advantage of starting this way is that your peaks will elute at the same time because you can use the same oven program.

Now when we look at the efficiency and separation of our sample we should get better chromatography when using hydrogen because the increased efficiency improves the resolution and when we look at method optimization we can start looking at running the sample at lower temperatures because products will elute at lower temperatures when you're running with hydrogen and one of the knock-on effects of being able to reduce the temperature of your GC Oven program is that you will decrease the time between samples because the oven cools faster and the lifetime of the column can actually be extended because there's less wear and tear because you're not having to heat it up as close to its maximum temperature as perhaps you would need to when using helium. So there can be a number of advantages of using hydrogen carrier gas in addition just to simply learning samples faster.

Of course, one of the questions that is often asked about nitrogen and hydrogen is in regards to safety of these gases and I'll just give you a little bit of information on nitrogen and hydrogen safety. Nitrogen is an inert gas, as indeed is helium, and it can cause oxygen depletion which means that it can displace oxygen and change the relative amount of oxygen in the atmosphere. Once oxygen levels drop below 18 % you actually will have impaired cognitive function meaning that you'll make mistakes and maybe think a little bit more slowly and once levels drop down to around 11% it's actually possible that people can suffer from irreversible brain damage as a result of lowered oxygen levels.

So, if we consider the use of cylinders or dewars for nitrogen supply there is potential for a large volume of nitrogen to quickly be released into the lab and significantly changing the oxygen level and oxygen content of the of the atmosphere and so there are significant dangers associated with the use of nitrogen cylinders and dewars and the use of a generator is actually a much safer and sometimes much more economical solution so do check the peak website for details of generators for whatever application you're looking at but we do have systems for GC applications.

If we consider hydrogen of course most people are aware that hydrogen is a flammable gas and it has a lower explosion level of 4.1% in atmosphere so if there's an ignition source and we have more than 4.1 % hydrogen in the atmosphere we can have an explosion or fire. Now if we take the example of a laboratory measuring by 5x5x3 meters then we've got a total volume of 75 cubic meters or 75,000 liters so the LEL in this particular lab would be just over 3000 liters so if we consider a large 50 liquid liter cylinder which contains around 9000 liters of hydrogen you can very quickly achieve or surpass the LEL with a significant

leak from the cylinder so there is significant danger associated with storing hydrogen in cylinders in laboratories.

Now if we contrast this with a hydrogen generator producing half a liter of hydrogen per minute it would take almost 7 days to produce the same volume of gas so this just over 3000 liters so hydrogen generator is often the preferred source of hydrogen for gas chromatography because it's a much safer and more controllable supply of the gas and if you want more information on hydrogen generators then have a look at the peak scientific website and there's plenty of information on there and also surrounding gas safety.

So now I'm just going to go over the major points involved in changing carrier gas from helium to hydrogen or nitrogen. So the first thing that you really should do is check whether your methods allow the use of nitrogen or hydrogen as an alternative to helium because some methods are actually locked on to helium so you're not able to change even if you wanted to for compliance purposes.

Now the chromatograms on the right show the same mixture being run with helium hydrogen and nitrogen so as you can see it is possible to achieve very similar, if not almost identical, results with the different carrier gases in terms of separation of the peaks. However as you may notice if you look at the x-axis of the horizontal axis the times vary depending on which carrier gas has been used. In this case with hydrogen offering the fastest analysis, helium medium-speed analysis and nitrogen slower analysis. So even though on the face of things that separation is the same, the times can vary.

So once we've established that we are able to change our method the next place that you should really go is to a method translation software. You can also do this in your GC software in the method setup - to change some of the parameters and see what the run times will look like but using a calculator like this one from Restek will allow you to play around with things like different column lengths, different column diameters and you can optimize the performance based on efficiency, speed or for the best column efficiency.

So what will happen is, as you can see on the left, you've got the original helium method and then you can select which gas you're translating the method to whether that's hydrogen or helium, and you can also look at keeping the column the same or the effect of changing the column and what it will do is calculate the oven program for you and also the pressures required, so the carrier gas pressure and this should give you some kind of indication of how your method will look when you change on the actual GC program.

In terms of hardware changes on the GC system, this mostly applies to GC-MS analysis. There's not actually that much that you would normally need to change on your GC if you're using a non-MS detector like an FID, TDC, ECD and so on. So first for example on GCMS you would need to check the pumping efficiency of the vacuum pump to make sure that it is capable of dealing with hydrogen because hydrogen is much lighter than helium so

the pump actually has a harder time pumping away the hydrogen that goes into the ion source.

Also looking at low nickel sources because nickel will actually facilitate hydrogenation reactions and this will reduce the background and reduce the opportunity for a reaction between your hydrogen carrier gas and sample. You can also look at, as I just mentioned before, alternative columns and using hydrogen in conjunction with the narrower column will overcome some of the effects of the reduced pressure that you may see and will also help in reducing the volume of hydrogen that actually goes into the source so it will actually help with the pumping efficiency by reducing the total volume of hydrogen entering the source. You can also start to look at shorter columns as well which can improve your chromatography.

Now one thing that you will almost certainly need to do if you're looking at hydrogen in place of helium is to replace the tubing between your gas supply and the GC. Stainless steel is normally recommended but lab grade copper should also work perfectly well for the supply of hydrogen. Lab ventilation is also a good idea, just a typical ventilation system or air-conditioning system that will replace the volume of air in the lab every few hours. Also in some labs people are quite wary of the hydrogen that's escaping through this split vent so you may want to consider putting an extractor over outlet from the split vent or potentially putting a line to a hood. I haven't done this myself because if you think back to the example I showed you before with the LEL, lower explosion level, of hydrogen it's very difficult to achieve this even if you are perhaps splitting out 100cc or 200ccs per minute it's going to take a long time to actually produce enough gas to reach the LEL in a typical lab and it's really very unlikely but if you are particularly concerned about this then you can vent to a fume hood or use an extractor. One other thing to consider of course when you change from helium to hydrogen or nitrogen is to change your septum and change the liner on the inlet of the GC. You certainly need to do that but you should be able to keep the rest of the system the same.

So once you've got the system set up with your alternative carrier gas you need to check the performance of the system so if you've changed from helium to nitrogen you need to check that the system is separating your sample and that everything looks good. if you are running GC-MS it's probably more likely that you are using hydrogen and the signal to noise can be reduced when using hydrogen but usually by a factor of two to five times and, as I mentioned before, if you're using nitrogen for GC-MS which is less often but some systems are capable of using nitrogen carrier gas, you should expect to see a reduction in sensitivity relative to helium of around twenty times so it can be significantly reduced.

So wherever possible if using G-CMs it's advisable to use sim detection selected ion monitoring which will help overcome some of loss of sensitivity when using an alternative

carrier gas. If you are using sim then normally you will know what you're looking for, some systems can do simultaneous sim and scan detection. In fact, all new systems will be able to so this might be an option for you as well if you're looking for unknowns and some known compounds. Now changing fragmentation patterns with GC-MS can also be a concern and can be a symptom of too much hydrogen moving from the column into the ion source. One way to combat this is to use a narrower column, a narrow bore column, which will reduce the volume of hydrogen entering the ion source at any one time, should help reduce the change of fragmentation. It won't entirely eliminate it but it should reduce the effects that are seen.

Peak tailing is often cited as a concern of analysts switching from helium to hydrogen and again, on a GC-MS system, one way to combat this is to follow guidelines from the instrument manufacturers regarding baking out the source. Agilent, for example, recommend baking the source and leaving the filament on overnight and this significantly reduces background that you see in the system so just look for any advice from your particular instrument manufacturer.

So now I'm just going to give you a couple of examples of applications where we've looked at hydrogen replacing helium for GC applications. The first is fatty acid methyl ester analysis, or fames analysis, and in this study we were looking at a 39 component standard and the customer was changing from helium to hydrogen because they had issues with supply and were also seeing increasing expense of helium.

So it's an FID method, GC FID method, and the first step that was taken was just to translate the method from helium to hydrogen but what we found was that some peaks co-eluted so we didn't get separation of all 39 components. So then we decided that the best place to start would be to match the linear velocity of the two gases. So if you think back to the software that I showed to you before where you can model the effects of changing carrier gas and column and so on. Well in this case it was the same column, GC setup was identical so that the oven program was the same and the only thing that was changed was the carrier gas so the linear velocity was also kept the same as for hydrogen as for helium. What this means is that you should get elution of each component at the same time in the hydrogen method as you did in the helium method. So with the unchanged retention times we then start to see the benefit of using hydrogen compared with helium. Since the flow of carrier gas was slightly above the optimal velocity for helium, but well into the optimal range for hydrogen, we got sharper narrower peaks. I'm running with hydrogen which you can see in the chromatograms at the bottom of the screen. So all the components separated identically but we've got a slightly better chromatography using hydrogen.

Now another common analysis, this time on GC-MS, is pesticide analysis. In this example we looked at 59 pesticides in a mixture, again using hydrogen carrier gas produced by a gas generator. Now the detection here was done in sim mode to increase sensitivity since we

knew the components we were looking for, and tested across a range of 50 ppb to 5 ppb. When we looked at the recovery rates of the different components, 2 compounds had higher than 10% RSD and the other 57 had less than 10% RSD so not seeing great variation, and the linearity of calibration standards was very good as you can see there for Fenitrothion.

The next application is on a GCMS triple quad and concerns the analysis of PAH and PCB compounds. These are both environmental pollutants but are typically analyzed using quite different methods, so PAHs are typically analyzed using HPLC with UV detection and the analysis time typically takes around 30 minutes. For PCBs traditionally these compounds have been analyzed using GC-ECV with an analysis time of around 60 minutes using helium carrier gas. The aim of this study was to look at the use of GC-MS to combine the analysis of these two types of compound. In particular, there are a number of critical separations such as PCB 28 and 31 which we had to be mindful of and so what was assessed here was analysis by single quad and by triple quad using hydrogen carrier gas and comparison with the traditional methods.

In terms of separation the critical separation of PCBs 28 and 31 was achieved as you can see in the chromatogram there and then when looking at the results of the GCMS or GCMS triple quad versus the traditional analysis, you can see that for the PCBs the recovery rate was in the same order of magnitude with perhaps a little bit more sensitivity for the GCMS triple quad and again for the PAH, there is a similar story with similar recovery rates for the compound regardless of the method but with the GCMS triple quad a little bit more sensitivity. Now, as you can see at the bottom, the total analysis time was just 11 minutes so this is a big potential time saving for labs who are able to switch from HPLC or GC ECD analysis to the GC-MS analysis which will work in single or triple quad. For more details the application note is available from the Peak website.

Now on to the last example which concerns the draw out lens which is a component of the Agilent ion source. If you look at the figure below the standard draw out lens dry out plate will have a three millimeter orifice but for use of hydrogen in conjunction with some compounds a six millimeter orifice is recommended, which can be ordered and can be fairly easily swapped for the three millimeter dry out plate. This gives the advantage of increasing sensitivity slightly when using hydrogen. So back to the different ways that we discussed before about overcoming some of the shortfalls of using hydrogen, this is another measure that you can take if you have an Agilent system in order to increase sensitivity.

We were interested in looking at the effect of the 6mm lens compared with the 3mm lens and hydrogen and helium, and particularly the effects on resolution and signal-to-noise. The table below shows three flow rates for each condition so we've got optimal flow rate, suboptimal and less optimal as a kind of medium option. What you can see if we just start with the results from helium and resolution, when we're in full scan at optimal flow rates

we're getting a value of 4.94, if we compare this to hydrogen with the 6mm lens for the value of 2.6 you can see that resolution is certainly better when we use helium at an optimal flow rate compared to hydrogen at an optimal flow rate. Then if you look in the second column there with the sim detection what you can see is that with hydrogen we're actually getting more resolution in sim mode than we get in helium in sim mode so we seem to be going a long way to improving things with when using hydrogen.

If we look at the signal-to-noise again comparing helium and hydrogen in full scan and Sim mode, we look at the optimal flow rate you can see that helium is far better than hydrogen in full scan mode with a signal-to-noise ratio of almost 2000 to compared to 200 so here, before I said that you'll typically see a 2 to 5 times reduction, here it's 10 times reduction almost but then if we compare this signal to noise in full scan with the signal-to-noise in Sim detection, at optimal flow rates you can see that with hydrogen we're actually getting very close to the performance that we get with helium. So again, back to the point about Sim mode, this is why you'll see many studies looking at hydrogen carrier gas running the system in Sim mode because it goes a long way to overcoming the sensitivity issues surrounding the use of hydrogen. I hope this gives you a bit more of an understanding of how or what the advantage of using sim detection can be.

Alright so as I mentioned, all the articles and applications which I've just covered and many more are available on the Peak Scientific website. There's a tab called learn and under learn there are articles and applications and we also have a knowledge base which has articles about how our systems work. There's lots of other information available on there about changing carrier gas or the use of generators and why gas generators could be advantageous for your lab so I would urge you to check there and if you're not able to find what you're looking for then feel free to contact us and we'll get back to you as soon as possible.

So I'd like to say thank you for your attendance today and thank you to SelectScience for hosting this webinar on behalf of Peak Scientific. If you have any questions please let me know.

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