

Hydrogen as Carrier Gas: Always Available, Cost Effective and Fast – A Personal Reflection

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Hydrogen is on the agenda again. Since the supply of helium has become a challenge, many labs are now considering the use of hydrogen as the carrier gas of choice. Most chromatographers agree that hydrogen is the best choice, because of the advantages on analysis time and availability, but safety management issues are the primary concerns with many chromatographers. Hydrogen can be generated safely in the lab and if you make the calculations, you will find that commercial gas generators are cost effective and will pay for their purchase price in a relative short time, particularly since the price of helium is high and unlikely to come down in the future. The focus of this paper will be to investigate the practical impact of using hydrogen in the lab and what other aspects need to be considered.

During my extensive working life in the analytical lab performing GC column evaluations at Chrompack, Varian Inc and for the last 6 years with Restek Corporation, the majority of column manufacturers have made a practice of testing columns using hydrogen since it is the 'fastest' carrier gas, and demonstrates the optimal performance of the column based on a combination of time and chromatographic efficiency. As a consequence the vast majority of the column test-reports supplied by manufacturers are based on the use of hydrogen carrier gas.

There are several topics to be considered when looking at the practical impact of changing to hydrogen as the carrier gas, these include;

- Safety aspects
- Impact on the chromatographic separation and peak response when existing methods are converted.
- Use of hydrogen with a MS detection system

One issue is of extreme importance: when moving to H₂ you must change oven temperature programmes, to obtain the same peak elution order (and get the full benefit of shorter retention times).

Safety

The first challenge to consider and for most labs the biggest hurdle is the safety aspect. [1]. When thinking about H₂, the 'Hindenburg' accident [2] always comes into

the memory, which gives a large negative feeling. Under certain circumstances hydrogen is explosive, but how can this risk be minimised in a GC? The answer is: The user needs to be aware of the potential risks and must eliminate such situations to occur.

Flow controlled vs pressure controlled analysis: In today's GC, there is a choice between using pressure or flow controlled analysis. In the case of using H₂ I would set up the system under 'flow control'. In terms of safety issues, the worst thing that can happen is that a fused silica capillary column breaks at the injection port. Using a flow controlled method, the total amount of H₂ that can enter the system, is the volume of injector + column, multiplied by the absolute pressure [3]. The digital pressure regulation of the carrier gas cannot build pressure so it

will detect a problem and the system will jump in "standby" mode, while displaying an alarm function. Even if hydrogen keeps on flowing, the amount is not enough to built up critical levels, see also [4]. Additionally the oven is turned off so there is no ignition source.

Safety systems: if this is not sufficient, one can always buy safety systems. Systems are available that 'suck' the oven-air and measure a possible presence of He or H₂ gas. It works in the same way as a leak detector or a gas sensor. Using these devices will be more expensive but it buys safety (Figure 1).

Metal capillary columns: To further decrease the risk, one can choose the option of using metal columns, which are much less likely to break than their silica counterparts. Such columns have been around for a long time for high temperature analysis like crude-oil-



Stand-alone



Integrated

Figure 1: Use Hydrogen sensors with alarm and event options

Simdist and Biodiesels, but they also perform very well for lower temperature applications. The inertness is remarkably good due to the Siltek deactivation. The functionalised silicon surface behaves for many applications similar (or better) than the natural silica, as demonstrated in Figure 2.

Hydrogen is explosive if there is an ignition source and concentrations are between 4 and 80%. To our advantage is that diffusion of H_2 is extremely fast which results in hydrogen being diluted very quickly, thus reducing risks of explosion. Hydrogen has been used for many applications and the risk of malfunction is there but it's extremely small if one understands what the real risks are. To put some context into the safety issue: we at Restek (and other manufacturers), have tested millions of columns using hydrogen as the carrier gas and never had an issue.

At a certain point, it requires common sense, like 'you do not light a cigarette when you are taking fuels at a gas station'. Using hydrogen is not different: you just have to be aware that it is combustible.

The splitted hydrogen may be perceived as a problem for the lab. In the old days we had a simple solution to get rid of the excess H_2 . It was simply burned using small torch next to the splitter, see Figure 3. This is not allowed anymore in today's lab policies as it's an 'open fire hazard'. Is there a risk for hydrogen built up in a lab? If someone makes some calculations, you will find that to build a 4% level it requires many days to get to that level, assuming it's a completely sealed room. Labs are ventilated quite intensive, so hydrogen built-up is not a realistic risk.

Impact on Separation and Response

Once the decision is made to use H_2 , one needs to optimise the method using this carrier gas. Figure 4 shows an example of a hydrocarbon mixture, analysed in the same GC, using helium and hydrogen. For hydrogen we used twice the velocity we used with helium. The components elute twice as fast with minor impact on efficiency. Since the peaks elute twice as quickly, and there is no loss in the efficiency, the peaks are 2x narrower, meaning they are also 2x higher.

It is quite simple to convert isothermal methods to hydrogen: the linear velocity is increased roughly by a factor of 2 and 50% of sample volume is injected using the same split ratio. This will result in the same peak-height (same sensitivity).

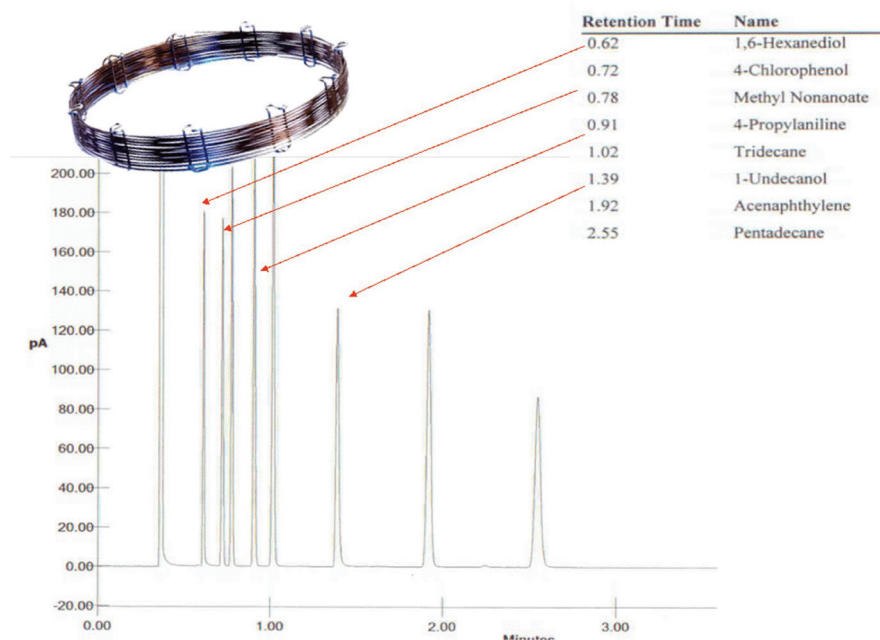


Figure 2: Test for inertness 10m x 0.32mm MXT coated with 0.1um Rtx-1 type film, @ 110 °C

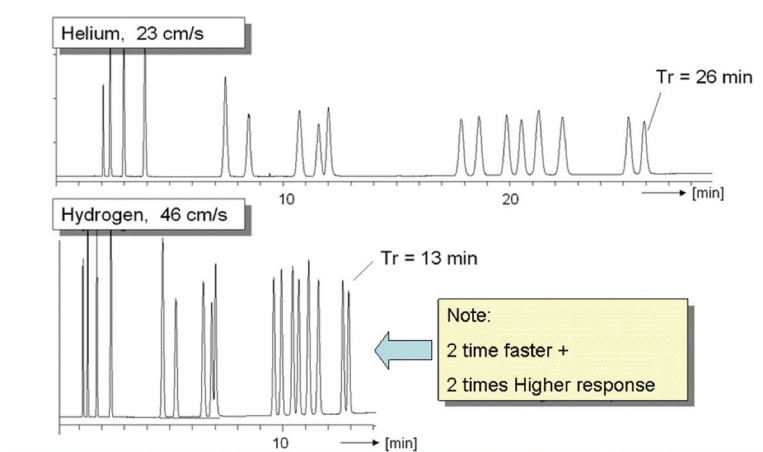


Figure 3: In the early days, excess hydrogen from Split was 'funneled' off in the lab.

Temperature programmed runs need some more attention, particularly if the same peak elution order is to be expected.

To realise this, a change of oven temperature program rate is required. The new program will make sure that the components will elute at the same elution temperature using hydrogen as with using helium. If this is not done, some separations will improve and some will go worse.

If the linear velocity increases roughly a factor 2, a 2x faster temperature program rate is used. Isothermal times have to be reduced by a factor 2. The result will be the same separation in about 50% of the time.

One can exactly calculate this, but there are also freeware programs available on the web. You can also use the helpdesk of

companies that are specialised in gas chromatography to help you with the calculation of your new settings.



Figure 4: Hydrocarbon mixture on Rt-Alumina BOND MAPD, using Helium and Hydrogen.

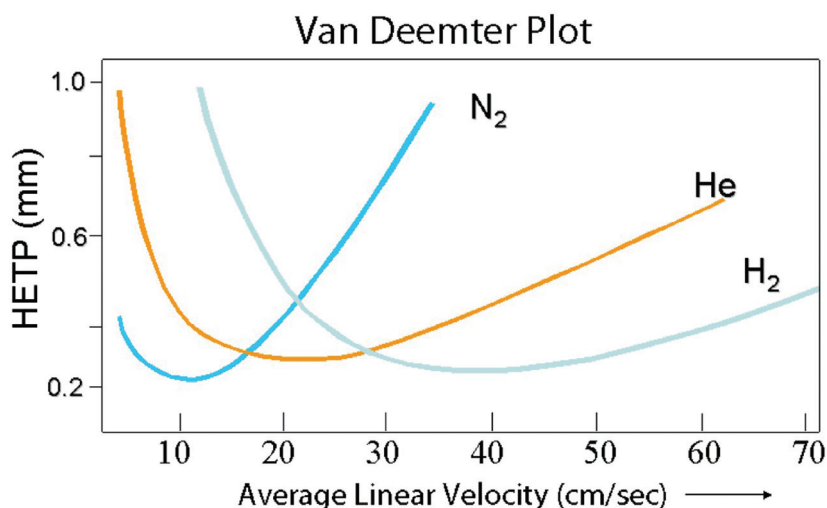


Figure 5: The effect of average linear velocity on column efficiency using three different gases. Hydrogen offers the fastest optimal velocity

The possibility of injecting less offers a big advantage, as only 50% of the original amount has to be injected, the contamination of the injection port liners will be 2 times less. Also column maintenance will be less, which is quite interesting for reducing maintenance and cost of analysis. This demonstrates a further cost saving associated with the change of carrier gas from helium to hydrogen.

Figure 5 shows the van Deemter plot which explains why this advantage for using hydrogen occurs [5,6].

If speed of analysis is a key driver, one can also apply hydrogen in combination with smaller diameter capillary columns (0.15mm instead of a 0.25mm). Figure 6 shows a fragrance separation on a 0.15mm Stabilwax column run with He and H₂. Here is no loss on separation efficiency and peak elution is

similar, while a shorter run time is obtained. This conversion can be done with all phases that are available on smaller diameter capillary columns. This combination allows run times to be reduced by almost a factor 4.

One can also choose for using thinner films, but the impact will be a reduced loadability, and as peaks elute at lower temperature, the peak shape for polar compounds will be challenged

Hydrogen and MS

With MS things get a little diffuse as instrument manufacturers have difficulty dealing with such questions. Last Pittsburgh Conference on Analytical Chemistry in US, I asked several instrument manufacturers about their recommendations and the reactions were not all similar.

What I learned was:

- H₂ in MS is generally not an issue, but if it's operated at 2x higher flow, vacuum pump must have enough capacity to pump away this flow. One can use a higher capacity pump or use a jet-splitter. However, it is easier is to choose a 0.18mm or 0.15mm ID Rxi-5Sil MS columns, which operates optimal at lower volumetric H₂ flow.
- Ionisation may be different. You cannot use NIST/WILEY reference databases. Practically, to be sure you need to create your own reference spectra; however, stable components like PCB, aromatics, dioxin do show similar spectra.
- H₂ may cause adsorption activity in ion source which may lead to a lower response and some tailing on polar components
- Running hydrogen through former 'helium' lines, may result in a higher initial background. Hydrogen has a 'scrubbing' effect of the gas lines that especially with sensitive detection systems may be detected.
- Sensitivity may be lower (may be compensated by optimising lens systems)
- Introduction of carrier gas / air mixtures will cause internal explosion: Not good for our MS, but probably good for service companies.

Some other concerns using Hydrogen as the carrier gas

Availability: the use of Hydrogen has also an economical component. While helium prices are increasing by the day, hydrogen prices are very low. One can produce hydrogen by a generator cutting carrier gas costs. In future, helium will only become more expensive and labs will have to deal with substantially reduced availability in the future. This is another viable reason to consider hydrogen and it's potential. Alternative, Nitrogen can also be considered for applications where maintaining similar resolution is not the key objective.

Reactivity

Hydrogen is a reducing gas. In conjunction with hot surfaces and adsorption surfaces, one can expect hydrogenation. A good example of this is with styrene analysis. In hot injector mode, the analyte will be converted

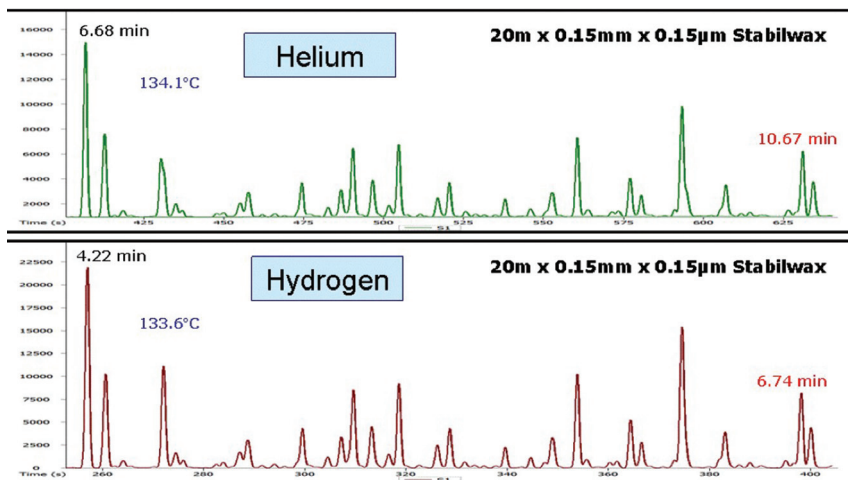


Figure 6: Replacing helium for hydrogen in fragrance analysis using a Stabil wax phase and 0.15mm columns

into ethylbenzene. Reactive olefins may show some reactivity when using alumina columns. This depends strongly on the type of alumina, deactivation, purity and temperature.

If reactivity in the column is suspected, one must;

- reduce the elution temperature
- use higher flow rates
- slow down temperature program
- and, if possible, use thinner films/shorter columns

Conclusion

The use of hydrogen has proved to be a good choice for speeding up separations. It may not have been implemented in many

labs, primarily due to safety considerations, but very few incidents have actually been reported. This is mainly due to the nature of the hydrogen carrier gas. One can simply decrease risks by using flow controlled methods as today's GC's will jump in standby mode if the pressure cannot be maintained. The application of more robust metal capillary columns will reduce column breakage risks. The use of hydrogen systems will further allow safe use of hydrogen as the carrier gas especially for implementing faster GC separations

Acknowledgements

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