Avoiding Safety Issues and Reaping the Benefits of Hydrogen as a Carrier Gas in GC

Matt James, Kirsty Ford, Tony Edge, Avantor

Introduction to explosive mixtures

One of the challenges of an analytical laboratory is making changes in an ever-changing world where external pressures often drive practical changes within the laboratory environment. Often these are in the form of new regulations, stipulating better more robust data, more sample analysis, or pressures from productivity, where financial pressures encourage the analytical scientist to reduce the analysis times. However, more recently the world of analytical chemistry has been targeted with another driver. The world is becoming more and more aware of the impact that the human race is having on valuable natural resources, and so terms like sustainability are being introduced into the laboratory environment.

One area that is being impacted is gas chromatography (GC). GC has been a front-line analytical technique for several decades and is routinely used for environmental, petrochemical, pharmaceutical, and food sample analysis [1, 2, 3, 4]. Although there has been a gradual move to perform the analysis of more polar compounds using HPLC, there is still a substantial amount of analysis being performed using this technique. The predominant carrier gas used in GC is helium, which is proving difficult to source. Helium is actually one of the most abundant elements in the universe, however on earth it is only generated through radioactive decay. It is very light and seeps through the earth only getting trapped by pockets of natural gas, which effectively means that it is a non-renewable resource. There is, thus, a drive in the industry to look at other possible carrier gases, with the benefits of reducing costs. The primary replacement carrier gas is hydrogen, and this article will look at the benefits and pitfalls associated with introducing hydrogen into a working laboratory, along with some other changes that will reduce analysis times without compromising the chromatographic performance of the GC system.

One of the major perceived challenges associated with the introduction of hydrogen is associated with safety. The reaction between air (oxygen) and hydrogen is stoichiometrically a trivial one, however the actual chemistry is very complex, and one that can exhibit a thermal runaway, or explosion under the correct conditions. Hydrogen gas forms combustible or explosive mixtures with atmospheric oxygen over a wide range of concentrations in the range 4.0% – 75% and 18% - 59% [5]. In terms of understanding why this reaction is so dangerous it is necessary to understand the chemistry.

The reduced hydrogen oxygen model [6], *Figure 1*, is often used to model the reaction, although this does not necessarily present a complete picture of all of the reaction mechanisms that are occurring, it does give an understanding of the underlying chemistry behind the observed phenomena.
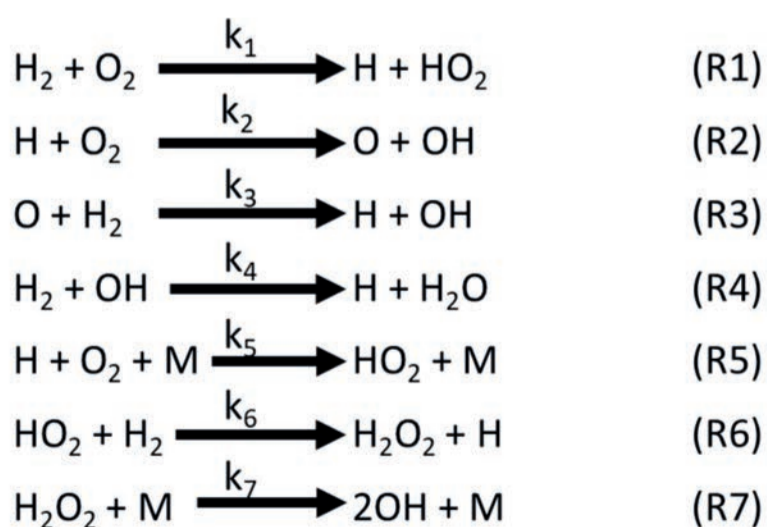

Figure 1. The reduced hydrogen – oxygen reaction scheme [6].

When solved, the reduced model generates two reaction states, a low energy one, and a high energy one which is associated with the thermal runaway or explosion. There is not a gradual transition between the two states and the difference can be quite dramatic when varying a parameter by only a small amount. The reaction scheme generates three explosion limits, in the form of a characteristic 'z' shape when looking at a pressure - temperature plot. Understanding of this reaction scheme is of particular importance to the petroleum and the automobile industries, since it is the basis of all combustion reactions [7, 8, 9]. Looking at the reaction scheme it is specifically R6 and R7 that form the basis of this explosive reaction when at atmospheric pressures. These reaction steps generate free radicals and water, the free radical propagates the reaction, whereas the formation of water generates heat, which in turn increases the rate of reaction. The reaction step that slows the reaction down is the wall termination or R5. The M here represents any gas phase collision partner. The idea that a reaction can have two very different reaction states is not unique to combustion reactions, and many other examples exist [10, 11] and in the world of mathematical modelling are referred to as part of catastrophe theory.
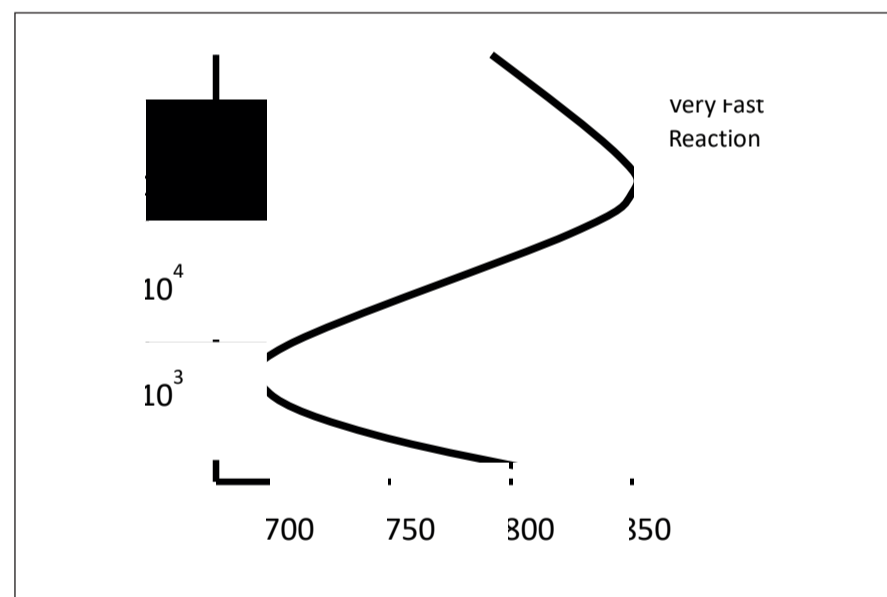

Figure 2. The three explosion limits that exist for the hydrogen oxygen reaction.

The non-linear nature of the reaction kinetics is itself fascinating as it can result in oscillatory behaviour when associated with continuous flow reactors, or in the presence of carbon monoxide have been shown to exhibit chaotic behaviour. Indeed, when the experimental data is plotted as a 2 dimensional plot where x(t) is plotted against x(t+n), where n is a regular time interval [12], higher levels of structure can be seen which is an indicative sign that the chemical kinetics are chaotic in nature. This experimental system has been investigated in some depth and other artifacts of a chaotic system have also been shown to exist including, bistability [13], period doubling bifurcations [14] and next maxima return plots [12].

Hydrogen is lighter, less viscous, and has a lower density than other fuels. As a consequence of these properties' hydrogen will disperse readily which means in a non-contained environment there is a reduced risk of building up high concentrations, however it does also mean that it is more likely to leak from any pipe work etc. This would suggest that in a large well ventilated room small leaks would not present a problem, however the major safety issue is the source of the hydrogen. The two most common sources of hydrogen that are used by modern chromatographers are gas cylinders, which will contain up to 50 L of gas pressurised to 200 bar, or a hydrogen generator which typically stores around 60 mL of gas pressurised to less than 10 bar. It is very evident that for the safety aware chromatographer that the hydrogen generator provides a substantially safer environment and one that could be readily employed within a laboratory, whereas a gas cylinder would require extra safety precautions, and would require the storage of the hydrogen cylinder outside of the laboratory facility.
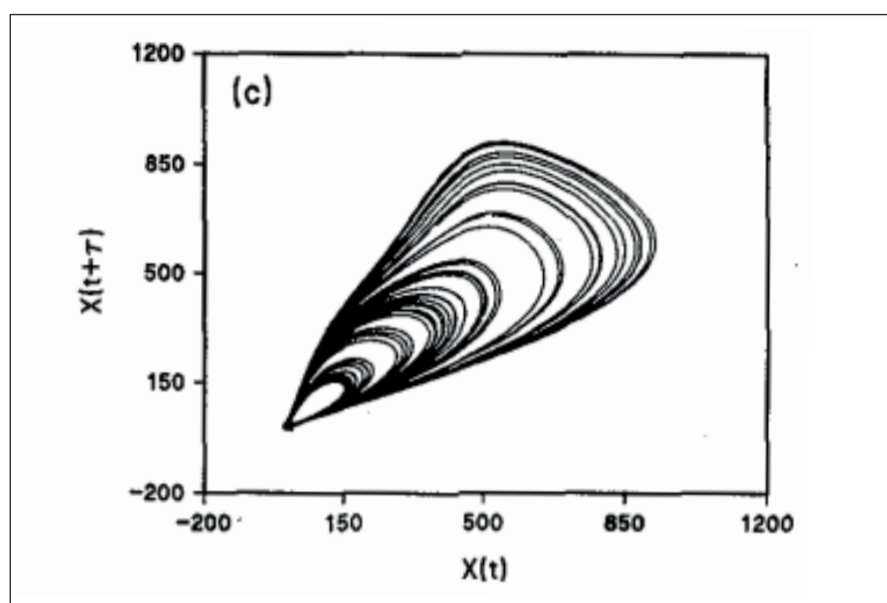
Figure 3. The mussel attractor found by Johnson et al. which is indicative of a chaotic system, reproduced with kind permission from [12].

Benefits of introducing hydrogen into the laboratory

In terms of the benefits associated with the introduction of hydrogen, there is a massive price differential, of approximately a factor of 20 (prices quoted in June 2023). This will depend on the purity of the gases being used but highlights a significant economic driver to look at alternative carrier gases. As well as the economic benefits associated with using hydrogen compared to helium, the higher diffusivity means that the optimal linear velocity is higher than that obtained when using helium. The higher diffusivity also means that there is a greater range over which the operating conditions do not have a significant effect on the chromatographic performance, allowing for even faster analysis times.

This can be explained by the Golay equation, *Equation 1* [15], which is a modified form of the van Deemter equation [16]. In GC performed with open tubular columns, the absence of a packed bed means that the eddy dispersion term is omitted, which is associated with the stochastic pathways a mobile phase molecule can have going through a packed bed. *Figure 4* shows a diagram of the chromatographic performance of hydrogen, nitrogen and helium (the three most common carrier gases) under isothermal conditions. For hydrogen it can be seen that the flow rate/linear velocity can be almost doubled without a loss in the chromatographic performance. However, this is not quite the case when running with temperature gradients where the temperature ramp rate for the oven also has to be changed. It should also be noted that the injection volume should also be changed to account for the higher linear velocity of the mobile phase, reducing it by approximately 50% when the flow rate is doubled.
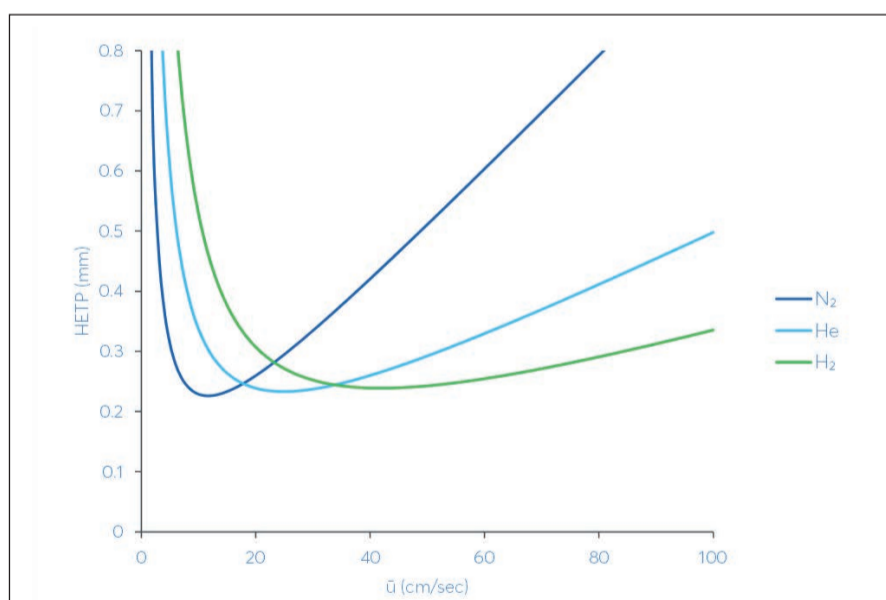

Figure 4. Golay plots showing the chromatographic performance for hydrogen, nitrogen and helium carrier gases.

Equation 1

The Golay equation [15]

$$du = \left(\frac{2D}{v_0} + \frac{(1 + 6k + 11k^2)v_0 r_0^2}{24(1 + k)^2 D} + \frac{k^3 v_0 r_0^2}{6(1 + k)^2 c^2 D_1} \right) dx_1$$

Where;

v_0 – linear velocity of the carrier gas

k – retention factor

r_0 – column radius

x – length of the column

u – measure of the peak width

D - Diffusion coefficient of analyte in the gas phase

D_1 – Diffusion coefficient in the stationary phase

Deterministic relationship with retention time / gradient

Further benefits associated with higher throughput and sustainability can also be achieved by a reduction in the film thickness, column diameter (both of which reduce the dispersion of the peak due to diffusion) or a decrease in the column length.

The following equations can be used to determine the system parameters required to optimise performance using a smaller i.d., shorter, reduced film thickness column with the subsequent sections demonstrating the effects of varying some of the parameters listed in *Equation 2*.

Equation 2

$$t_{g2} = t_{g1} \frac{v_2}{v_1} \frac{\beta_2}{\beta_1} \frac{l_1}{l_2} \qquad\qquad T_2 = T_1 \frac{v_1}{v_2} \frac{\beta_1}{\beta_2} \frac{l_2}{l_1}$$

Where;

t_{g1}, t_{g2} - temperature gradient for original and new conditions

v_1, v_2 - linear velocity of gas for original and new conditions

T_1, T_2 - hold time for isothermal part of separation for original and new conditions

β_1, β_2 - phase ratio for original and new conditions

l_1, l_2 - length of column for original and new conditions

The use of narrow i.d. and thin film columns, coupled with very fast temperature gradients, is often referred to as Fast GC [17]. Significant improvements in the assay performance can be achieved without the need to make changes to the system set-up using Fast GC column dimensions ((20 m × 0.15 mm × 0.15 µm for example) compared to conventional column dimensions (30 m × 0.25 mm × 0.25 µm). The improved peak efficiencies obtained using a Fast GC column, without compromise in peak resolution, can be obtained provided:

• The ratio of column length to i.d. remains the same
• The column stationary phase should not alter
• The column phase ratio (β) is consistent between the two columns.

Further improvements in productivity can be obtained by combining higher optimal linear velocity, with an increase in the temperature ramp rate.
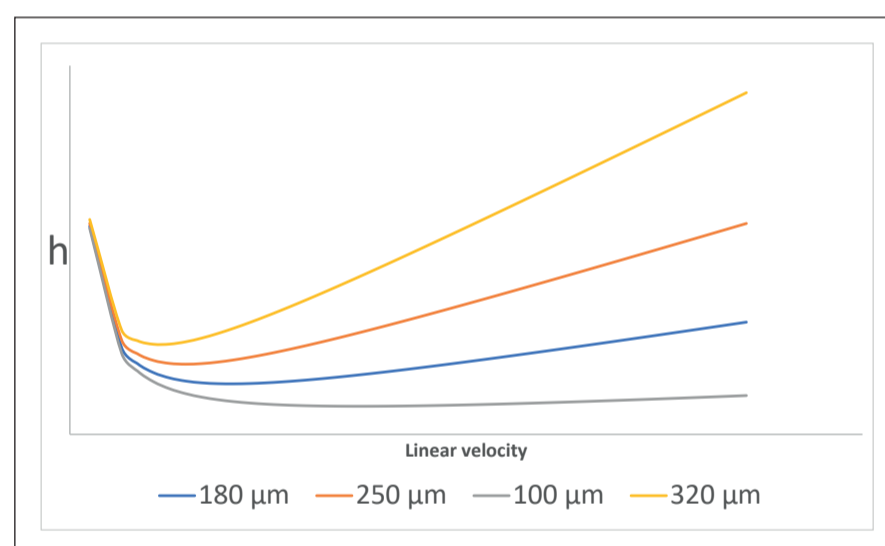

Figure 5. Effect of reducing the column diameter on the chromatographic performance when using GC.

Figure 5 illustrates that by reducing the column diameter; efficiency increases and as a consequence so does the resolution. The efficiency is always greater in the narrower bore column, thus shorter columns can be used to reduce analysis time, whilst offsetting the reduced efficiency arising from shorter column length. *Table 1* shows normalised efficiency for column length and diameter.

Table 1. Comparisons of the efficiency relative to column length and diameter compared to a 30 m x 0.25 mm column.

Column I.D (mm)	Column length (m)				
	60	30	20	15	10
0.15	3.3	1.7	1.1	0.8	0.6
0.18	2.8	1.4	0.9	0.7	0.5
0.25	2.0	1.0	0.7	0.5	0.3
0.32	1.6	0.8	0.5	0.4	0.3
0.53	0.9	0.5	0.3	0.2	0.2

Another advantage of using a narrow bore column is that optimal linear velocity of carrier gas also increases, which allows shorter analysis time. There are, however, some practical considerations with the use of narrow bore columns, including lower sample loading capacity which means that higher split ratios or reduced sample injection may be required to prevent column overload.

The effect of the increased carrier gas flow on the temperature gradient is to effectively decrease the temperature gradient relative to the time the compounds stay on the column. This results in the peak capacity increasing due to the peak widths getting narrower and the temperature gradient effectively being decreased.

Keeping the phase ratio consistent

If the phase ratio *(Equation 3)* is kept consistent, then the elution order of compounds will be the same. *Table 2* shows that a 0.25 mm x 0.25 µm GC column has the same phase ratio as a 0.15 mm x 0.15 µm column, so will show ,relatively, the same elution order of the compounds. However, the efficiency on the 0.15 mm column diameter is greater, allowing for a similar separation to be performed with a shorter column length.

Equation 3

β – Phase ratio of the column
d_c – Column diameter (µm)
d_f – Film thickness (µm)

$$\beta = \frac{d_c}{4d_f}$$

Table 2. Phase ratio values to ensure correct dimensions are selected for optimising methods.

Column diameter, d_c (mm)	Film thickness, d_f (µm)										
	0.15	0.18	0.25	0.5	1	1.4	1.5	1.8	2.65	3	5
0.15	250	208	150	75	38	27	25	21	14	13	8
0.18	300	250	180	90	45	32	30	25	17	15	9
0.25	417	347	250	125	63	45	42	35	24	21	13
0.32	533	444	320	160	80	57	53	44	30	27	16
0.53	883	736	530	265	133	95	88	74	50	44	27

It is therefore evident that reducing the column diameter improves the efficiency and will also reduce the amount of carrier gas that is required, however it also reduces the loadability of the stationary phase.

Conclusion

Replacing helium with hydrogen can be performed without any serious safety concerns arising if the appropriate source of hydrogen is used.

The benefits associated with this are substantial not only in terms of significantly reduced carrier gas costs, but also in the ability to use this as a steppingstone to supercharge the chromatography, by moving to FAST GC. The resulting benefits in reduced analysis times, and even further reductions in carrier gas costs due to the lower flow rates utilised. It is often the case that individuals use the introduction of one change to allow for bigger changes to occur, and in the case of moving to hydrogen, it is not a case of increasing safety issues, but more of improving the separation, reducing costs and reducing analysis times.

References

1. F. J. Santos and M. T. Galceran, J. Chromatogr. A., vol. 1000, pp. 125-151, 2003.

2. C. Witschi and E. Doelker, European Journal of Pharmaceutical and Biopharmaceutics, vol. 43, pp. 215-242, 1997.

3. K. Ahang, J. W. Wong, D. G. Hayward and P. Yang, Comprehensive Analytical Chemistry, vol. 61, pp. 55-95, 2013.

4. K. Kimata, K. Iwaguchi, S. Onishi, K. Jinno, R. Eksteen, K. Hosoya, M. Araki and N. Tanaka, J. Chromaogr. Sci., vol. 27, pp. 721-728, 1989.

5. H. Dagdougui, R. Sacile, C. Bersani and A. Ouammi, Hydrogen infrastructure for energy applications, C. 7. -. H. L. S. a. R. Issues, Ed., Academic Press, 2018, pp. 127-148.

6. L. Newcomb, M. Marucci and J. Green, "Explosion limits of hydrogen-oxygen mixtures from," Physical Chemistry Chemical Physics, vol. 30, no. 23, pp. 15746 - 157752, 2018.

7. R. R. Baldwin and R. W. Walker, "The role of radical-radical reactions in hydrocarbon oxidation," Combustion and flame, vol. 21, no. 1, pp. 55-67, 1973.

8. D. L. Baulch, J. F. Griffiths, W. Kordylewski, R. Richter, S. K. Scott and P. Gray, "Experimental Studies of the Oscillatory Combustion of Hydrogen in a Stirred Flow Reactor," Philosophical transactions of the Royal Society of London. Series A: Mathematical, physical, and engineering sciences, vol. 337, pp. 199-210, 1991.

9. O. M. Egeiban, J. F. Griffiths, J. R. Mullins and S. K. Scott, "Explosion hazards in exothermic materials: Critical conditions and scaling rules for masses of different geometry," International Symposium on Combustion,, vol. 19, no. 1, pp. 825-833, 1982.

10. R. S. Zahler and H. J. Sussmann, "Claims and accomplishments of applied catastrophe theory," Nature, vol. 269, pp. 759-763, 1977.

11. J. B. Rosser, "The rise and fall of catastrophe theory application in economics: Was the baby thrown out with the bathwater?," Journal of Economic Dynamics and Control, vol. 31, pp. 3255-3280, 2007.

12. B. R. Johnson, J. F. Griffiths and S. K. Scott, "Oscillations and chaos in CO + O2 combustion," Chaos, vol. 4, no. 1, pp. 387-395, 1991.

13. H. Wang, T. Shen, S. Duan, Z. Chen and X. Xu, "Bistability for CO oxidation: An understanding from extended phenomenological simulations," ACS Catalysis, vol. 9, pp. 11116 - 11124, 2019.

14. A. T. Winfree, "The prehistory of the Belousov-Zhabotinsky oscillator," Journal of Chemical Education, vol. 61, pp. 661-663, 1984.

15. M. J. Golay, Gas Chromatography, D. Desty, Ed., London: Butterworths, 1958, pp. 62-64.

16. J. J. van Deemter, F. J. Zuiderweg and A. Klikenberg, "Longitudinal diffusion and resistance to mass transfer as causes of non ideality in chromatography," Chemical Engineering Science, vol. 5, pp. 271 - 289, 1956.

17. E. Matisová and M. Dömötörová, J. Chromatogr. A. , pp. 199 - 221, 2003.

Read, Share and Comment on this Article, visit: www.labmate-online.com/article