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The Effects of Carrier Gas Viscosity and Diffusion on Column Efficiency in Capillary Gas Chromatography

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INTRODUCTION

Viscosity is the resistance of a liquid or gas to flow. The viscosity of a gas is determined by two factors: (1) the molecular weight of the gas, and (2) its temperature. When the temperature or molecular weight of the gas is increased, its viscosity is also increased. In a chromatographic system, with a constant pressure drop, an increase in viscosity results in a decrease in the linear velocity of the carrier gas, ultimately resulting in lower column efficiency.

The objective of this study is to determine the effects of carrier gas viscosity of hydrogen and helium on column efficiency, particularly when employing thin films. When using thin films, mass transfer in the stationary phase becomes negligible and mass transfer in the mobile phase predominates. It was hypothesized that when employing thin films, hydrogen would be the carrier gas of choice due to its higher diffusiveness and lower viscosity. The combination of the previous factors should lead to faster analyses and higher column efficiency.

PROCEDURE

1. Compared the analysis times of a benzene, toluene, m-xylene, p-xylene and o-xylene mixture for hydrogen and helium at 40°C, 60°C, 80°C and 100°C (See **table 1**).
2. Compared the efficiency of the last eluting peak o-xylene for both Hydrogen and Helium (See **table 2**).
3. Compared the resolution of the isomers p-xylene and m-xylene at 40°C, 60°C, 80°C and 100°C (See **table 3**).
4. Mass Transfer in the mobile phase was calculated for Hydrogen and Helium at 200°C, 250°C, and 275°C (See **figure 3**).

INSTRUMENTATION

The instrument was a Hewlett Packard model 5890 series II Gas Chromatograph with a flame ionization detector and a Hewlett Packard model 7673 auto sampler; the column is a HP-5 (95% Methyl- 5% Phenyl Polysiloxane) 0.20 mm x 0.20 μm x 12 meter narrow bore capillary column. A Packard Instruments 9400 Hydrogen Generator produced the hydrogen that supplied both the carrier gas and supported the FID.

RESULTS

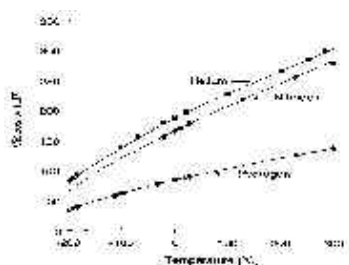


Figure 1: Shows the viscosity of hydrogen, helium, and nitrogen as a function of temperature (1).

TABLE 1: COMPARISON OF RETENTION TIMES FOR HYDROGEN AND HELIUM

Temperature	Hydrogen (min)	Helium (min)	% Faster Analysis
40°C	6.50	9.15	41.5
60°C	2.98	4.18	40.3
80°C	1.66	2.35	41.0
100°C	1.14	1.58	38.24

Table 1 illustrates the effect of viscosity on retention time. For all gases, as temperature increases, viscosity increases. Hydrogen's viscosity is influenced less by temperature than helium's is (**figure 1**), so it is easier to maintain higher linear velocities with hydrogen. This ultimately results in faster analysis times, particularly at high temperatures.

TABLE 2: EFFICIENCY COMPARISON OF HYDROGEN AND HELIUM

Temperature	Hydrogen	Helium	% Improvement
40°C	4.48E4	4.47E4	0.18

60°C	4.13E4	4.08E4	1.21
80°C	3.87E4	3.70E4	4.43
100°C	3.51E4	2.04E4	41.9

It was noted from previous research that there is a significant increase in column efficiency when using hydrogen (see footnote 2). However, what is most curious is that the difference in the efficiency between hydrogen and helium seemed to increase as the temperature increased. This phenomenon is attributed to the fact that the viscosity of helium increases more rapidly with temperature than does the viscosity of hydrogen (see **figure 1**). This causes slower mass transfer in the mobile phase and lower column efficiency when using helium.

TABLE 3: RESOLUTION COMPARISON OF HYDROGEN AND HELIUM

Temperature	Hydrogen	Helium	% improv. using H2
40°C	3.46	3.37	2.60
60°C	2.71	2.66	1.80
80°C	1.62	1.54	5.18
100°C	1.08	0.88	18.6

The most detrimental effect of increasing viscosity is that the target analyte has more difficulty partitioning through the mobile phase to the surface of the stationary phase and vice versa. This phenomenon results in slow mass transfer of the analyte and increased band broadening (See **figure 2 and table 3**). However, due to the smaller molecular size of hydrogen, it takes less effort for the analyte to diffuse through the mobile phase. This results in sharp and narrow peaks.

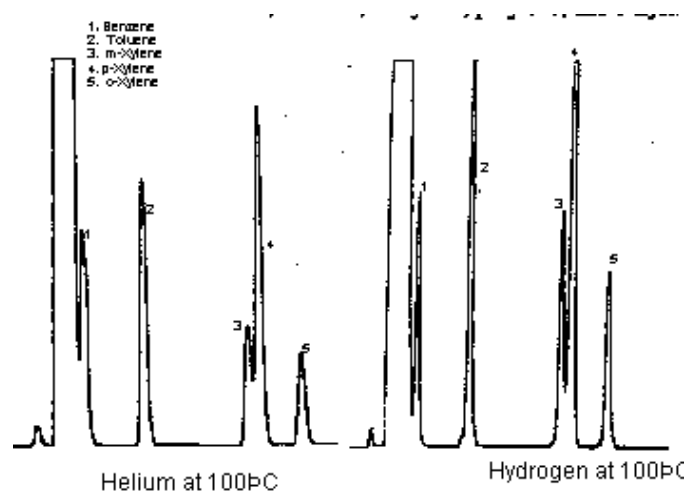


Figure 2: Illustration of improvement in efficiency and resolution when using hydrogen.

Mass transfer in the mobile phase is a function of capacity factor, column radius, and the diffusion coefficient of the solute in the mobile phase. The mass transfer data illustrates that hydrogen as a carrier gas has a higher rate of mass transfer than helium. Due to the larger molecular diameter of helium, it is more difficult for the solute molecules to penetrate the gas layer; as a result, the rate of diffusion is slower.

Figure 3 clearly shows that the rate of mass transfer in the gas phase increases with temperature and decreases with molecular weight, and that the rate of mass transfer is consistently faster when hydrogen is used as the carrier gas. One would expect the rate of mass transfer to decrease with increasing temperature due to the increased viscosity of the carrier gas. It was hypothesized that the more viscous the mobile phase, the slower the rate of mass transfer in the gas phase. However, when the temperature increases, the diffusiveness of the solute in carrier gas increases more than the viscosity, which results in faster mass transfer in the gas phase. Thus, the diffusiveness in the carrier gas plays a more important role than viscosity on column efficiency.

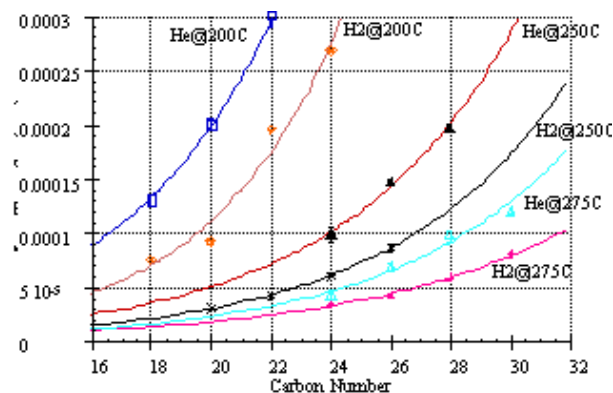


Figure 3: Mass Transfer Data for Hydrogen and Helium at 200°C, 250°C, and 275°C.

CONCLUSION

When using thin films, mass transfer in the stationary phase becomes negligible and mass transfer in the mobile phase dominates. This means that the role of the carrier gas dominates and that hydrogen becomes the best carrier gas. The primary goal in capillary gas chromatography is to produce as many theoretical plates as possible. This minimizes HETP, which is desirable. This report proves that when using thin films, hydrogen is the carrier gas of choice due to its faster diffusion in the gas phase and its lower viscosity.

Dr. Harold McNair is Professor of Chemistry at Virginia Polytechnic and State University. Stephanye Armstrong is currently a graduate student at VPI&SU.

References

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