

## The Effect of Temperature on Compound Elution Order in Gas Chromatography

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### Introduction

A compound's vapor pressure inside of a (Gas Chromatography) GC column is a function of two opposing forces. The first opposing force is the vaporization of the compound. The second opposing force is the strength of the intermolecular interactions between the compound and the stationary phase. Higher temperatures will increase a compound's vapor pressure, whereas stronger intermolecular interactions with the phase will decrease a compound's vapor pressure. At any one time, it is a combination of these two forces that determines what proportion of the injected compound will be in the mobile phase and what proportion will be in the stationary phase.

Since a compound can only elute through the column when it is in the mobile phase, it is the vapor pressure that determines retention time.<sup>1</sup> The easiest way to control a compound's vapor pressure in a GC is through the GC oven. By creating an oven program tailored to the analytes, a GC analyst can manipulate compound retention times and even change the elution order.

Note: Care must be taken when identifying peaks after a change in oven program, as an inadvertent change in elution order can occur.<sup>2</sup>

### Experiment

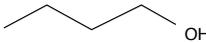
An Agilent 6890 gas chromatograph coupled to an Agilent 5973 MSD is used for the experiment. Four injections of a benzene/butanol mixture are made, each using a different oven program. All other samples and GC parameters remain constant.

### Results and Discussion

The four chromatograms seen in **Figure 1** show the reversal in elution order of two compounds, benzene and butanol. This elution order reversal was achieved by changing only the oven program. Oven program (A) was isothermal at 30 °C, then sequentially the temperature ramp was increased in increments of 10 °C/min (B, C and D) until a ramp of 30 °C/min was reached. Initially, under isothermal conditions, benzene eluted before butanol, but as the temperature ramp increased the two compounds began to co-elute and then eventually separate in the reversed elution order. By comparing the boiling points and structures of these two compounds the switch in elution order can be explained.

The boiling points for both benzene and butanol are listed in **Figure 2**. Of these, benzene has the lower relative boiling point by 37 °C. However, benzene also has stronger interaction with the Zebron™ ZB-5MSi stationary phase (**Figure 3**) due to pi-pi bonding with the phenyl groups in the phase. This form of interaction which does not exist for butanol, suppresses the volatilization of benzene.

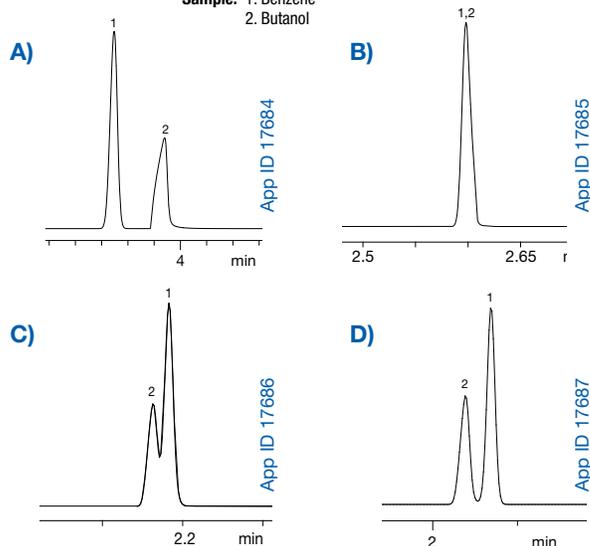
**Figure 2.**  
Compound boiling points

 Benzene Boiling Point 80 °C	 Butanol Boiling Point 117 °C
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**Figure 1.**

Chromatograms showing elution order change for Benzene and Butanol

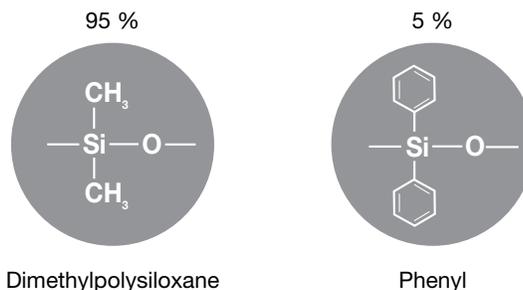
**Column:** Zebron ZB-5MSi  
**Dimensions:** 30 meters x 0.25 mm x 0.50 µm  
**Part No.:** 7HG-G018-17  
**Injection:** Split 50:1 @ 250 °C, 1.0 µL  
**Carrier Gas:** Helium @ 55 cm/sec (constant flow)  
**Oven Program:** Variable  
**Detector:** FID @ 250 °C  
**Note:** 50 ppm in DMSO  
**Sample:** 1. Benzene  
 2. Butanol



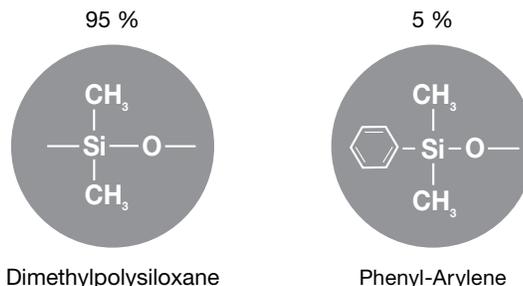
**Figure 3.**

Zebron ZB-5MSi and ZB-5ms stationary phases

#### Zebron ZB-5MSi



#### Zebron ZB-5ms



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Under 30 °C isothermal conditions, benzene has greater presence in the mobile phase than butanol because the oven temperature is closer to benzene's boiling point than to butanol's boiling point. As the oven ramp is increased butanol's vapor pressure increases at a greater rate than benzene's. This is because butanol has less interaction with the phase, so its vapor pressure is more affected by a change in temperature, as discussed by Grob.<sup>3</sup> Consequently, butanol elutes earlier relative to benzene with each increase in the temperature ramp.

## Conclusion

When analyzing via GC, two factors need to be taken into consideration, a compound's boiling point and its ability to interact with the stationary phase. These properties determine analyte vapor pressure and give a GC analyst the ability to manipulate the elution order of a chromatographic run. The extent in which each of these properties is exhibited is governed largely by the oven program. As a result, the desired separation can be achieved by changing the oven program to suit the compounds being analyzed. In addition, it is advised that the elution order be verified after any substantial change in the oven program. This will ensure that the elution order is not inadvertently rearranged.

## References

1. Hively, R.A. and R.E. Hinton, J.Gas Chromatoraphy. 6 (1968) 203-217.
2. Mehran M. et al., HRC, 14 (1991) 745-750.
3. Grob, R.L. (1995). Modern practice of gas chromatography, (3rd edition): Theory of gas chromatography (pp.100). New York: John Wiley & Sons, Inc.

## Ordering Information

### Zebtron ZB-5MSi GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
<b>15-Meter</b>			
0.25	0.25	-60 to 360/370	7EG-G018-11
<b>30-Meter</b>			
0.25	0.25	-60 to 360/370	7HG-G018-11
0.25	0.50	-60 to 360/370	7HG-G018-17
0.32	0.25	-60 to 360/370	7HM-G018-11
0.32	0.50	-60 to 360/370	7HM-G018-17
<b>60-Meter</b>			
0.25	0.25	-60 to 360/370	7KG-G018-11

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