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Retention Cross-over Phenomenon in Gas Chromatography—Can the Mystery be Revealed? Part 1

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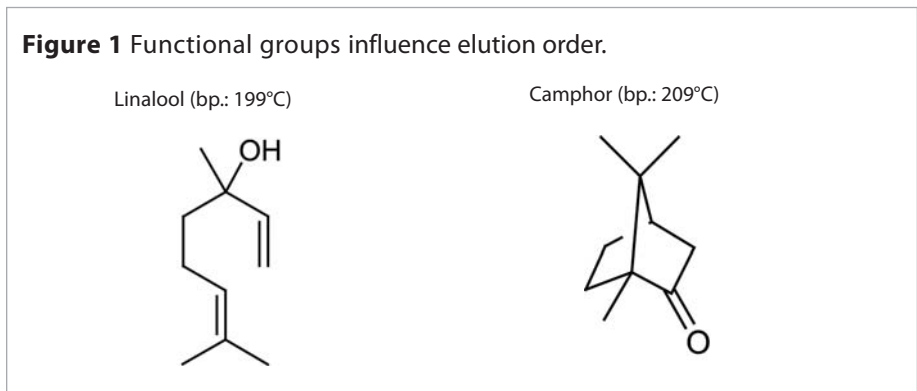
Have you ever faced changes in elution order after modifying the column temperature or the heating rate in the temperature program of the GC analysis of complex samples? This so-called cross-over phenomenon, which can lead to problems in peak identification, has been a well-known mystery in GC for decades.¹ But, so far, the physico-chemical background is still not well understood.

The cross-over phenomenon is very common when separating compounds with different functional groups on polar stationary phases. For example, we observed a reversal in the elution order for components like linalool and camphor on a polyethylene glycol column (Carbowax 20M) after changing the column temperature programming rate: at 5°C/min. linalool elutes before camphor but at 3°C/min. camphor will elute first. Effects like this are often observed when essential oils are analyzed or, to be more precise, when the GC methods are optimized. The reversal of the elution order is mainly explained as a result of the different temperature-dependencies of the intermolecular interactions, which are responsible for the retention: London-type dispersion forces and induction forces are independent of temperature, whereas the orientation forces and hydrogen bridge bonds depend strongly on the temperature (Figure 1).

However, this explanation is only half the truth and we should examine the influence of column temperature on retention in some more detail. It is generally known that the column temperature is one of the two most important variables in GC (the other being of course the nature of the stationary phase). In partition GC, the effect of temperature on the solute partition coefficient K is given by the van't Hoff relationship $\ln K = HS/RT_c + C$ (with HS being the molar heat of solution of solute). From this follows the fundamental correlation between column temperature T_c and retention factors:

$$\ln k' = HS/RT_c + C' - \ln \beta$$

where k' is the retention or capacity factor ($k' = t'R/tM$) and β the column phase ratio. This equation indicates that the retention decreases logarithmically as the column temperature increases.



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Retention Cross-over Phenomenon in Gas Chromatography- Can the Mystery be Revealed? Part 1

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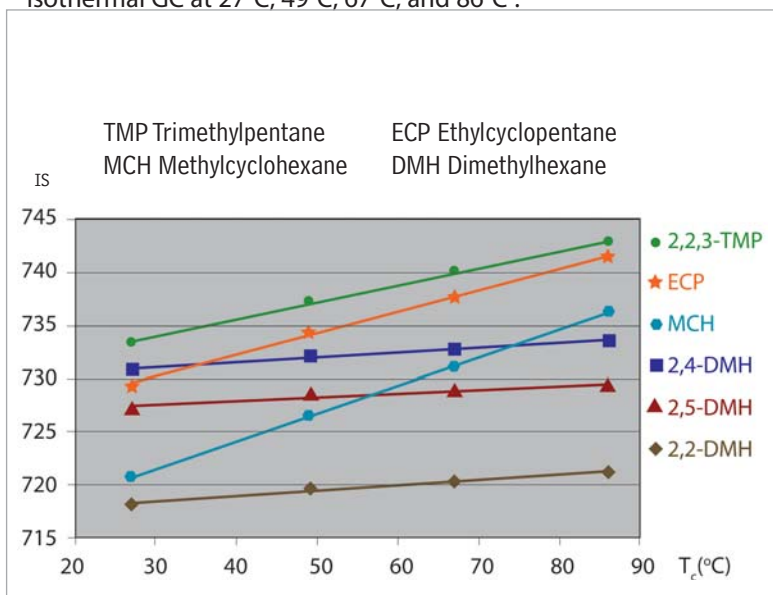
Therefore, the dependence of the retention time upon column temperature is usually expressed graphically as the log of the retention parameter (net retention time t'_R or retention factor k' or retention index I) vs. T_c or $1/T_c$, where T_c is the absolute column temperature. In many cases, the plots are linear over the temperature range employed and, furthermore, the lines are approximately parallel to each other indicating that there is little change in selectivity by changing the column temperature in isothermal mode. This is valid for chemically similar compounds. But closer inspection reveals that some lines diverge slightly in their slope and even cross each other (Figure 2).² The practical implication is coelution of the two compounds at the temperature where the lines intersect. By further changing the column temperature the compounds are again separated but in reverse elution order. As mentioned above, this kind of behavior is often experienced when compounds of different chemical nature are analyzed on moderate to highly polar stationary phases.

But not only compounds with different functional groups will behave this way! In the next issue of the Restek Advantage, you will see examples of aliphatic versus cyclic compounds or cyclic compounds differing in their ring number, and the cross-over effect on non-polar columns.

References:

- Mehran M. et al., HRC, 14 (1991) 745 – 750.
- Hively, R.A. and R.E. Hinton, J. Gas Chromatogr. 6 (1968) 203 – 217.

Figure 2 Retention indices on squalane (IS) as a function of T_c for isothermal GC at 27°C, 49°C, 67°C, and 86°C².



more to reveal!

See the next issue of the Restek Advantage for Part 2 of Retention Cross-over Phenomenon in Gas Chromatography- Can the Mystery be revealed?

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Tradeshhow Schedule

We'd be happy to talk with you at any of the following meetings or shows. We'll post our booth numbers as they become available to us.

June, 2007

Date: June 3-7
Show: 55th ASMS Conference on Mass Spectrometry
Location: Indiana Convention Center, Indianapolis, IN

Date: June 4-7
Show: 30th International Symposium on Capillary Chromatography (ISCC)
Location: Dalian World Expo Centre, Dalian, P.R. China (Booth 80)

Date: June 11-14
Show: Metabolomics Society 3rd Annual Conference
Location: Renold Building, The University of Manchester, Manchester, UK

Date: June 17-21
Show: HPLC 2007
Location: International Convention Centre, Ghent, Belgium

July, 2007

Date: July 17-19
Show: Semicon West 2007
Location: Moscone Center, San Francisco, CA

Date: July 22-25
Show: Florida Pesticide Residue Workshop (FPRW)
Location: TradeWinds Island Grand, St. Pete Beach, FL

August, 2007

Date: August 19-23
Show: ACS 234th National Meeting & Exposition
Location: Boston, MA

Date: August 20-24
Show: National Environmental Monitoring Conference (NEMC)
Location: Hyatt Regency, Cambridge, MA

Date: August 26-31
Show: T2007 - TIAFT (International Conference) (NEMC)
Location: Seattle Sheraton, Seattle, WA

For latest updates, see our Tradeshhow Calendar at www.restek.com/ontheroad.

Seminar Schedule

Date	Cat. #	City	State
GC Hands-On Maintenance and Troubleshooting			
6/13	65552	Lafayette Hill	PA
Comprehensive Capillary GC			
6/12	65551	Lafayette Hill	PA
6/15	65553	Wilmington	DE
6/19	65554	Cleveland	OH
6/20	65555	Buffalo	NY
6/22	65556	Pittsburgh	PA
7/23	65560	Idaho Falls	ID
7/25	65561	Boise	ID
7/26	65562	Spokane	WA
Comprehensive HPLC			
7/9	65557	Chicago	IL
7/11	65558	Madison	WI
7/13	65559	Kansas City	MO

Register at www.restek.com/seminar