

IN THIS ISSUE

Editorial

Retention Cross-over Phenomenon in Gas Chromatography—Can the Mystery be Revealed? Part 2 ..... 2

Chemical/Petrochemical

New MXT-Biodiesel TG Column Line ..... 3

Pharmaceutical

Optimize Selectivity & Efficiency in UHPLC Separations ..... 6

Environmental

Faster Organochlorine Pesticide Sample Throughput ..... 8

Resolving the Benzo(j)fluoranthene Challenge ..... 10

Foods, Flavors & Fragrances

Analysis of Nitrofurans in Honey ..... 11

Clinical/Forensics

Why Derivatize? ..... 12

Sample Preparation

Superior Fractionation of Extractable Petroleum Hydrocarbons ..... 14

Restek Performance Coatings

Prevent Mercury Loss During Transport and Storage ..... 16

Protect Sample Integrity and Prolong Sampling System Lifetime ..... 17

HPLC Accessories

Hub-Cap Mobile Phase Accessories ..... 18

GC Accessories

Cool Tools (Fused Silica Column Cutters) ..... 19

Peak Performers (Column-to-Column Connections) ..... 20

Tech Tip

Get Connected! ..... 22

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Carbo-Prep, Crossbond, Hydroguard, Integra-Gap, MX, Pinnacle, Press-Tight, Resprep, Rtx, Rxi, SeCure, Silcosteel, Siltek, Sulfinert, Uniliner, Vu-Union, Vu2 Union

Other Trademarks

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# Retention Cross-over Phenomenon in Gas Chromatography—Can the Mystery be Revealed? Part 2

By Werner Engewald, Ph.D., Professor Emeritus, University of Leipzig, Institute of Analytical Chemistry, Leipzig, Germany; engewald@uni-leipzig.de



In the last issue of the Restek Advantage (2007.02), I showed some examples of the cross-over phenomenon on polar (polyethyleneglycol) columns. Here in Part 2, we will examine the cross-over phenomenon on nonpolar columns.

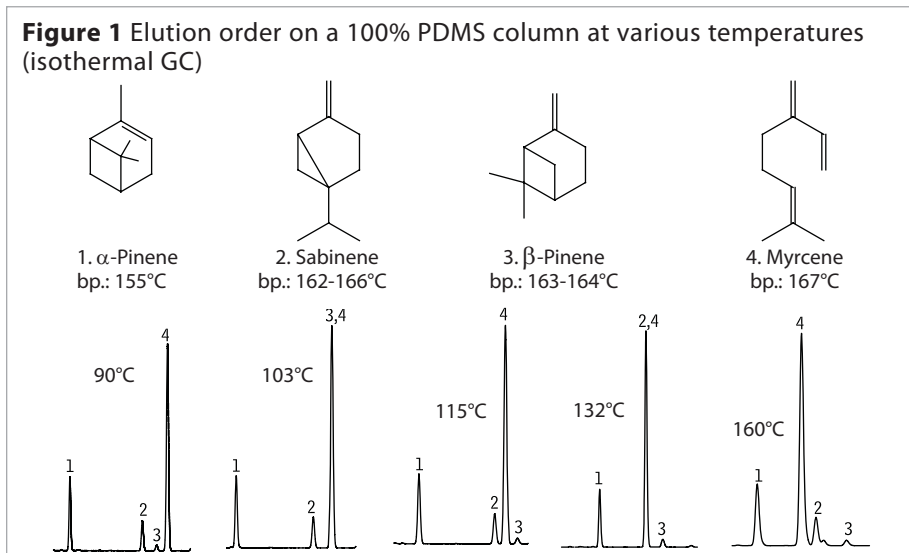
It is known to a lesser extent that changes in peak elution order also occur on nonpolar or weakly polar stationary phases for hydrocarbons that differ only in their carbon skeleton, e.g. aliphatic versus cyclic compounds or cyclic compounds differing in their ring number. The terpenes sabinene,  $\beta$ -pinene and myrcene are given as an example in Figure 1. The cross-over effect was observed on a polydimethylsiloxane phase with 5% phenyl (60m, 0.25mm ID, 1 $\mu$ m film thickness) as well as on a 100% polydimethylsiloxane phase (60m, 0.32mm ID, 0.5 $\mu$ m film thickness). The column temperature was increased from 90°C to 160°C using isothermal mode. The elution order changed from sabinene,  $\beta$ -pinene, myrcene at 90°C to myrcene, sabinene,  $\beta$ -pinene at 160°C. What could be the reason for this effect? A closer look at the molecular structure shows that sabinene and  $\beta$ -pinene are double ring systems whereas myrcene is an aliphatic hydrocarbon.

Other interesting analyte pairs prone to cross-over on methylsiloxane phases at different column temperatures are *o*-xylene/*n*-nonane, naphthalene/dodecane, as well as 1,2,3-trimethylbenzene/*n*-decane. In the latter case we also observe coelution and cross-over at different temperature programming rates. At a heating rate of 2°C/min., *n*-decane elutes before 1,2,3-trimethylbenzene, at 5°C/min. coelution occurs, and at 20°C the aromatic hydrocarbon is the first peak (100% PDMS column, 12m, 0.2mm ID, 0.33 $\mu$ m film thickness, starting temperature 35°C). It seems obvious that the geometry of the molecule, e.g. cyclic versus open chain, contributes to the cross-over phenomenon.

Nevertheless, I have this long-standing friendly discussion with a former student of mine, who persistently points out that the examples we have been looking at so far are always pairs of conjugated versus nonconjugated compounds and that  $\pi$  interactions, specifically with phenyl modified phases, should be taken into account.

Let's, therefore, go back to the structure of substances presented in Figure 2: they are exclusively saturated aliphatic and alicyclic hydrocarbons. The data in Figure 2 are from Hively and Hinton (1968) and in that paper the relative retention and retention indices of approxi-

Continued on page 23.



# Retention Cross-over Phenomenon in Gas Chromatography—Can the Mystery be Revealed? Part 2

Continued from page 2

mately 250 compounds were measured on a squalane stationary phase at four temperatures.<sup>1</sup> From these data one can identify numerous reversals in elution order of aliphatic and cyclic hydrocarbons. The solute interactions with a squalane stationary phase, the most nonpolar stationary phase one can use, are largely a result of dispersion interactions. The authors stated that the magnitude of temperature variation is a function of the size of the molecule expressed by the cross-sectional area of the molecules, which should also prove my point in my next discussion over coffee with my former student.

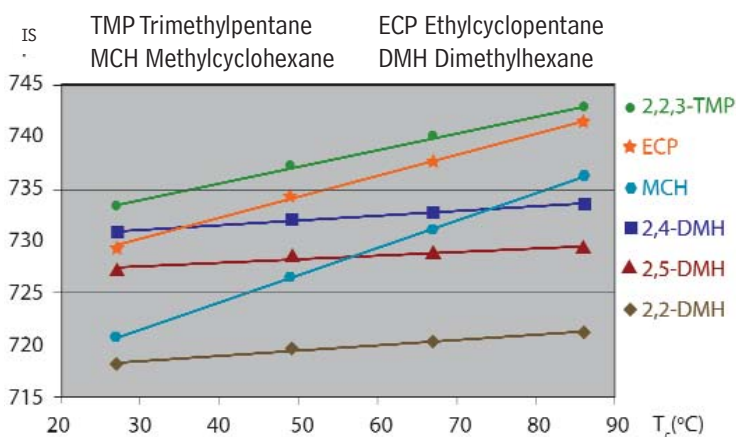
Finally, coming back to our first example in Part 1, both components not only show different functional groups, they also differ in their carbon skeleton (Figure 3). Linalool is an aliphatic alcohol and camphor is a bi-cyclic ketone, which means that not only the functional groups but also the difference in molecular geometry will contribute to the cross-over phenomenon.

What can we learn from this discussion? Peak overlapping and cross-over in peak elution order caused by variation of column temperature or temperature programming rate can occur not only on polar stationary phases for compounds with different functional groups but also on nonpolar or weak polar stationary phases for compounds that differ in their carbon skeleton. The analyst should, therefore, carefully examine the structure of the compounds to be separated if the information is available. Furthermore, it is recommended to study analyte retention carefully at various temperatures for difficult separations as an important aspect of method optimization.

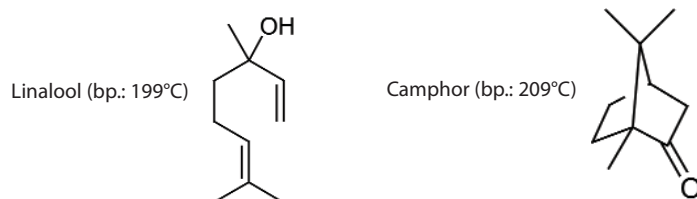
References:

1 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°C.<sup>1</sup>



**Figure 3** Functional groups influence elution order.



## Tradeshaw 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.

### September, 2007

Date	September 2-7
Show	Dioxin 2007
Location	Hotel Okura, Tokyo
Date	September 13
Show	New Jersey Mass Spectrometry Discussion Group Annual Vendor Show
Location	DoubleTree Hotel, Somerset, NJ
Date	September 16-20
Show	AOAC International 121st Annual Meeting & Expo
Location	Hyatt Regency Orange County, Anaheim, CA
Date	September 25-28
Show	Midwestern Association of Forensic Scientists (MAFS)
Location	Park Place Hotel, Traverse City, MI
Date	September 26-28
Show	Vapor Intrusion Conference
Location	Providence, RI

### October, 2007

Date	October 2-4
Show	ISA Expo 2007
Location	Reliant Center, Houston, TX
Date	October 10-12
Show	ACIL National Meeting
Location	InterContinental Hotel Buckhead, Atlanta, GA
Date	October 13-20
Show	Society of Forensic Toxicology (SOFT)
Location	Chapel Hill, NC
Date	October 16-17
Show	Gulf Coast Conference
Location	Moody Garden Convention Center, Galveston, TX
Date	October 18-21
Show	Beijing Conference & Exhibition on Instrument Analysis
Location	Beijing Exhibition Center, Beijing, China, Booth #00
Date	October 30-November 1
Show	Chem Show
Location	Javits Convention Center, New York, NY
Date	October 30-November 2
Show	2007 SEMA Show
Location	Las Vegas Convention Center, Las Vegas, NV
Date	October 31-November 3
Show	33rd Annual NEAFS Meeting
Location	The Sagamore Resort, Bolton Landing, NY

### November, 2007

Date	November 1
Show	2007 ANACHEM Symposium
Location	Burton Manor, 27777 Schoolcraft Road, Livonia, MI
Date	November 7-9
Show	3rd International Symposium on Recent Advances in Food Analysis
Location	Diplomat Hotel-Conference Center, Prague, Czech Republic
Date	November 11-15
Show	Eastern Analytical Symposium (EAS)
Location	Garden State Convention & Exhibit Center, Somerset, NJ
Date	November 11-15
Show	2007 AAPS Annual Meeting and Exposition
Location	San Diego Convention Center, San Diego, CA
Date	November 28-30
Show	31st Int'l Symposium on Capillary Chromatography & Electrophoresis
Location	Hotel Albuquerque, Albuquerque, NM

For latest updates, see our Tradeshaw Calendar at [www.restek.com/ontheroad](http://www.restek.com/ontheroad).