Short communication

On retentivity tuning by flow in the second column of different comprehensive two dimensional gas chromatographic configurations☆

Ján Krupčík [a,*], Pavel Májek [a], Roman Gorovenko [a], Pat Sandra [b], Daniel W. Armstrong [c]

[a] Institute of Analytical Chemistry, FCHPT, STU, Radlinskeho 9, 81237 Bratislava, Slovak Republic
[b] Research Institute for Chromatography, Kortrijk, Belgium
[c] Department of Chemistry and Biochemistry, University of Texas Arlington, Arlington, TX 76019-0065, USA

ABSTRACT

Retentivity tuning in comprehensive two dimensional GC separations of aliphatics (linear and cyclic hydrocarbons) and aromatics in gasoline by changing the carrier gas flows in the column series at constant working temperature parameters of both columns is discussed. Comprehensive 2D techniques studied include GC × GC with cryogenic and differential flow modulation and non-modulated transfer (NMT). In all configurations, the first dimension was a non-polar column and the second dimension a polar column. Using three different flows (0.6, 1.0 and 1.4 mL/min) of helium carrier gas in cryogenic modulated GC × GC illustrated that, as expected, retention of the solutes on the ^{1}D and ^{2}D columns increased but the separation quality was nearly constant. A change of carrier gas pressure ($p_m = 175$–125 kPa) on the ^{1}D and ^{2}D columns joint point at constant inlet pressure ($p_i = 525$ kPa) in NMT, induces an increase of the carrier gas flow rate on the ^{1}D and a decrease on the ^{2}D column, respectively. The higher retentivity of the ^{2}D column improved the group type separation of aliphatic/cyclic hydrocarbons and aromatics and a higher distribution of aromatics on the 2D retention plane was noted. Retentivity tuning was also performed in flow modulated GC × GC by operating the ^{1}D column at 0.8 mL/min and the ^{2}D column at 20 and 26 mL/min. The higher retentivity at 20 mL/min improved the group type separation of aliphatic/cyclic hydrocarbons and aromatics in the 2D retention plane.

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1. Introduction

Two columns of different polarity are often coupled in series to improve gas chromatographic (GC) separations of complex mixtures. The following techniques can be differentiated: one dimensional dual column chromatography (1D), two-dimensional chromatography (2D) and comprehensive two-dimensional chromatography (GC × GC).

The overall polarity of a GC capillary column series depends on the relative contributions of individual column polarities and due to the gas compressibility, even on the column order. The 1D configuration, however, does not generally yield comprehensive separations on the two column series as the final separation leads to a convolution of the individual column retentions:
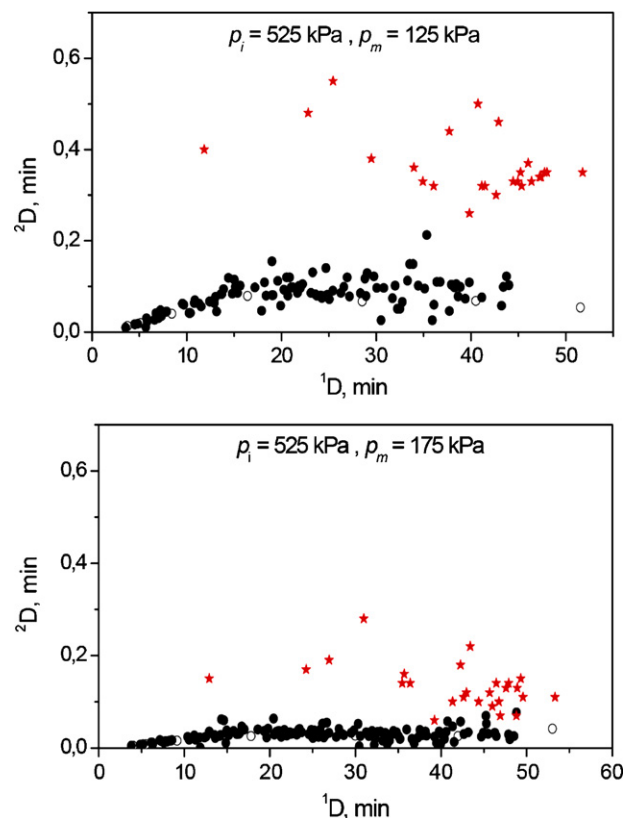
$$t_{R,i,AB} = t_{R,i,A} + t_{R,i,B}.$$

An interface device (modulator) between two columns, as used in GC × GC separations, accumulating narrow bands from the ^{1}D effluent for fast re-injection into the ^{2}D column, maintains the separation of peaks accomplished on the ^{1}D column [1–5]. Separations in ^{1}D are commonly performed on conventional capillary columns (20–30 m in length, 0.2–0.5 mm ID and 0.2–0.5 μm d_f) [3–5] although Kohl et al. recently demonstrated that for GC × GC separation of very complex samples, long ^{1}D columns (e.g. 100 m) and operation at optimum flow conditions should be used [6]. The separation on the ^{2}D column (typically 1–5 m in length, 0.1–0.2 mm ID and 0.1–1 μm d_f) should be very fast (usually around 5 s or less). The higher is the orthogonality between the ^{1}D and ^{2}D columns, the better is the separation [4–6]. Columns may be placed in one or two independently heated ovens. GC × GC separations of complex samples are usually performed under temperature programming conditions. The experimental set-up requires two ovens if the temperature program for the ^{1}D column is different from that of the ^{2}D column. Optimization of GC × GC working parameters most often involves finding ways to tune the contribution of the ^{2}D column retentivity (^2t_R) to the overall retentivity of the selected column set. The following strategies are commonly used in GC × GC praxis to tune ^{2}D column retentivity when both
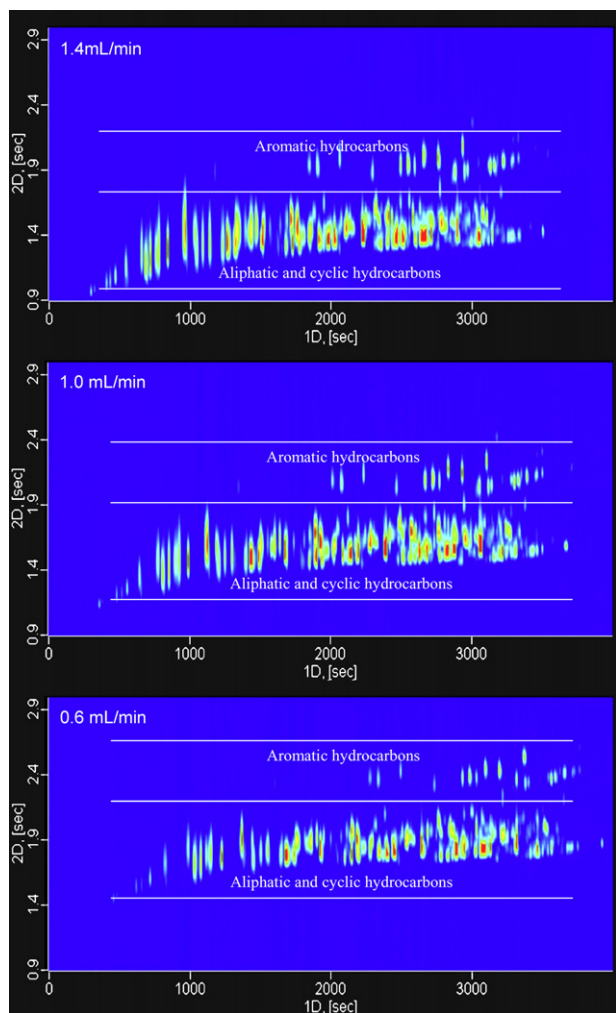
Fig. 1. Cryogenic modulated GC × GC-TOFMS total ion contour plots for gasoline using PONA (^{1}D) and BPX-50 (^{2}D) column series using various flows of helium carrier gas.

Fig. 2. Distribution of retention times for gasoline on a 2D retention plane (Apex plots) obtained by NMT. Labels: ○ – n-alkanes, ● – branched and cyclic alkanes and ★ - aromatic hydrocarbons.

columns are placed in one GC oven: (i) an increase of ^{1}D + ^{2}D column series flow decreases retentivity of both columns and corresponding peaks elute at lower temperature, (ii) a decrease of ^{1}D + ^{2}D column series flow increases retentivity of both columns and corresponding peaks elute at higher temperature, (iii) an increase in the temperature gradient induces that corresponding peaks enter ^{2}D at a higher temperature which reduces ^{2}D retentivity [7]. Retentivity of both columns can moreover be changed by varying the temperature and/or temperature program parameters if ^{1}D and ^{2}D columns are placed in two independently heated ovens.

In this contribution we present data on retentivity tuning by changing the flows in different comprehensive two dimensional GC configurations namely cryogenic and differential flow modulation and non-modulated transfer (NMT) [8]. Note that in GC × GC using cryogenic modulation, the columns are mostly directly connected in series without adjustment of pressure or flow at the connection point between the two columns. This was the procedure used in this work. Tranchida et al. reported the use of split-flow before the second dimension to obtain close-to-optimal gas velocity to increase the second dimension efficiency [9]. In both non-modulated transfer (NMT) as in differential flow modulation of the ^{1}D effluent, joint point pressure or flow adjustment is common praxis.

2. Experimental

2.1. Cryogenic modulation GC × GC

A LECO Pegasus 4D (LECO Corporation, St. Joseph, MI, USA) consisting of an Agilent 7890 gas chromatograph and automatic liquid sampler HP 7683 (Agilent, Palo Alto, CA, USA) equipped with a split/splitless injector, dual-stage thermal modulator and secondary oven and connected to a Time-Of-Flight Mass Spectrometer (TOFMS) was used. 0.2 µL of gasoline (Russian crude oil distillation fraction 97.6–173.6 °C) was injected at 250 °C with a split ratio 500:1. The mass range scanned from m/z 29 to 450 with an acquisition rate of 100 spectra/s was used. Helium was used as a carrier gas at 0.6, 1.0 or 1.4 mL/min constant flow. A PONA (50 m, 200 µm ID coated with a 0.5 µm film of polydimethylsiloxane, (Supelco, Bellefonte, PA, USA) was used as ^{1}D column. This column was directly coupled to the ^{2}D column consisting of BPX-50 (1.8 m, 100 µm ID coated with a 0.24 µm film of 50%-diphenyl–50%-dimethyl polysilphenylene-siloxane (Supelco, Bellefonte, PA, USA). The primary oven was programmed from 45 °C (15 min) to 180 °C (5 min) at 1.6 °C/min. The temperature offset between the secondary and primary oven was 5 °C. The modulation frequency was 3 s. The temperature offset of modulation was 50 °C. The temperature of the transfer line was 280 °C. The temperature of the ion source was 250 °C. Electron impact ionization energy was 70 eV.

2.2. Non-modulated 2D GC separation

For the non-modulated 2D GC separation an Agilent 5890 Gas Chromatograph (Agilent Technologies, Wilmington, DE, USA) was used. The GC instrument was equipped with electronic
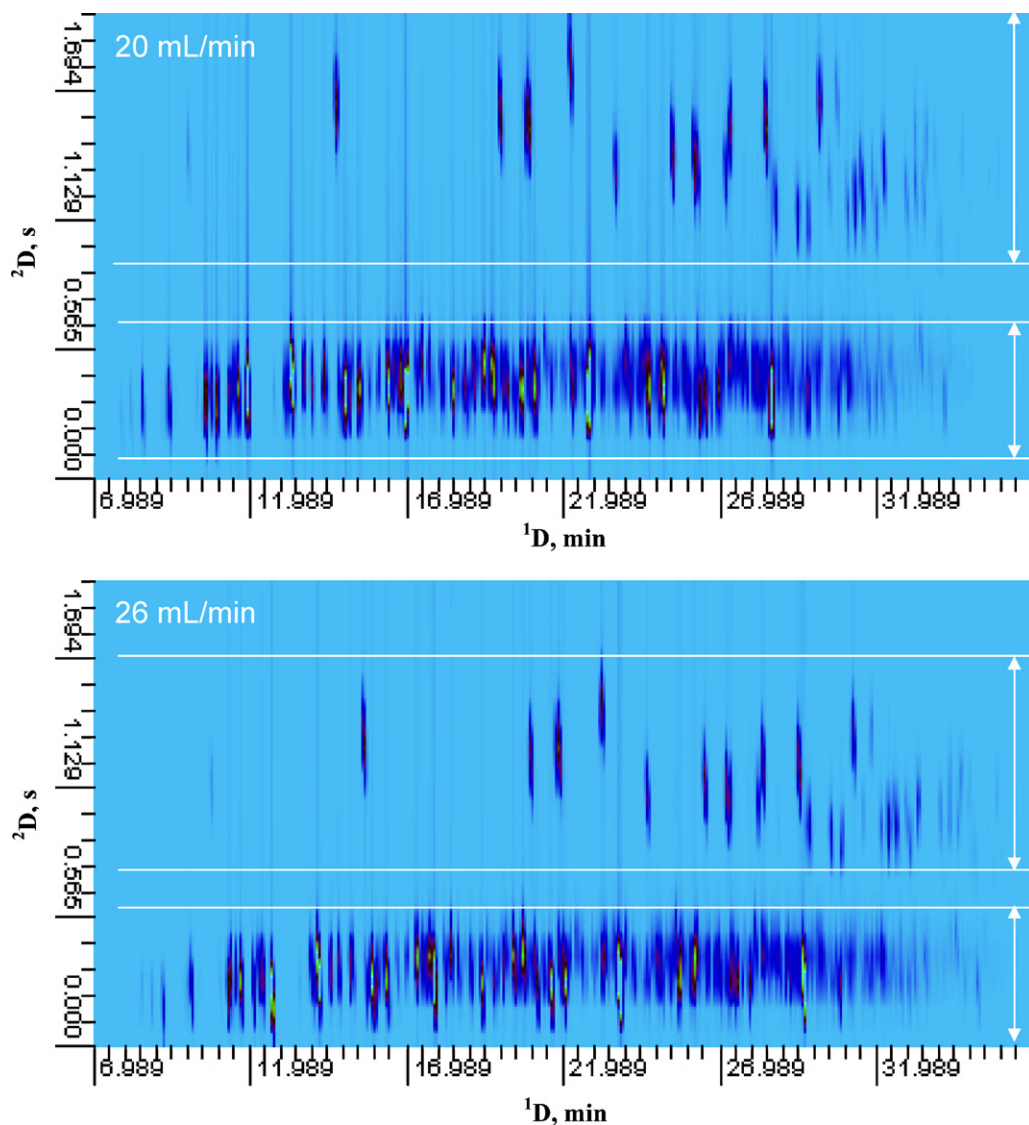
Fig. 3. Flow modulated GC × GC-QMSD total ion contour plots for gasoline using SPB-Octyl (^{1}D) and SLB-IL-59 (^{2}D) column series using various flows of helium carrier gas on the ^{2}D column.

pressure control (EPC), two split/splitless injectors and two flame ionization detectors (FIDs) capable of producing a digital signal at a sampling rate of 200 Hz. Helium was used as a carrier gas. A schematic of the non-modulated 2D GC instrument is depicted in Supplementary Data. A non-polar capillary column (Petrocol, 100 m, 0.25 mm ID, coated with a 0.5 μm film of poly-dimethylsiloxane) was used in the first dimension and an ionic liquid capillary column SLB-IL59 (1,8, 100 μm ID coated with a 0.24 μm film of 1,12-di(tripropyl-phosphonium)dodecanebis(tri-fluoromethanesulfonyl)imide) in the second dimension. Both columns were delivered by SUPELCO, Bellefonte, PA, USA). 0.1 μL of gasoline was injected manually at 250 °C with a split ratio of 500:1. The separation was performed using a temperature program from 45 °C (15 min) at 1.6 °C/min to 180 °C (5 min). The effluents of the ^{1}D and ^{2}D columns were monitored with the two FIDs heated at 300 °C. The signal from the FIDs was processed by ChemStation Software (Agilent Technologies, Palo Alto, CA, U.S.A). Complete details of the instrumental set-up as well as evaluation of the non-modulated 2D GC configuration are described in [8].

2.3. Flow modulated GC × GC

An Agilent 7890 gas chromatograph equipped with differential flow modulator (DFM), flame ionization detector (FID) and a 5975 quadruple mass spectrometric detector (QMSD) (Agilent Technologies, Wilmington, DE) was used. A non-polar SPB-Octyl column (50 m, 250 μm ID coated with a 0.25 μm film of poly(50%-methyl-50%-octyl)siloxane phase) was used as ^{1}D column and connected through a differential flow modulator to an ionic liquid capillary column SLB-IL59 (5 m, 250 μm ID coated with a 0.25 μm film of 1,12-di(tripropylphosphonium)dodecanebis-(trifluoromethanesulfonyl)imide). Both columns were delivered by SUPELCO, Bellefonte, PA, USA. The outlet of the ^{2}D column was connected via splitter to FID and QMSD using restrictors (120 cm × 0.25 mm ID of deactivated fused silica tubing for FID and 50 cm × 0.10 mm ID of deactivated fused silica tubing for MSD) [10]. Helium was used as a carrier gas at 0.8 mL/min flow on the ^{1}D column and 20 or 26 mL/min flow on the ^{2}D column. The temperature of both columns was programmed from 40 °C (4 min) to 180 °C (5 min) at 3 °C/min. The modulation frequency was 3 s (2.9 s to fill

Table 1
Dependence of retention times (in s) for benzene, toluene, ethyl benzene, p + m-xylenes and o-xylene in cryogenic GC × GC-TOFMS on Petrocol/BPX-70 column series using three different flows of helium carrier gas.

BTEX	0.6 mL/min		1.0 mL/min		1.4 mL/min	
	^1t_R	^2t_R	^1t_R	^2t_R	^1t_R	^2t_R
Benzene	939	2.18	738	1.74	621	1.49
Toluene	1596	2.33	1347	2.04	1185	1.88
Ethylbenzene	2274	2.37	2016	2.08	1845	1.93
m + p-Xylene	2337	2.36	2076	2.06	1905	1.92
o-Xylene	2496	2.42	2235	2.13	2061	1.99

and 0.1 s to flush). The temperature of FID was 250 °C. The temperature of the transfer line to ion source was 280 °C. The temperature of the ion source was 250 °C. QMSD with electron impact ionization (EI) at 70 eV was used in TIC mode. Stored mass range was m/z 40–450 with an acquisition rate of 2.8 spectra/s was. 1 μL of gasoline was injected into at 250 °C with a split ratio of 1000:1.

3. Results and discussion

Fig. 1 shows the GC × GC-TOFMS total ion contour plots for the hydrocarbons present in the gasoline sample on the PONA (^{1}D) and BPX-50 (^{2}D) column series registered at various helium carrier gas flows. This figure illustrates an increase of the retention times of the hydrocarbons with a decrease in helium flow on both ^{1}D and ^{2}D columns, as depicted in Table 1 for benzene, toluene, ethylbenzene and the xylenes. However, the group type separation seems not to be affected by this increase of retention times.

It should be noted that the ^{1}D and ^{2}D columns are placed in two independently heated ovens. This also allows to tune the retentivity of the solutes by changing the working temperature parameters of ^{1}D and ^{2}D columns. Studying this was not the aim in this work.

Fig. 2 shows the dispersion of the hydrocarbons on a 2D retention plane (Apex plots) constructed from the data obtained by the separation of gasoline on a Petrocol + SLB-IL59 column series with a constant inlet pressure (p_i = 525 kPa) and two various column joint point intermediate pressures (p_m = 125 and 175 kPa) using non-modulated transfer (NMT) of the first column effluent [8]. Details in relation with the use of the NMT method for determination of retention times needed for the construction of Fig. 2 are depicted in Supplementary Data. The figure demonstrates that a decrease of column joint point pressure (p_m), at a constant inlet pressure (p_i), induces an increase of the carrier gas flow rate on the ^{1}D column and a reduction of it on the ^{2}D column, respectively. The contribution of the ^{2}D column retentivity to the column series retentivity is higher due to a decreasing carrier gas flow in this column. Fig. 2 also demonstrates that the higher retentivity on the ^{2}D column improves the group type separation of aliphatic/cyclic hydrocarbons and aromatics as well as a higher and better distribution of the aromatics on the 2D retention plane.

From the principle of flow modulation in GC × GC, it follows that the flow in ^{1}D and ^{2}D columns must be very different. It has been stated that the flow in the ^{2}D column has to be at least twenty times higher than that in the ^{1}D column. This also allows to tune the retentivity in the chosen column series. Fig. 3 depicts the flow modulated GC × GC separation of the gasoline sample on the non-polar SPB-Octyl and ionic liquid SLB-IL59 column series with 0.8 mL/min ^{1}D column flow rate and two different flow rates in ^{2}D namely 20 mL/min and 26 mL/min. It is clear from the figure that the higher retentivity of the ^{2}D column at 20 mL/min improves the group type separation as well as a slightly higher distribution of aromatic hydrocarbons on the 2D retention plane. Detailed evaluation of both chromatograms shows: (i) a dependence of retention span on the flow rate for aromatics (1.3 s for 20 mL/min flow and 0.9 s for 26 mL/min), (ii) almost no dependence of the retention span on flow rate for aliphatic and cyclic hydrocarbons (0.6 s), (iii) slightly higher retention of aliphatic and cyclic hydrocarbons at 20 mL/min flow rate, and (iv) small retention changes in the first dimension. The last two observations are currently studied in detail and will be published separately.

4. Conclusions

A change in the carrier gas flow in cryogenic GC × GC influences the retention in both columns but has little influence on the separation of the column series. In non-modulated comprehensive 2D separations, a change of carrier gas pressure at the joint point of ^{1}D and ^{2}D and at constant inlet pressure, allows to fine-tune the retentivity as illustrated for the group type separation aliphatic/cyclic hydrocarbons and aromatics. It was confirmed that flow modulated GC × GC allows to a certain extent to tune retentivity of ^{1}D and ^{2}D column series by changing the ^{2}D column flow. The contribution of the ^{2}D column retentivity increases with reduction of carrier gas flow in this column.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.03.042.

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