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Retention time locking procedure for comprehensive two-dimensional gas chromatography

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ABSTRACT

In gas chromatography (GC) reproducible retention times are in many cases highly favorable or in some cases even required. In one-dimensional GC, retention time shifts can be eliminated or minimized using a procedure called retention time locking (RTL). This procedure is based on adjusting the (constant) column head pressure. Unfortunately, this RTL procedure cannot be used in comprehensive two-dimensional gas chromatography (GC × GC) given the fact that peaks will shift in both dimensions. Adjusting the column head pressure in GC × GC will only minimize or eliminate the primary retention time shifts. In this paper, a fast and easy to perform, two-step retention time locking procedure for two-dimensional gas chromatography (2D-RTL) is proposed and its feasibility is demonstrated. This 2D-RTL procedure involves adjustment of the column head pressure or constant column flow, followed by the adjustment of the so-called effective secondary column length. The secondary column length is increased or decreased, simply by moving it stepwise through the modulator. It is demonstrated that retention time shifts in both the primary- and secondary-dimension, which may occur after e.g. replacing the column set, can be minimized to less than half peak base width. The proposed 2D-RTL procedure is used successfully for approximately 1 year in our laboratory.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC), introduced by Liu and Phillips [1], is a powerful analytical technique for the analysis of complex samples. One of the main advantages of GC × GC is its high separation power making this technique ideal for unraveling complex mixtures. Another main advantage is that GC × GC provides structured chromatograms in which compounds with similar chemical properties appear as distinct groups in the two-dimensional chromatogram. Nowadays, GC × GC is used to solve all kinds of real-life analytical problems in a wide variety of fields such as food [2,3], biological [4,5], environmental [6,7] and petrochemical [8,9] areas.

As in one-dimensional GC, retention time shifts in GC × GC are in many cases undesired. Reproducible retention times are highly favorable or even required for visually comparing 2D chromatograms, when using 2D templates for group-type analysis, when using 2D chromatograms as chemical fingerprints, or when applying all kinds of chemometric operations.

The problem of retention time shifts in 1D-GC can be solved by a procedure called retention time locking (RTL), introduced by Blumberg and Klee [10]. RTL allows one to maintain equal retention times for the same or different columns as long as both columns have the same type of stationary phase and equal nominal phase ratio. Using RTL, chromatograms can be reproduced accurately from one column to another or from one GC to another. RTL is achieved simply by adjusting the column head pressure. Since the introduction of RTL many applications can be found in the literature [11–14].

However, in GC × GC retention times may or will shift in both the primary- and the secondary-dimensions. Locking both dimension retention times in GC × GC cannot be achieved by only adjusting the column head pressure. Given the fact that no retention time locking tools exists for GC × GC, only post-analysis alignment techniques for eliminating retention time shifts in both dimensions have been reported in the literature [15–18].

In this paper, a GC × GC retention time locking procedure is proposed and its feasibility is demonstrated. The proposed 2D-RTL procedure involves two main steps. The first step is locking the primary retention times by adjusting the column head pressure or the constant column flow. The second step is locking the secondary retention times by adjusting the effective secondary column length. The effective secondary column length, which can be defined as the length measured from the modulator to the detec-

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tor, can be adjusted by stepwise moving the second column through the modulator. The main idea of this procedure is that the part of the secondary column which is positioned in front of the modulator does not contribute to the secondary-dimension separation and does not have a significant influence on the primary-dimension separation.

2. Experimental

2.1. Chemicals

Grob test mixtures were purchased from Restek® (Restek Corporation, Bellefonte, PA).

2.2. Instrumental

All GC × GC-FID analyses were carried out on a Leco (St. Joseph, MI, USA) GC × GC system equipped with an Agilent 7683 autosampler, a hot split/splitless injector and a flame ionization detector (FID). Three VF-1MS columns (50 m × 0.25 mm; 0.4 μm film thickness) and three VF-17MS columns (10 m × 0.10 mm; 0.2 μm film thickness) were purchased from Varian B.V. (Middelburg, The Netherlands).

2.3. Software

GC × GC instrument control and data processing was performed by Leco ChromaTOF® software (St. Joseph, MI, USA) version 3.25. For all calculations Microsoft® Office Excel 2003 (Redmond, WA, USA), was used.

2.4. Chromatographic conditions

In all experiments using a Grob test mixture a non-polar VF1-MS column was used for the first dimension separation and a medium-polar VF17-MS column (variable length) was used for the second-dimension separation. The primary and secondary columns are attached by means of a pressfit (Varian, Palo Alto, CA, USA) or Meltfit® (Nlisis Chromatography BV, Veldhoven, The Netherlands) connector. The GC × GC instrument was operated under temperature-programmed conditions from 40 °C, held for 0.2 min, to 280 °C for the primary GC oven and from 45 °C, held for 0.2 min, to 285 °C for the secondary GC oven; both at a temperature rate of 5 °C min^{-1}. The secondary oven was only used to connect the secondary column from the modulator directly to the primary GC oven; so both columns are situated in the primary GC oven. The modulation time was 3 s. The temperature of the modulator hot jets was 15 °C higher than the actual primary oven temperature, and the pulse time was set to 1 s. Helium was used as the carrier gas. All separations were carried out using a constant head pressure or constant column flow. The injection volume was 1 μL. The injector temperature was 280 °C. A split injection with a split ratio of 100:1 was applied for all analyses. The FID was operated at a temperature of 300 °C, using a data-acquisition rate of 200 Hz.

A naphtha sample was used in order to demonstrate the 2D-RTL procedure with a real-life sample. For these experiments two different column sets were used. A non-polar 50 m × 0.25 mm × 0.4 μm VF1-MS column was used for the first-dimension separation and a medium-polar 1.5 m × 0.10 mm × 0.2 μm VF17-MS for the second-dimension separation. The GC × GC instrument was operated under temperature-programmed conditions from 50 °C, held for 0.5 min, to 320 °C for the primary GC oven and from 55 °C, held for 0.5 min, to 325 °C for the secondary GC oven; both at a temperature rate of 3 °C min^{-1}. The secondary oven was only used to connect the secondary column from the modulator directly to the primary GC oven; so both columns are situated in the primary GC oven. The modulation time was 4 s.

2.4.1. Original column set, method and retention times

Column set A is defined as the original column set. The analysis method using a constant column head pressure of 41.75 psi and a secondary column length of 1.50 m is defined as the original method. The retention times obtained using the original column set (set A) and the original method are defined as the original retention times.

For the experiment with the naphtha sample, both constant pressure and constant flow modes were used. For these experiments, column set A is defined as the original column set. The constant pressure method uses a constant column head pressure of 55 psi and the constant flow method uses a constant column flow of 1 ml/min. Both methods are defined as the original methods. The retention times obtained using the column set A, and the original methods are defined as the original retention times.

2.4.2. Run-to-run repeatability

In order to determine the repeatability a Grob mixture was analyzed four times using the original column set A, and the original analysis method.

2.4.3. Retention time shifts due to differences in column sets

A Grob mixture was analyzed to determine retention time shifts due to differences in column sets on three different column sets (A, B and C) using the original analysis method.

2.4.4. 2D-RTL procedure

In order to demonstrate the feasibility of the 2D-RTL procedure a new column set, in which the secondary column length was approximately 15 cm longer than in the original secondary column length, was installed. The extra 15 cm was situated after the modulator so contributing to the second-dimension separation. Before installing, the first 25 cm of the secondary column (modulator side) was graduated by marking the column every centimeter using a heat resistant paint. The extra 15 cm can be required in case the new second-dimension retention times are significantly lower compared to the original retention times.

The first step of the 2D-RTL procedure is locking the first dimension. For this a Grob mixture is analyzed at five different column head pressures or at five different constant column flows, in the range of the column head pressure or column flow as used in the original method ±20%. From the dependence of the retention time of a target compound on column head pressure or column flow, the new column head pressure or column flow, at which the primary retention of the target compound matches its original primary retention time, is calculated and has to be set into the analysis method to lock the primary retention time.

The second step of the 2D-RTL procedure is locking the second-dimension. For this a Grob mixture is analyzed, using the locked primary-dimension method, at five different effective secondary column lengths: the effective secondary column length as installed ±15 cm. Shortening the effective secondary column length has to be done by sliding the secondary column through the modulator making use of the painted markings. Next, the delta second-dimension retention times (original retention time of the target compound minus the new obtained retention time) of the target compound are plotted against the sliding distance measured in centimeters. From this plot, the sliding distance at which the secondary retention of the target compound matches its original secondary retention time, is calculated. Next a Grob mixture is analyzed again in order to check the 2D-RTL result.

This procedure is limited to modulator-types in which it is possible to lengthen of shorten the effective secondary column length by

sliding the secondary column through the modulator; these types can be referred to as so-called pass-through modulators. A similar approach could also be used for single-stage loop-type modulators in which the position of the loop is displaced across the secondary column length.

Furthermore, the part of the secondary column length situated before and after the modulator should preferably reside in the same thermal zone, more specifically the length of secondary column that resides in each thermal zone (column part situated before modulator, in modulator, after modulator and in transfer line or in detector) must stay the same before and after sliding the column through the modulator. Therefore, the current setup precludes the use of a separate thermal zone (secondary oven) for the second-dimension separation.

3. Results and discussion

3.1. Run-to-run repeatability

The run-to-run repeatability was determined by analyzing a Grob mixture four times using the original column set A, and the original analysis method. The results are given in Table 1. The results for the primary and secondary retention time repeatability are given in Tables 1 and 2, respectively.

The retention time in the first dimension is determined by the modulated peak, which has the largest peak area of all modulated peaks belonging to a single compound. The first dimension retention time is not a continuum but is expressed as the product of the number of the second-dimension chromatogram and the modulation time. The run-to-run primary retention time variation for the 12 compounds in the Grob mixture is better than the modulation period of 3 s ($n = 4$). As a consequence, no differences in the primary retention times, from run-to-run could be determined. The peak widths at peak base (W_b) in the primary-dimension have been estimated by multiplying the number of modulated peaks, belonging to the single compound, with the modulation period of 3 s.

The run-to-run second-dimension retention time variation of the 12 compounds in the Grob mixture is on average better than 10 ms for peaks having an average peak base width (W_b) of approximately 100 ms.

3.2. Retention time shifts due to differences in column sets

In order to get a rough idea about the influence of (small) manufacturing differences in GC columns, including small differences in the positioning of the column set, a Grob mixture was analyzed using three different column sets (column sets A, B and C). It has to be noted that all columns are new and were ordered at the same supplier at the same time, so large variations in the column parameters and stationary phase properties by manufacturing variations or usage are not expected. For each analysis the original analysis method was used. Installation of the column sets and analysis was performed by one person. The results are summarized in Table 3.

Analysis on column set B shows a shift of all peaks to higher primary retention times and to lower secondary retention times. Analysis on column set C shows a shift of all peaks to higher primary and secondary retention times. Furthermore, a correlation between the retention time and the absolute retention time shift is clearly visible; the absolute peak shift increases at higher primary and secondary retention times.

It is obvious that shifts in the primary retention times can be caused by small changes in the primary column dimensions (^{1}L, ^{1}dc, ^{1}df), however these shifts may also be caused by changes in the secondary column dimensions (^{2}L, ^{2}d$_c$) given the fact these changes also influence the pressure drop across both the secondary and primary column. The same is true for shifts in the secondary retention times, these can be caused by small changes in the secondary column dimensions (^{2}L, ^{2}d$_c$, ^{2}d$_f$) or by small changes in the primary column dimensions (^{1}L, ^{1}d$_c$). Furthermore, in case of temperature-

Table 1
Grob mix run-to-run repeatability of the first dimension retention times.

Compound name	Average peak width (s)	Analysis #1 (s)	Analysis #2 (s)	Analysis #3 (s)	Analysis #4 (s)
Butanediol	9	591	591	591	591
n-Decane	9	1092	1095	1095	1095
Octanol	9	1212	1212	1212	1212
Nonanal	9	1275	1275	1275	1275
Dime-phenol	9	1287	1287	1287	1287
n-Undecane	9	1299	1299	1299	1299
Ethylhexanoic acid	12	1302	1302	1302	1302
Dime-aniline	9	1410	1410	1410	1410
Me-decanoate	12	1689	1689	1689	1689
Me-undecanoate	9	1857	1857	1857	1857
Dicyclohexylamine	12	1899	1899	1899	1899
Me-dodecanoate	9	2016	2016	2016	2016

Table 2
Grob mix run-to-run repeatability of the second-dimension retention times.

Component	Average peak width (W_b) (ms)	#1 (ms)	#2 (ms)	#3 (ms)	#4 (ms)	Average (ms)	CV (%)
Butanediol	143	1835	1815	1815	1820	1821	0.5
n-Decane	89	1350	1350	1345	1350	1349	0.2
Octanol	88	1780	1775	1770	1775	1775	0.2
Nonanal	88	1845	1840	1840	1840	1841	0.1
Dime-phenol	109	2425	2410	2415	2420	2418	0.3
n-Undecane	76	1415	1415	1415	1415	1415	0.0
Ethylhexanoic acid	108	1810	1805	1805	1805	1806	0.1
Dime-aniline	117	2705	2700	2700	2700	2701	0.1
Me-decanoate	82	1870	1870	1870	1875	1871	0.1
Me-undecanoate	81	1915	1915	1910	1915	1914	0.1
Dicyclohexylamine	92	2125	2120	2120	2125	2123	0.1
Me-dodecanoate	81	1965	1965	1955	1960	1961	0.2

Table 3
Retention time shifts determined by analysis of a Grob mixture by three different column sets (column sets A, B and C) using the original analysis method.

Compounds	W_b	W_b	Original column set A		Column set B		Column set C	
	^{1}tr (s)	^{2}tr (ms)	^{1}tr (s)	^{2}tr (ms)	Δ^1tr (s)	Δ^2tr (ms)	Δ^1tr (s)	Δ^2tr (ms)
Butanediol	9	143	591	1815	27	−55	0	110
n-Decane	9	89	1095	1345	30	−20	3	80
Octanol	9	88	1212	1770	33	−45	6	100
Nonanal	9	88	1275	1840	36	−55	6	100
Dime-phenol	9	109	1287	2415	36	−90	6	135
n-Undecane	9	76	1299	1415	33	−25	6	75
Ethylhexanoic acid	12	108	1302	1805	36	−60	9	105
Dime-aniline	9	117	1410	2700	36	−105	6	155
Me-decanoate	12	82	1689	1870	39	−50	9	105
Me-undecanoate	9	81	1857	1910	42	−45	12	105
Dicyclohexylamine	12	92	1899	2120	42	−55	12	115
Me-dodecanoate	9	81	2016	1955	45	−50	12	110

programming, a compound eluting at a different primary retention time, caused by a change in the primary and/or the secondary column dimension, will enter the secondary column at a different oven temperature, which will lead to a secondary retention time shift. In summary, peaks may shift in both directions and the direction and degree of shift cannot be predicted.

3.3. 2D retention time locking procedure

3.3.1. Locking the first dimension

After installing a new column set, in which the secondary column length was approximately 15 cm longer, a Grob mixture was analyzed at five different column head pressures. In Table 4 the original primary retention times (measured using column set A) and the retention time shifts measured at the different constant column head pressures are given for all Grob mix compounds. The results clearly indicate a primary retention time shift of 60–80 s, for all compounds when analyzing the Grob mixture using the original analysis method having a constant head pressure of 41.75 psi.

An overlay of the 2D chromatograms of the Grob mixture analyzed by the original column set A and the original analysis method and the 2D chromatogram of the Grob mixture analyzed by the newly installed column set and the original (not locked) analysis method is given in Fig. 1.

The results of methyl decanoate were used to calculate the constant column head pressure at which the retention time difference compared to the original retention time of methyl decanoate (1689 s) is zero. The plot of the constant column head pressure versus the primary retention time shift is given in Fig. 2.

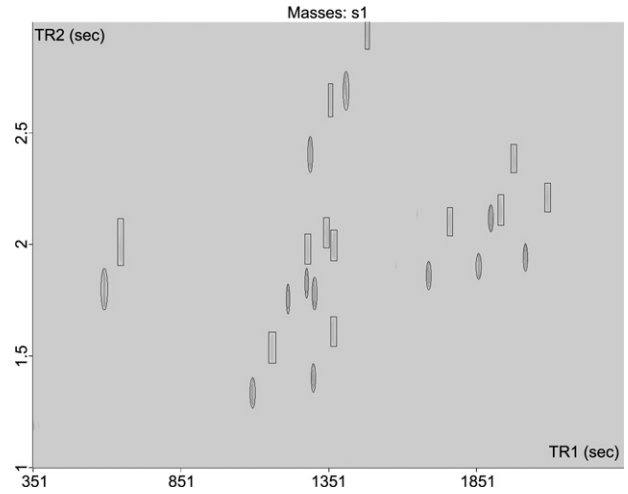

Fig. 1. Overlay of the 2D chromatogram of a Grob mixture obtained using column set A (ellipses) and a new installed column set (rectangles) both obtained using the original analysis method.

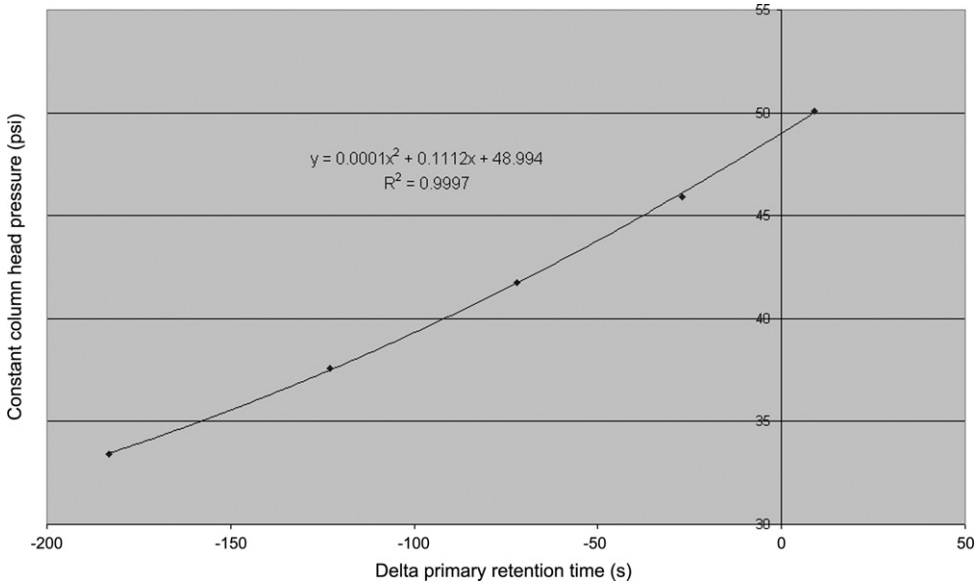

Fig. 2. Primary retention time shift of methyl decanoate compared to its original retention time as a function of the constant column head pressure.

Table 4
Differences in retention times, compared to the original retention times, measured at different constant column head pressures.

Column head pressure (psi)	41.75 Original (column set A) ^{1}tr (s)	33.40 Δ^1tr (s)	37.58 Δ^1tr (s)	41.75 Δ^1tr (s)	45.93 Δ^1tr (s)	50.10 Δ^1tr (s)
1,4-Butanediol	591	−150	−99	−57	−21	9
n-Decane	1095	−171	−114	−63	−24	15
Octanol	1212	−174	−117	−66	−27	12
Nonanal	1275	−177	−120	−69	−27	12
Dime-phenol	1287	−183	−123	−69	−27	12
n-Undecane	1299	−177	−117	−66	−24	12
Ethylhexanoic acid	1302	−174	−117	−66	−27	12
Dime-aniline	1410	−189	−126	−72	−27	12
Me-decanoate	1689	−183	−123	−72	−27	9
Me-undecanoate	1857	−183	−126	−75	−30	9
Dicyclohexylamine	1899	−192	−129	−78	−30	12
Me-dodecanoate	2016	−186	−126	−75	−30	9

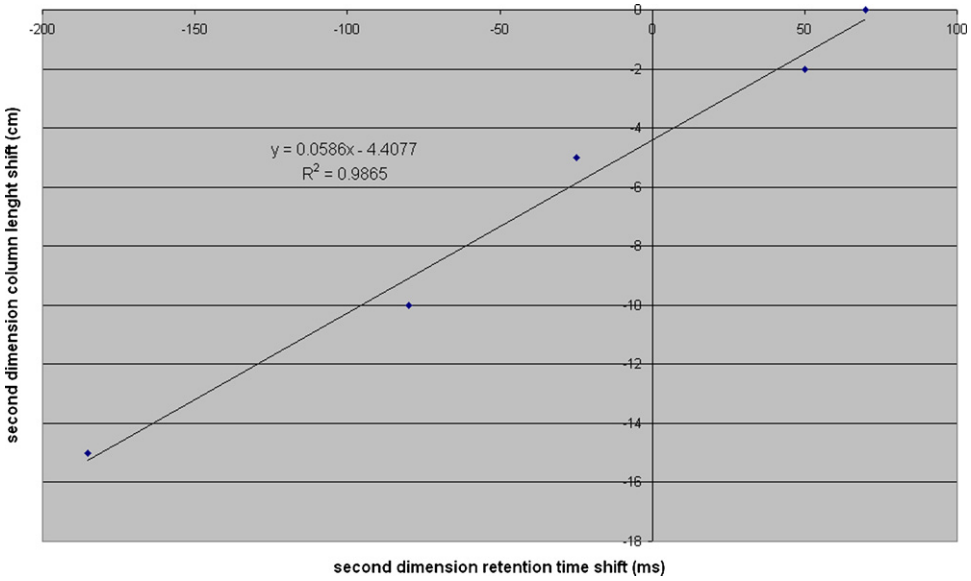

Fig. 3. Secondary retention time shift of methyl decanoate compared to its original retention time as a function of the secondary column length shift.

Using the plot function as given in Fig. 2, the column head pressure at which the retention time of methyl decanoate matches its original retention time can be calculated. The calculated locked constant head pressure is 48.99 psi. This pressure was set into the analysis method used for locking the secondary-dimension.

3.3.2. *Locking the second-dimension*

In order to lock the second-dimension a Grob mixture was analyzed, using the locked primary-dimension method, at five different effective secondary column lengths. In Table 5 the original secondary retention times and the retention time shifts measured with different effective secondary column lengths are given for all Grob mix compounds.

The results of methyl decanoate were used to calculate the secondary column length shift at which the retention time difference compared to the original retention time of methyl decanoate (1670 s) is zero. The plot of the secondary column shift versus the secondary retention time shift is given in Fig. 3.

Using the plot function as given in Fig. 3, the secondary column length shift at which the retention time of methyl decanoate matches its original retention time can be calculated. The calculated

Table 5
Differences in retention times, compared to the original retention times, measured at different effective secondary column lengths.

Secondary column length shift (cm)	Original (column set A) ^{2}tr (ms)	0 ^{2}tr (ms)	−2 ^{2}tr (ms)	−5 ^{2}tr (ms)	−10 ^{2}tr (ms)	−15 ^{2}tr (ms)
1,4-Butanediol	1815	85	70	−10	−70	−160
n-Decane	1350	40	35	−25	−70	−135
Octanol	1775	65	55	−30	−75	−180
Nonanal	1840	70	55	−25	−80	−180
Dime-phenol	2410	105	80	−20	−90	−230
n-Undecane	1415	45	35	−30	−70	−145
Ethylhexanoic acid	1805	65	55	−25	−85	−170
Dime-aniline	2700	105	80	−20	−115	−265
Me-decanoate	1870	70	50	−25	−80	−185
Me-undecanoate	1915	70	50	−30	−90	−190
Dicyclohexylamine	2120	80	50	−30	−95	−215
Me-dodecanoate	1965	60	45	−35	−100	−205

Table 6
Differences in primary retention times, compared to the original retention times, measured at different effective secondary column length.

Secondary column length shift (cm)	Original (column set A) ^{1}tr (ms)	0 ^{1}tr (s)	−2 ^{1}tr (s)	−5 ^{1}tr (s)	−10 ^{1}tr (s)	−15 ^{1}tr (s)
1,4-Butanediol	591	3	3	3	3	3
n-Decane	1095	6	6	6	6	3
Octanol	1212	3	3	3	6	0
Nonanal	1275	3	3	3	6	0
Dime-phenol	1287	3	3	3	6	0
n-Undecane	1299	3	3	6	6	3
Ethylhexanoic acid	1302	3	3	3	6	0
Dime-aniline	1410	3	3	6	6	3
Me-decanoate	1689	0	0	3	6	0
Me-undecanoate	1857	0	0	0	3	−3
Dicyclohexylamine	1899	0	0	3	6	−3
Me-dodecanoate	2016	−3	0	0	3	−3

secondary retention time shift is −4 cm. The secondary column was positioned to −4 cm.

In Table 6, the differences in primary retention times, compared to the original retention times, measured at different effective secondary column lengths, are given. These results clearly show that there is no significant correlation of shifting the secondary column through the modulator, thereby lengthening or shortening its effective length, on the primary retention times.

After completing the locking procedure, a Grob mixture was analyzed again. The results are summarized in Table 7. Both the primary and secondary retention time shifts are, on average, minimized to less than 0.5 W_b.

An overlay of the 2D chromatograms of the Grob mixture analyzed by the original column set A and the original analysis method and the 2D chromatogram of the Grob mixture analyzed by the new installed column set and the locked analysis method is given in Fig. 4.

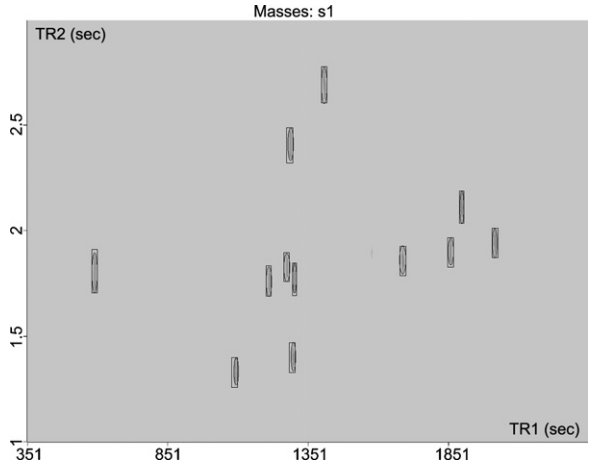

Fig. 4. Overlay of the 2D chromatogram of a Grob mixture obtained using column set A and the original analysis method (ellipses) and a new installed column set (rectangles) obtained by using the locked primary- and secondary-dimension analysis method.

3.4. Real-life sample

The naphtha sample was analyzed using column set A, and both the original methods, utilizing constant pressure and constant flow. The 2D chromatogram of the sample obtained using the column set A, and the original constant pressure method (pressure is 55 psi) is given in Fig. 5. In Fig. 5, five peaks are indicated which are used to check the performance of the 2D-RTL procedure. After installing column set B, the naphtha sample was analyzed again using both unlocked methods. Next, the 2D-RTL procedure was applied and the naphtha sample was analyzed once more using both locked methods. The constant pressure, used in the constant pressure method was, was changed from 55.00 to 50.47 psi in order to lock the primary-dimension. The constant column flow, used in the constant column flow method, was changed from 1.50 to 1.30 ml/min, in order to lock the primary-dimension. For both methods, the secondary column length was shortened 4.5 cm in order to lock the secondary-dimension. In Table 8, the 2D-RTL results of five different peaks are summarized. The five peaks are well spread over the

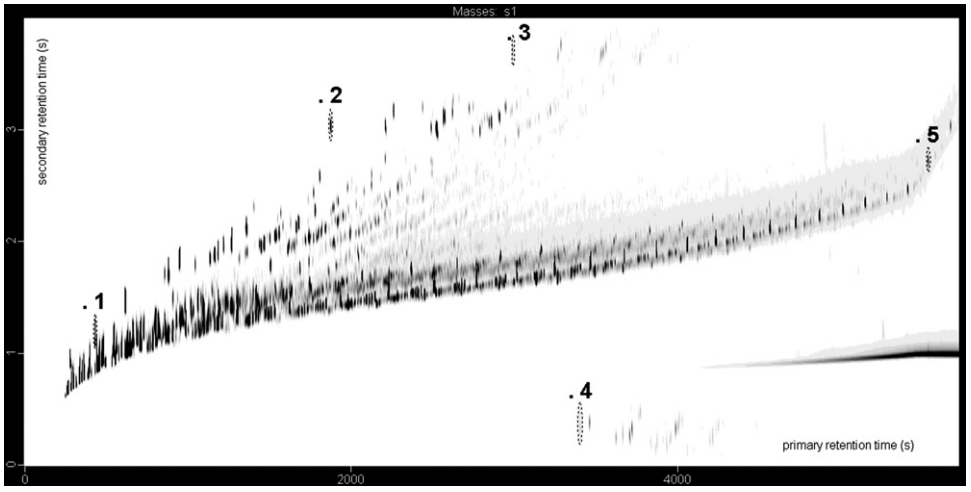

Fig. 5. 2D chromatogram of a naphtha sample analyzed using column set A and the original constant pressure method.

Table 7
Summarized results of the locking procedure.

Compounds	Original		Original		Not locked		Locked primary-dimension		Locked primary-and secondary-dimension	
	^{1}tr (s)	^{2}tr (ms)	^1W_b (s)	^2W_b (ms)	Δ^1tr (s)	Δ^2tr (ms)	Δ^1tr (s)	Δ^2tr (ms)	Δ^1tr (s)	Δ^2tr (ms)
1,4-Butanediol	591	1815	9	143	−57	−205	3	−85	3	−5
n-Decane	1095	1350	9	89	−63	−195	6	−40	6	15
Octanol	1212	1775	9	88	−66	−215	3	−65	3	15
Nonanal	1275	1840	9	88	−69	−215	3	−70	3	15
Dime-phenol	1287	2410	9	109	−69	−250	3	−105	3	5
n-Undecane	1299	1415	9	76	−66	−205	3	−45	3	20
Ethylhexanoic acid	1302	1805	12	108	−66	−215	3	−65	3	10
Dime-aniline	1410	2700	9	117	−72	−255	3	−105	6	5
Me-decanoate	1689	1870	12	82	−72	−240	0	−70	3	15
Me-undecanoate	1857	1915	9	81	−75	−245	0	−70	0	20
Dicyclohexylamine	1899	2120	12	92	−78	−265	0	−80	3	15
Me-dodecanoate	2016	1965	9	81	−75	−255	−3	−60	0	25

Table 8
Results of the 2D-RTL procedure.

Peak no.	Column set A		Column set B Not locked		Column set B Locked		Column set A vs. B	
	^{1}tr (s)	^{2}tr (s)	^{1}tr (s)	^{2}tr (s)	^{1}tr (s)	^{2}tr (s)	Δ^1tr (s)	Δ^2tr (ms)
Constant pressure mode								
1	432	1.18	400	1.15	428	1.16	−4	−20
2	1876	3.04	1816	3.23	1868	3.07	−8	20
3	2992	3.72	2932	3.91	2988	3.72	−4	0
4	3400	0.37[a]	3344	0.57[a]	3400	0.35[a]	0	−20
5	5536	2.74	5492	2.65	5540	2.70	4	−30
Constant column flow mode								
1	532	1.38	496	1.40	528	1.39	−4	10
2	1948	2.97	1892	3.14	1944	3.00	−4	40
3	2988	3.50	2932	3.67	2984	3.53	−4	30
4	3368	0.08[a]	3316	0.23[a]	3368	0.08[a]	0	0
5	5508	2.25	5468	2.12	5512	2.25	4	0

[a] These peaks are wrapped around.

whole 2D chromatogram and are therefore assumed to be representative for the whole chromatogram.

The results given in Table 8 clearly indicate a significant retention time difference between column set A and B when using the original, non-locked, methods. After performing the 2D-RTL procedure, retention time shifts are on average minimized to less than 0.5 W_b for both constant pressure and constant column flow methods.

4. Conclusions

A fast and easy two step 2D-RTL procedure is proposed and its feasibility is demonstrated. The results show that significant primary and secondary retention time shifts can be minimized to less than 0.5 W_b when applying this procedure. The two step procedure consists of locking the first dimension by adjusting the constant head pressure or constant column flow, followed by locking the second-dimension by adjusting the effective secondary column length. Locking the second-dimension, by moving the second-dimension column trough the modulator, thereby shortening or lengthening only its effective length, does not have a significant effect on the already locked primary retention times. The 2D-RTL procedure is limited to so-called pass-through modulators, however the applicability to single-stage loop-type modulators will be part of our future research.

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