Journal of Chromatography A, 1218 (2011) 3159–3165

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Retention time locking procedure for comprehensive two-dimensional gas chromatography

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ARTICLE INFO

Article history:
Available online 21 September 2010

Keywords:
Retention time locking
Gas chromatography
Two-dimensional gas chromatography
Retention times

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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doi:10.1016/j.chroma.2010.08.065

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