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DOI

[10.1016/j.chroma.2012.11.004](https://doi.org/10.1016/j.chroma.2012.11.004)

Publication date

2012

Document Version

Author accepted manuscript

Published in

Journal of Chromatography A

[Link to publication](#)

Citation for published version (APA):

Mommers, J., Knooren, J., Dutriez, T., Ritzen, E., & van der Wal, S. (2012). Temperature-tunable selectivity in comprehensive two-dimensional gas chromatography. *Journal of Chromatography A*, 1270, 305-309. <https://doi.org/10.1016/j.chroma.2012.11.004>

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Temperature-tunable selectivity in comprehensive two-dimensional gas chromatography

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ARTICLE INFO

Article history:

Received 15 September 2012

Received in revised form 31 October 2012

Accepted 1 November 2012

Available online 6 November 2012

Keywords:

Tunable chromatography

Tunable selectivity

GC × GC

Dual-oven

ABSTRACT

A temperature-tunable two-dimensional gas chromatography setup, consisting of three capillary columns with different selectivity, is described. In this setup the selectivity of the primary dimension can be tuned by adjusting the temperature offset of two in series-coupled capillary columns, both columns being part of the primary dimension and positioned in two separate GC ovens. The overall GC × GC separation can be optimized by altering the selectivity of the primary dimension. Besides tuning selectivity, in order to achieve optimal separation, this 2D-GC setup also offers enhanced opportunities for qualitative analysis. Sequentially altering the selectivity of the primary dimension enables one to identify groups of compounds which show similar chromatographic retention behavior.

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC), introduced in 1991 by Liu and Phillips [1], is a powerful analytical technique providing structured chromatograms and high separation power, making this technique ideal for analyzing complex samples. Despite the high separation power of this technique, coelutions of target determinants still may occur.

In this paper we describe a temperature-tunable two dimensional gas chromatography setup in which the column selectivity of the primary dimension can be altered for solving critical coelutions of target determinants. In our approach, the primary dimension consists of two columns coupled in series in which the second column is positioned in a separate GC oven. This second in series-coupled primary column should have different retention characteristics, in terms of selectivity and retention mechanism, compared to the other two columns. The contribution of the second in series-coupled primary column, which is positioned in the second oven, can be altered by adjusting the temperature offset of this oven compared to the main oven and thereby the overall selectivity of the primary dimension can be tuned. The contribution of the second in series-coupled primary column to the overall first

dimension retention time can be increased by lowering the temperature offset and can be decreased or minimized by increasing the temperature offset.

Tuning of column selectivity for one dimensional gas chromatography has extensively been described in literature. In most publications column selectivity is tuned by means of controlling the pressure at the junction point of two different in series-coupled capillary columns [2–15]. This approach, however, requires a T-connector and an extra carrier gas supply. Another approach for tuning selectivity is optimizing the temperatures for series-coupled columns in dual-oven gas chromatographic systems [16–19]. Column temperature has a significant effect on selectivity, especially for polar phases and compounds.

To our knowledge, tuning strategies for comprehensive two-dimensional gas chromatography, based on temperature or pressure tuning the selectivity of the primary dimension by using series-coupled columns has not been described in the literature yet.

Besides optimizing the resolution by tuning the selectivity of the primary dimension, our tunable 2D-GC setup also offers enhanced opportunities for qualitative analysis. Altering stepwise the contribution of the second in-series coupled primary column, which has different retention characteristics compared to the first in series-coupled primary column and second dimension column, enables the opportunity to identify groups of compounds which show similar chromatographic retention behavior (similar interactions) with the stationary phase of the second in series-coupled primary column.

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2. Experimental

2.1. Test mixtures and samples

All experiments were carried out with a homemade test mixture containing 38 compounds and two different industrial plant samples. The test mixture contained 500 μL of each of the following compounds: diethylketone, 3,3-dimethyl-2-butanone, 2,4-dimethyl-3-pentanone, 3-methyl-2-pentanol, 3-methyl-2-pentanone, 3-methyl-2-butanone, 2-methoxyethanol, 2-pentanone, methyl-cyclohexane, 3-methoxy-propionitrile, isobutyronitrile, propionitrile, 1-pentanal, 3-methyl-2-butanol, butanal, 1-hexanol, isobutanol, 1-butanol, benzene, cyclohexane, 1-propanol, hexane, dimethylsulfoxide, ethanol, heptane, n-butylacetate, chloroform, ethylacetate, diethylether, 2-cyanoethylether and also 100 μL of each of the following compounds: allylcyanide, methyl-cyclopentane, ethyl-cyclopentane, crotononitrile, 2-pentanol, 2-hexen-1-ol, 3-hexanol, and 2-hexanol.

2.2. Instrumental

All GC $\times$ GC-FID analyses were carried out on a Leco (St. Joseph, MI, USA) GC $\times$ GC system, equipped with a secondary GC-oven which is positioned inside the main GC-oven, an Agilent 7683 autosampler, a hot split/splitless injector and a flame ionization detector (FID). Instrument control and data processing was performed by Leco ChromaTOF[®] software (St. Joseph, MI, USA) version 3.25. For all calculations Microsoft[®] Office Excel 2007 (Redmond, Washington, VWA, USA), was used.

A schematic overview of the tunable two-dimensional gas chromatographic setup is given in Fig. 1. In order to be able to tune the overall GC $\times$ GC selectivity, all three capillary columns must have different retention characteristics.

Column 1 is a non-polar 25 m $\times$ 0.25 mm, 1.2 μm film thickness CPSil8CB column, purchased from Varian (Middelburg, The Netherlands). This column is coupled in series with a polar 5 m $\times$ 0.25 mm, 0.5 μm film thickness Stabilwax[®]-DB column (column 2, Restek, Bellefonte, PA, USA). The Stabilwax[®]-DB-column is installed in the second GC-oven (oven-2). The other end of this column is coupled to a 2 m $\times$ 0.1 mm, 0.08 μm film thickness polar ionic liquid SLB[®]-IL59 column (column 3), purchased from Sigma-Aldrich (St. Louis, MO, USA). The ionic liquid column is installed in oven-1 and passes through the modulator. All capillary column connections were made by using SilTite[™] μ -Unions,

purchased from SGE Europe (United Kingdom). When performing two-dimensional gas chromatography, the in series coupled columns 1 and 2 make up the tunable primary dimension and column 3 the secondary dimension. Due to temperature controlling restrictions of this GC $\times$ GC system, oven-2 must be programmed at least 5 $^{\circ}\text{C}$ higher than the temperature of oven-1.

2.3. Chromatographic conditions

For all experiments, oven-1 was held for 1 min at 50 $^{\circ}\text{C}$ and next programmed to 180 $^{\circ}\text{C}$. Oven-2 was programmed having a positive temperature offset, for both the initial and final oven temperature, of 5, 10, 15, 20, 25, 30, 35 or 40 $^{\circ}\text{C}$ compared to oven-1. The temperature rates, for both ovens, were 3 $^{\circ}\text{C min}^{-1}$. A modulation time of 3.5 s was used. All separations were carried out using a constant helium flow of 1.2 ml/min. The injector temperature was 280 $^{\circ}\text{C}$, using a split ratio of 1:50 and an injection volume of 1 μL . The FID was operated at a temperature of 300 $^{\circ}\text{C}$, using a data-acquisition rate of 200 Hz.

3. Results and discussions

3.1. Influence of oven-2 temperature offset on primary dimension separation

In Fig. 2, part of the primary dimension 1D-chromatograms of the test mixture, measured at different oven-2 temperature offsets, are given. The lower the oven-2 temperature offset the more the Stabilwax[®]-DB column will contribute to the primary dimension separation. In Fig. 2 it can clearly be seen that the most polar compounds 1, 3, 4, 7, 9 and 10, shift to higher retention times when lowering the oven-2 temperature offset. The relation between the oven-2 temperature offset and the retention of the polar compounds can be described by a quadratic function. In this example, the primary dimension separation can be tuned by adjusting the temperature offset to 10 $^{\circ}\text{C}$, in order to achieve a full baseline separation for all 10 compounds.

3.2. Influence of the temperature of oven-2 offset on two-dimension separation

In Fig. 3 an overlay is given of the two-dimensional chromatograms of the analysis of the test mixture measured at different oven-2 temperature offsets. The highlighted and colored peaks are

Fig. 1. Schematic overview of the tunable two-dimensional gas chromatography set-up.

Fig. 2. Influence of oven-2 temperature offset on the primary dimension separation; analysis of a test mixture at different oven-2 temperature offsets (1 = ethanol; 2 = ethyl ether; 3 = 1-propanol; 4 = propanenitrile; 5 = hexane; 6 = ethylacetate; 7 = chloroform; 8 = cyclohexane; 9 = isobutyronitrile; 10 = 2-methyl-1-propanol).

measured with an oven-2 temperature offset of 40 °C, the dark/gray peaks are measured sequentially with an oven-2 temperature offset of 35, 30, 25, 20, 15, 10 and 5 °C.

In Fig. 3 it clearly can be seen that the influence of lowering the oven-2 temperature offset is not the same for all compounds. The compounds in box A, all nonpolar compounds, do not shift when lowering the offset temperature indicating that these non-polar compounds have zero affinity with the polar Stabilwax®-DB column. The compounds in the boxes B have significant retention on the polar ionic liquid SLB®-IL59 column but almost no retention on the polar Stabilwax®-DB column. However, the compounds in the boxes C have significant retention on the polar ionic liquid SLB®-IL59 column and also significant retention on the polar Stabilwax®-DB column. The compounds in the boxes C are not

Fig. 3. Influence of oven-2 temperature offset on the two-dimensional separation; analysis of a test mixture at different oven-2 temperature offsets; highlighted colored peaks are measured with a positive oven-2 offset of 40 °C, colorless peaks are sequentially measured with an positive offset of 35, 30, 25, 20, 15, 10 and 5 °C.

susceptible to hydrogen bonding with the polyethylene glycol stationary phase of the Stabilwax®-DB column. The compounds in the boxes B however are susceptible to hydrogen bonding. This result clearly demonstrate the different retention characteristics of the polar Stabilwax®-DB-column and the polar ionic liquid SLB®-IL59 column: compounds with similar retention on the ionic liquid SLB®-IL59 column, for example peak B' (3-methyl-2-pentanone) and C' (1-pentanol) in Fig. 3, show different retention behavior on the Stabilwax®-DB column. So, by changing the oven-2 temperature offset, the overall selectivity of the primary dimension column can be altered. Partly or fully coeluting peaks, which have adequate different selectivity's on the Stabilwax®-DB-column and the polar ionic liquid SLB®-IL59 column may be separated simply by tuning the oven-2 temperature offset.

In Fig. 4 the secondary dimension retention times of the test mix compounds are plotted against the primary retention time differences measured when analyzing the test mix applying a temperature oven-2 offset of 40 °C and 5 °C. These measured retention time differences are related to the retention of the compounds on the polar Stabilwax®-DB column (column-2).

In this plot three different groups, A, B and C can be identified. The compounds in group A (e.g. cyclohexane, hexane, heptane, diethylether, methylcyclopentane, ethylcyclopentane) show almost no retention on the secondary dimension column and their retention is not influenced by altering the temperature offset of the polar Stabilwax®-DB column (column-2). Compounds in group A are all nonpolar compounds showing low retention on both polar columns. The compounds in group B (e.g. diethyl ketone, 3,3-dimethyl-2-butanone, 2,4-dimethyl-3-pentanone, 3-methyl-2-pentanone, 3-methyl-2-butanone, 2-pentanone, 1-pentanal, butanal) show significant retention on the secondary dimension column and low retention on the polar Stabilwax®-DB column (column-2). All these compounds are significantly polar however are not able to undergo strong hydrogen bonding with the stationary polyethylene glycol phase of the polar Stabilwax®-DB column. The compounds in group C (3-methyl-2-pentanol, 2-methoxyethanol, 3-methyl-2-butanol, 1-hexanol, isobutanol, 1-butanol, 1-propanol, ethanol, 2-pentanol, 2-hexen-1-ol, 3-hexanol,

Fig. 4. Analysis of test mixture by tunable GC $\times$ GC applying an oven-2 temperature offset of 40 °C and 5 °C; secondary dimension retention times plotted against the delta primary retention time. Group A are nonpolar compounds; group B are polar compounds, not able to undergo hydrogen bonding; group C are polar compounds, able to undergo hydrogen bonding.

and 2-hexanol) show significant retention on the polar Stabilwax®-DB and the ionic liquid SLB®-IL59 column. All these compounds are polar and able to undergo hydrogen bonding with the stationary phase of the polar Stabilwax®-DB column.

This example clearly demonstrates that the selectivity of the primary dimension in this GC $\times$ GC setup can be tuned and also that this tunable GC $\times$ GC setup can be used for the identification of compound groups which have different retention behavior on both the Stabilwax®-DB and the ionic liquid SLB®-IL59 column.

3.3. Analysis of real-life industrial plant samples

In Fig. 5, part of the two-dimensional chromatogram the industrial plant sample A, measured at different oven-2 offset temperatures, is given. A few coelutions or critical separations, measured with an oven-2 temperature offset of 40 °C, are indicated by the yellow circles. When lowering the temperature offset, so increasing the contribution of the Stabilwax®-DB column, the separation of the critical pairs improves. For the critical pairs in the yellow circle B, it can clearly be seen that one peak shows relatively more retention on the Stabilwax®-DB column compared to the other peaks, leading to a full separation at lower oven-2 temperature offsets. The critical separations indicated in the yellow circles A and C are coelutions of compounds which are wrapped-around with peaks which are non-polar and not wrapped-around. At lower oven-2 temperature offsets the wrapped-around compounds have more retention on the Stabilwax®-DB column, compared to the non wrapped-around peaks. Lowering the oven-2 temperature offset has no or little effect on the non-polar compounds, while the more polar coeluting compounds show more retention on the Stabilwax®-DB column.

Of course, in complex chromatograms concurrently a decrease of resolution of other compounds will occur, so careful optimization is required. Temperature-tuning GC $\times$ GC thus will offer an alternative and convenient screening-strategy for very complex samples.

In Fig. 6, part of the two-dimensional chromatogram of the industrial plant sample B, measured at an oven-2 offset temperature of 40 °C and 10 °C, is given. At an offset of 40 °C, the low intensity peaks A and B coelute with the large intensity peak C. When lowering the temperature offset to 10 °C, peaks A and B can be fully separated from peak C. Compounds A and B undergo more retention on the Stabilwax®-DB column than compound C.

Fig. 5. Analysis of the industrial plant sample A by tunable GC $\times$ GC applying an oven-2 temperature offset of 40 °C, 30 °C, 20 °C, 10 °C and 5 °C; yellow circles A, B and C indicate coelutions or critical separations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Analysis of the industrial plant sample B by tunable GC $\times$ GC applying an oven-2 temperature offset of 40 °C and 10 °C; A, B and C indicate the target determinants.

4. Conclusions and discussions

By using the temperature-tunable two dimensional gas chromatography setup described in this paper it is possible to tune the selectivity of the first dimension separation. In this setup the primary dimension exists of two in series-coupled columns, a non-polar CPSil8CB and a polar Stabilwax®-DB column, in which the latter is positioned in a separate GC-oven and a polar ionic liquid SLB®-IL59 as the secondary dimension column. By altering the temperature offset of the separate GC-oven the contribution of the second, primary dimension, and column (Stabilwax®-DB) can be changed and thereby changing the overall primary dimension selectivity.

It is essential that all three columns have different retention characteristics in order to optimize the overall two-dimensional separation. However, the type of stationary phase and also the column dimensions of the in series-coupled second primary dimension column should be selected carefully; the contribution of this second column to the overall GC $\times$ GC separation may not lead to a significant decrease in orthogonality.

Furthermore, besides optimizing the resolution by tuning the selectivity of the overall primary dimension, this temperature tunable GC $\times$ GC setup also offers enhanced opportunities for qualitative analysis. By changing stepwise the contribution of the second in series-coupled primary column (Stabilwax®-DB), simply by changing the oven-2 temperature offset, groups of compounds which have different retention behavior on a polar Stabilwax®-DB and a polar ionic liquid SLB®-IL59 can be identified. In fact, in this setup the extra column can be seen as a virtual third dimension. For example, it was demonstrated that polar compounds which are susceptible to hydrogen bonding, e.g. alcohols, are relatively more retained when lowering the oven-2 temperature offset, so thereby increasing the Stabilwax®-DB retention contribution, than polar compounds which are not susceptible to strong hydrogen bonding e.g. ketones.

Besides the described temperature-tunable GC $\times$ GC setup also other related configurations could be applied for tuning the overall two-dimensional selectivity. A similar approach could be used to tune the selectivity of the secondary dimension. For this, two in series-coupled secondary columns having similar internal diameters and in which one of the two columns is positioned in a separate GC oven, the overall selectivity of the secondary dimension could be tuned by optimizing the temperature offset. However, the main disadvantage of this setup is the fact that the extra dimension column, including a required column connector, which are positioned after the GC $\times$ GC modulator, would lead to extra band broadening and also to a higher, in general less favorable, midpoint pressure.

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