Rapid determination of thermodynamic parameters from one-dimensional programmed-temperature gas chromatography for use in retention time prediction in comprehensive multidimensional chromatography

By: Teague M. McGinitie1, Heshmatollah Ebrahimi-Najafabadi1,2 and James J. Harynuk1

Submitted to: *J. Chromatogr. A.*

October 2013

Corresponding Author:

James J. Harynuk

[1] Department of Chemistry

 University of Alberta

 Edmonton, Alberta, T6G2G2, CANADA

 James.harynuk@ualberta.ca

[2] Department of Medicinal Chemistry,

 School of pharmacy,

 Guilan University of Medical Sciences,

 Rasht, Iran

Key Words:

Comprehensive two-dimensional gas chromatography; gas chromatography; retention time; prediction; thermodynamics

Abstract:

A new method for estimating the thermodynamic parameters of Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* for use in thermodynamic modeling of GC×GC separations has been developed. The method is an alternative to the traditional isothermal separations required to fit a three-parameter thermodynamic model to retention data. Herein, a non-linear optimization technique is used to estimate the parameters from a series of temperature-programmed separations using the Nelder-Mead simplex algorithm. With this method, the time required to obtain estimates of thermodynamic parameters a series of analytes is significantly reduced. This new method allows for precise predictions of retention time with the average error being only 0.2 s for 1D separations. Predictions for GC×GC separations were also in agreement with experimental measurements; having an average relative error of 0.37 % for *1tr* and 2.1 % for *2tr*.

***1 Introduction:***

Predictive models of GC retention can be useful for several tasks including the optimization of separation conditions [[[1]](#endnote-1)] and the identification of unknown peaks in chromatograms [[[2]](#endnote-2)]. With comprehensive techniques such as GC×GC becoming more prevalent, predictive models that can provide accurate retention information for these separation modes (ideally in both separation dimensions) are also required. The complexity associated with optimizing a comprehensive two-dimensional separation (e.g. GC×GC) is exponentially greater than that for the optimization of a one-dimensional separation. This complexity arises due to the interdependence of the separation conditions in the two dimensions. Consequently, changes made to one dimension (i.e. column geometry, column chemistry, temperature, or flow) will affect the conditions experienced by analytes in both dimensions of the separation [[[3]](#endnote-3)]. Given the large number of variables that could be optimized in a GC×GC separation it would be advantageous to use predictive models to aid in the optimization process.

 Predictive modeling could also be used as a tool to interpret the information contained within the structured retention patterns observed in GC×GC. Using a model of chromatographic retention for one- or multi-dimensional separations, an extra layer of information to confirm the identity of a compound could be provided. This ability to identify compounds in a sample on the basis of retention information and mass spectral data would be particularly useful in distinguishing structural isomers which are often difficult (or impossible) to distinguish by mass spectrometry alone. The need for such interpretive tools is clear when one considers that GC×GC chromatograms frequently contain thousands (or even tens of thousands) of peaks eluting across a two-dimensional plane [[[4]](#endnote-4)].

A variety of models exist for the prediction of retention behavior in 1D GC and while the field of GC×GC is relatively new, several attempts have already been made to create predictive models suitable for multidimensional gas chromatography. One of the first predictive models to be adapted to GC×GC used calculated vapour pressures derived from the Kovats retention indices in order to estimate retention times [[[5]](#endnote-5)]. This work introduced the usage of isovolatility curves to estimate the retention of analytes in the second dimension. Western and Marriott [[[6]](#endnote-6)] then refined this technique through the use of timed injections of alkane standards. Since then there have been several variations of this technique for use in GC×GC of which most are centered on the use of relating retention index to an analyte’s partition coefficient in order to model retention behavior. Several authors including Vendeuvre [[[7]](#endnote-7)], Pang [[[8]](#endnote-8)], Arey [[[9]](#endnote-9)] and Seeley [[[10]](#endnote-10)] have adapted these methods in various ways.

RI-based models have the advantage of an extensive library of RI data from which to work, at least for some stationary phases. However, the generation of isovolatility curves remains technically difficult on most instruments and can be time consuming [[[11]](#endnote-11)]. Furthermore, it has been argued that the use of alkanes as retention index standards is not necessarily appropriate for the second dimension in GC×GC [[[12]](#endnote-12)]. Despite these limitations for GC×GC, the popularity of RI models remains high, with several new studies conducted within the last few years [[[13]](#endnote-13), [[14]](#endnote-14)] and a recent review by von Muehlen and Marriott [[[15]](#endnote-15)].

With the rise of GC×GC, thermodynamic modeling of retention times is being revisited by several research groups. Zhu et al. used thermodynamics predicted from isovolatility curves to predict the retention indices of alcohols [[[16]](#endnote-16)]. While Lu et al. estimated enthalpic and entropic parameters to predict retention times for a variety of pyridines [[[17]](#endnote-17)]. The manner by which these estimations were performed worked incredibly well for optimizing a specific separation on the instrument used to collect the data. However, it is unclear how easily predictions could be ported from one system to another. Thewalim et al. used a two-parameter thermodynamic model to estimate retention times for various column sets [[[18]](#endnote-18)]. Dorman et al. also used a thermodynamic model based on ΔH and ΔS to predict the retention times of select components from the Grob mixture in a GC×GC separation [[[19]](#endnote-19)] , and Zhu et al. have used thermodynamic modeling to predict retention times of alkanes and PAHs in GC×GC separations [[[20]](#endnote-20)].

Thermodynamic-based models are attractive for several reasons, first thermodynamic models can account for changing operating conditions while maintaining accuracy, assuming that the model accurately accounts for the temperature dependence of the thermodynamic parameters over the range of temperatures studied [[[21]](#endnote-21)]. This is an advantage over models based on specific properties (such as RI) which have a dependence on oven temperature and ramp rate [[[22]](#endnote-22)]. The second advantage that thermodynamic models hold is that they do not require determinations of isovolatility curves. As our previous research has shown, accurate prediction of *1tr* and *2tr* in GC×GC using thermodynamics is possible provided the analytes’ thermodynamic parameters are known for each stationary phase involved [[[23]](#endnote-23)].

Regardless of the advantages thermodynamic modeling offers, its widespread usage is hampered by the unavailability of a library or other repository of thermodynamic data for a wide range of molecules. Without a library of thermodynamic data for a large cross section of analytes on a variety of stationary phases, thermodynamic predictions will largely remain in the realm of academic curiosities and small custom applications. Towards this end, we have previously outlined a standardized approach to estimate an analyte’s thermodynamic parameters in a way that permits their use in inter-laboratory studies [[[24]](#endnote-24)]. The same research introduced an automated method for the collection of thermodynamic data which reduced the required operator time necessary to perform careful manual injections to gather data.

Despite these refinements, the collection of thermodynamic data remains a time-consuming endeavor. Using our previous approach, a minimum of six isothermal separations performed in triplicate were required to obtain accurate thermodynamic parameters for a single compound. While it may be possible to run a solution that contains several analytes of interest, the nature of isothermal chromatography limits the utility of this approach. To date, the work of Dorman et al [19] appears to be the only example of an approach that uses temperature-programmed separations to obtain thermodynamic data for a two-parameter thermodynamic model of the GC separation. The problem with two-parameter thermodynamic models of GC separations is that the enthalpy (*ΔH*) and entropy (*ΔS*) of the GC process are assumed constant; however, these terms are in fact observed to be temperature-dependent over the range of temperatures commonly experienced by an analyte in temperature-programmed GC separations. For more accurate predictions over the range of temperatures typical of temperature-programmed GC, the change in adiabatic molar heat capacity (*ΔCP*) must be considered in order to account for the temperature-dependence of (*ΔH*) and (*ΔS*).

Herein we demonstrate a method whereby thermodynamic information for a three-parameter model of the GC process can be rapidly collected and calculated for multiple analytes based on data obtained from a series of temperature-programmed separations. This rapidly collected data can then be used with existing models for the prediction of GC or GC×GC separations.

***1.1 Theory***

 In order to accurately predict retention in a gas chromatographic separation it is necessary to estimate the changes in enthalpy and entropy of the analyte at some reference temperature, Δ*H*(*T0*) and Δ*S*(*T0*), respectively, as well as the change in its adiabatic molar heat capacity, Δ*CP*. In previous works [20, 22, [[25]](#endnote-25), [[26]](#endnote-26), [[27]](#endnote-27), [[28]](#endnote-28), [[29]](#endnote-29)] these parameters have been estimated through a series of isothermal separations from which a regression of the partition coefficient, *K*, against temperature, *T*, provides estimates for Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* through Equations 1-4 [21].

 (1)

 (2)

 (3)

 (4)

These thermodynamic estimates are then used in a time summation model based on the method of Snijders et al [30] to arrive at the retention time. The difference between the Snijders approach and ours is that at each step the value of the partition coefficient is recalculated based on the thermodynamic parameters for the compound, and the model is adapted for GC and GC×GC predictions [22]. In brief, the distancetraveled by an analyte which is initially at a position *xn* along the column during a brief interval of time is calculated. The time interval is sufficiently small for both the carrier gas velocity and retention factor of the analyte to be assumed constant. Thus, at the end of interval *n*, the analyte is at position *x(n+1)*.Then, the local velocity of the carrier gas and partition coefficient are recalculated based on the new position in the column and changes in oven temperature and/or inlet pressure and the distance traveled in the subsequent time interval is calculated. The process repeats until the total distance traveled by the analyte exceeds the length of the column.

 In this study, a nonlinear optimization procedure is used to estimate the thermodynamic parameters that would be required for an analyte to exhibit the retention times observed in a series of temperature-programmed separations. Here we combined the previously used time summation model with the Nelder-Mead simplex algorithm [31]. However, any other optimization technique such as genetic algorithms, particle swarm optimization, or Quasi-Newton techniques could in principle be used to minimize the error values of the predicted retention times. The Nelder-Mead simplex was chosen because it is simple, fast, and has high reproducibility. The simplex starts with four vertices as there are three thermodynamic parameters and then it sequentially moves through the experimental domain by a reflection, an expansion, or a contraction [32].

Using the absolute retention times for the analyte of interest across a series of temperature-programmed separations, thermodynamic estimates for Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* are obtainable. To help ensure the accuracy and robustness of the approach, data from four temperature ramps are used with a leave-one-out optimization strategy. For each analyte, the algorithm uses an initial guess for each of Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* to build the model under three temperature ramps and then proceeds to predict the retention time of the forth temperature ramp. The Nelder-Mead simplex algorithm proceeds to minimize the difference between the actual and predicted retention times for each temperature ramp by changing each of the three thermodynamic estimates. A sum of squares was used to test the fitness of the algorithm. In order to increase the likelihood of finding the optimal solution, the procedure was repeated 10 times with new random guesses of Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* (within some broad constraints) for each iteration. Once the algorithm reaches its optimal solution, the values of the thermodynamic parameters can be used in the traditional time summation model to make predictions in both 1D and GC×GC modes.

**2. Experimental**

**2.1 Chemicals**

A single standard mixture comprised of alkanes, alcohols and ketones was used in all experiments. n-Alkanes ranging from undecane to tetradecane were obtained from Sigma-Aldrich (Oakville, Ontario). 2-Undecanone, 2-dodecanone, and 2-tridecanone were purchased from Alfa-Aesar (Ward Hill, MA). Primary alcohol standards ranging from 1-undecanol to 1-tetradecanol were also purchased from Sigma-Aldrich. The standard mixture was prepared at a concentration of 1000 ppm in toluene (Sigma-Aldrich). Methane from the laboratory natural gas supply was used as a dead time marker when needed.

***2.2 Instrumental***

A 7890A gas chromatograph (Agilent Technologies, Mississauga, ON) equipped with a split/splitless injector, flame ionization detector, and a capillary flow technology (CFT) GC×GC modulator was used for all experiments. The GC was used in both 1D and 2D separation modes. Regardless of the mode used injections were performed in split mode with a split ratio of 100:1 and an inlet temperature of 280 °C. The flame ionization detector was maintained at a temperature of 250 °C with a data sampling rate of 200 Hz. 99.999 % Hydrogen (Praxair, Edmonton, AB) was used as a carrier gas. For GC×GC operations the modulation period was set at 1.5 s with a flush time of 0.15 s for all experiments. One-dimensional separations were carried out on a Supelco SLB5ms (30 m × 0.25 mm; 0.25 µm df; 5 % phenyl substituted polydimethylsiloxane), Supelco SPB50 column (30 m × 0.25 mm; 0.25 µm df; 50 % phenyl substituted polydimethylsiloxane), and Supelcowax (30 m × 0.25 mm; 0.25 µm df; polyethylene glycol). In GC×GC mode the primary column for all experiments was a Supelco SLB5ms (15 m × 0.1 mm; 0.1 µm df). The secondary column was a Supelcowax (3 m × 0.25 mm; 0.25 µm df).

All separations were performed under constant-flow conditions. For all one-dimensional separations the flow was set at 1.1 mL·min-1. In GC×GC, flows of 0.6 mL·min-1 and 21.3 mL·min-1 were set for the primary and secondary columns, respectively. The separations for both 1D and GC×GC runs were initialized at 30 °C, with the oven temperature programmed at ramp rates of 3, 5, 8, 10, 12, 16, and 20 °C·min-1 to 230 °C, with a hold time of one minute at the beginning and end of the run.

Raw data files for GC×GC separations were exported from Chemstation (Agilent) as text files and then converted using a custom script written in MATLAB 7.10.0 (The Mathworks, Natick, MA) into a format that was then imported into ChromaTOF 4.33 (Leco Corporation, St. Joseph, MI) for GC×GC processing. During processing, wrap around in the second dimension was calculated through the method developed by Micyus et al. [33]. Thermodynamic estimations, GC, and GC×GC retention time predictions were calculated using custom scripts written in MATLAB.

**3. Results and discussion**

***3.1 Method Validation***

Validation of the method was carried out via several independent checks. The thermodynamic optimization method was first validated through the use of a leave-one-out (LOO) methodology. In this case the input data set consisted of the collected retention times for the test mixture using 3, 5, 12, and 20 °C·min-1 temperature-programmed runs. For each analyte, three of the four ramps were included in a training set which was used by the model to obtain an estimate for Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP.* This estimation was repeated ten times and the best of these ten estimates (based on the minimal prediction error for the fourth ramp which was left out) was used for Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* for this combination of temperature ramps. This process was repeated three times, leaving out a different ramp each time. Once the LOO process was complete, the final estimate of the thermodynamic parameters was calculated from the average of the best values found in each of the LOO iterations. Figure 1 illustrates the procedure for the validation process including training set creation and parameter optimization. Table 1 provides an example of the estimated thermodynamic parameters using the training sets for dodecane, dodecanone and dodecanol along with the comparison of the experimental and predicted retention times for the ramp that was left out for all three stationary phases investigated. Similar data for the remaining analytes is provided in the supplemental data. The average error in the predicted retention times for all analytes using the LOO validation on the 5% phenyl, 50% phenyl and wax column were 0.2 s, 0.8 s, and 0.3 s respectively; with the largest error across all analytes and columns being 3.6 s. For all three columns there was no significant difference in the errors of prediction between fast or slow ramp rates, nor was there any relationship between the time an analyte spends in the column and the accuracy of the prediction.

A second validation was performed by using thermodynamic parameters estimated using the LOO approach to predict the retention times of analytes using three additional temperature ramps (8, 10, and 16 °C·min-1) as an external data set. This validation was performed to ensure the success of the predictions outside of the training set as the leave-one-out method incorporates data from the validation set when determining the average thermodynamic parameters. Again for all columns studied the predicted and experimental values for the retention times of analytes for the three ramps were in agreement, with the average error for all analytes being 0.1 s, 0.3 s, and 0.4 s for the 5 % phenyl, 50 % phenyl and wax columns, respectively. Using the parameters that we estimated in this work, the average error in retention time for all predictions of all analytes across all temperature ramps used was 0.1 s (5 % phenyl), 0.3 s (50 % phenyl), and 0.2 s (wax). Table 2 shows the results for all retention time predictions made for these one-dimensional separations.

The thermodynamic data collected from this new method were compared to data collected previously using the older isothermal approach as another validation of the results. This comparison is shown for the 5 % phenyl and wax columns in Table 3. The 5 % phenyl column shows agreement between the two methods with the average relative error for Δ*H*(*T0*), and Δ*S*(*T0*) being 0.67 % and 1.22 % respectively. For the wax column there is a slightly higher deviation between the two methods with an average error of 2.82 % and 5.35 % for Δ*H*(*T0*), and Δ*S*(*T0*). In both cases Δ*CP* exhibits a larger error between the two methods however; due to the relatively small contribution of Δ*CP* and the fact that it is treated as a constant in this approach, this is expected and not critical to the performance of the models.

A further advantage of the new method for determining thermodynamic parameters in GC is that with it we were able to significantly reduce the required analysis time for the determination of the thermodynamic parameters Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP*. By taking the sum of the retention times used to estimate the thermodynamic parameters for each analyte in our previous study [22] it was determined that on average 250 minutes of instrument run time are required per analyte, for a total analysis time of 41.6 hours to collect data for ten compounds. In comparison, using the same ten analytes and the new method based on temperature-programmed GC, only two hours of instrument time were required to obtain all necessary data. This represents a 95% reduction in the time required to collect thermodynamic data. If one considers that data for mixtures of 20 or more compounds could be easily collected in the same two-hour time period using this approach, especially with a multivariate detector (e.g. MS, AED, or IR) to aid in identifying and tracking closely and coeluting peaks, then the magnitude of the time savings increases dramatically.

***3.2 GC×GC Predictions***

Using the estimated thermodynamic parameters for each analyte, predictions were performed for GC×GC separations. All previously used temperature ramps were again used in the GC×GC separations. Before predictions were made the, exact column length was measured and then methane was used as a void time marker to estimate for the average column inner diameter. The average film thickness of each column was estimated by the use of undecanol as a marker as previously described [22]. Proper estimation of the column inner diameter and stationary phase film thickness is critical as small variations from the listed nominal values exist for both and can have a dramatic impact upon the success of the predictions. The column inner dimensions for the primary and secondary columns were calculated to be 102.5 µm and 262.5 µm, respectively. The film thicknesses for the primary and secondary columns were estimated to be 0.101 µm and 0.290 µm. To compare the predicted and experimentally determined second-dimension retention times, *2tr*, the wraparound of the analytes eluting from the second-dimension column were determined using the method developed by Micyus et al. [28].

Table 4 lists the experimental and predicted values for all compounds in both the primary and secondary dimensions across all temperature ramps studied. The predicted *1tr* were in agreement with the experimentally determined values with an average relative error of 0.37 %. The average relative error in the prediction of *2tr* was slightly higher at 2.09 %. The worst estimates for the predicted retention times in both *1tr* and *2tr* were found to be from the 3 °C·min-1 experiment; however, the relative error in this case was in line with the predictions made for all other temperature ramps. Figures 2 and 3 show the predicted peak apexes overlaid with the actual chromatogram and illustrate the high precision with which these predictions are made. The accuracy of the predictions in this study are on par with those from data that was obtained using isothermal runs. With the previous study [22] having an average relative error in *1tr* of 0.64 % and 2.22 % for *2tr*.

***4. Conclusions***

We have demonstrated a way in which temperature-programmed separation data can be used to rapidly obtain estimates for the thermodynamic parameters Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* that govern the behavior of analytes in GC. It was demonstrated that accurate data could be obtained from only four temperature-programmed runs which decreases the time required to collect thermodynamic information significantly. These parameters were then used for the prediction of retention times in GC×GC with a high degree of accuracy.. This new method to estimate the thermodynamic parameters for a GC separation makes the generation of libraries of thermodynamic data for GC separations a realistic, attainable goal.

**Acknowledgements**

Funding for this research was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Alberta Innovates Technology Futures. We would like to thank Syncrude Ltd. Canada for the use of facilities and the industrial contribution towards an NSERC IPS scholarship for T. McGinitie.

**References**

**Table/Figure Captions**

Table 1. Results for the leave-one-out (LOO) analysis of the four temperature ramps used to estimate the thermodynamic parameters of Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP*. The ramp listed was excluded from the optimization; the experimental and predicted retention times for the left-out ramp are shown.

Table 2. Comparison of the experimentally determined and predicted retention times using the average of the determined parameters Δ*H*(*T0*), Δ*S*(*T0*), and Δ*CP* from each LOO analysis.

Table 3. Comparison of thermodynamic parameters estimated using isothermal method and temperature-programmed method.

Table 4. Comparison of unwrapped experimental primary and secondary retention times with thermodynamically predicted values for each temperature program tested.

Figure 1. Flowchart for the process of estimating thermodynamic parameters including method validation

Figure 2. Chromatogram of 3 °C·min-1 temperature ramp; white squares depict predicted peak apex. 1-4 undecane, dodecane, tridecane, tetradecane. 5-7 undecanone, dodecanone, and tridecanone. 8-11 undecanol, dodecanol, tridecanol, tetradecanol

Figure 3. Chromatogram of 8 °C·min-1 temperature ramp; white squares depict predicted peak apex. 1-4 undecane, dodecane, tridecane, tetradecane. 5-7 undecanone, dodecanone, and tridecanone. 8-11 undecanol, dodecanol, tridecanol, tetradecanol

Figure 4. Chromatogram of 20 °C·min-1 temperature ramp; white squares depict predicted peak apex. 1-4 undecane, dodecane, tridecane, tetradecane. 5-7 undecanone, dodecanone, and tridecanone. 8-11 undecanol, dodecanol, tridecanol, tetradecanol

Table 1.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
| Compound |   | LOO Ramp | Estimated ΔH (To) (kJ·Mol-1) | Estimated ΔS (To) (J·K-1·Mol-1) | Estimated ΔCp (J·K-1·Mol-1) | Experimental Retention Time (min) | Predicted Retention Time (min) | Error (s) |
| Dodecane | 5 % Phenyl Column (SLB5ms) | 3 | -51.59 | -80.15 | 87.45 | 25.039 | 25.043 | -0.3 |
| 5 | -51.56 | -80.07 | 86.80 | 17.748 | 17.745 | 0.2 |
| 12 | -51.56 | -80.05 | 87.86 | 10.014 | 10.015 | -0.1 |
| 20 | -51.56 | -80.05 | 87.86 | 7.337 | 7.338 | -0.1 |
| Average Value | -51.57 | -80.08 | 87.49 |   |   | 0.1 |
| 50 % Phenyl Column (SPB50) | 3 | -44.31 | -63.81 | 199.88 | 21.780 | 21.792 | -0.7 |
| 5 | -44.28 | -63.73 | 195.71 | 15.873 | 15.867 | 0.4 |
| 12 | -44.26 | -63.65 | 197.56 | 9.362 | 9.363 | -0.1 |
| 20 | -44.27 | -63.69 | 195.43 | 7.033 | 7.033 | 0.0 |
| Average Value | -44.28 | -63.72 | 197.14 |   |   |   |
| Wax Column (Supelco Wax) | 3 | -42.34 | -69.22 | 32.02 | 13.231 | 13.230 | 0.1 |
| 5 | -42.36 | -69.25 | 31.23 | 10.405 | 10.407 | -0.1 |
| 12 | -42.36 | -69.26 | 31.96 | 6.812 | 6.808 | 0.2 |
| 20 | -41.90 | -67.96 | 49.16 | 5.371 | 5.377 | -0.3 |
| Average Value | -42.24 | -68.93 | 36.09 |   |   | 0.2 |
| 1-Dodecanol | 5 % Phenyl Column (SLB5ms) | 3 | -63.88 | -98.21 | 126.12 | 36.743 | 36.752 | -0.5 |
| 5 | -62.14 | -93.63 | 89.83 | 24.865 | 24.877 | -0.7 |
| 12 | -63.90 | -98.26 | 128.02 | 13.043 | 13.042 | 0.1 |
| 20 | -63.89 | -98.26 | 129.38 | 9.172 | 9.175 | -0.2 |
| Average Value | -63.45 | -97.09 | 118.34 |   |   | 0.4 |
| 50 % Phenyl Column (SPB50) | 3 | -61.90 | -92.13 | 180.80 | 37.777 | 37.757 | 1.2 |
| 5 | -59.41 | -85.55 | 129.07 | 25.642 | 25.678 | -2.2 |
| 12 | -62.23 | -92.95 | 183.88 | 13.537 | 13.538 | -0.1 |
| 20 | -62.27 | -93.07 | 183.24 | 9.565 | 9.553 | 0.7 |
| Average Value | -61.45 | -90.93 | 169.25 |   |   |   |
| Wax Column (Supelco Wax) | 3 | -65.12 | -94.19 | 70.15 | 42.413 | 42.403 | 0.6 |
| 5 | -65.30 | -94.64 | 71.98 | 28.357 | 28.360 | -0.2 |
| 12 | -65.38 | -94.84 | 72.74 | 14.548 | 14.547 | 0.1 |
| 20 | -65.86 | -96.10 | 81.38 | 10.082 | 10.083 | -0.1 |
| Average Value | -65.41 | -94.94 | 74.06 |   |   | 0.1 |
| 2-Dodecanone | 5 % Phenyl Column (SLB5ms) | 3 | -59.34 | -90.05 | 84.94 | 33.761 | 33.750 | 0.7 |
| 5 | -59.33 | -90.00 | 83.13 | 23.053 | 23.062 | -0.5 |
| 12 | -59.37 | -90.13 | 83.63 | 12.268 | 12.268 | 0.0 |
| 20 | -59.38 | -90.15 | 82.80 | 8.700 | 8.695 | 0.3 |
| Average Value | -59.36 | -90.08 | 83.62 |   |   |   |
| 50 % Phenyl Column (SPB50) | 3 | -58.50 | -86.52 | 170.57 | 35.056 | 35.030 | 1.6 |
| 5 | -58.49 | -86.43 | 166.89 | 23.982 | 23.997 | -0.9 |
| 12 | -58.61 | -86.76 | 171.27 | 12.827 | 12.835 | -0.5 |
| 20 | -58.65 | -86.88 | 168.07 | 9.133 | 9.118 | 0.9 |
| Average Value | -58.56 | -86.65 | 169.20 |   |   |   |
| Wax Column (Supelco Wax) | 3 | -54.63 | -78.03 | 47.07 | 33.366 | 33.362 | 0.26 |
| 5 | -54.93 | -78.83 | 55.07 | 22.936 | 22.935 | 0.06 |
| 12 | -54.95 | -78.89 | 54.96 | 12.304 | 12.302 | 0.14 |
| 20 | -55.00 | -79.02 | 57.89 | 8.745 | 8.748 | -0.20 |
| Average Value | -54.88 | -78.69 | 53.75 |   |   |   |

Table 2.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |
|  |  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
| Compund | Column | TemperatureRamp °C·min-1 | Experimental tr (min) | Predicted tr (min) | Difference (s) |
| dodecane | 5 % Phenyl Column (SLB5ms) | 3 | 25.039 | 25.040 | -0.1 |
| 5 | 17.748 | 17.747 | 0.1 |
| 12 | 10.014 | 10.013 | 0.0 |
| 20 | 7.337 | 7.337 | 0.0 |
| 8 | 12.997 | 12.995 | 0.1 |
| 10 | 11.246 | 11.245 | 0.1 |
| 16 | 8.381 | 8.382 | 0.0 |
| 50 % Phenyl Column (SPB50) | 3 | 21.780 | 21.783 | -0.2 |
| 5 | 15.873 | 15.868 | 0.3 |
| 12 | 9.362 | 9.363 | -0.1 |
| 20 | 7.033 | 7.033 | 0.0 |
| 8 | 11.907 | 11.905 | 0.1 |
| 10 | 10.419 | 10.420 | -0.1 |
| 16 | 7.947 | 7.948 | -0.1 |
| Wax Column (Supelco Wax) | 3 | 13.231 | 13.232 | 0.0 |
| 5 | 10.405 | 10.405 | 0.0 |
| 12 | 6.812 | 6.810 | 0.1 |
| 20 | 5.371 | 5.372 | 0.0 |
| 8 | 8.280 | 8.283 | -0.2 |
| 10 | 7.402 | 7.433 | -1.9 |
| 16 | 5.948 | 5.947 | 0.1 |
| dodecanol | 5 % Phenyl Column (SLB5ms) | 3 | 36.743 | 36.747 | -0.2 |
| 5 | 24.865 | 24.867 | -0.1 |
| 12 | 13.043 | 13.043 | 0.0 |
| 20 | 9.172 | 9.172 | 0.0 |
| 8 | 17.498 | 17.498 | 0.0 |
| 10 | 14.866 | 14.867 | 0.0 |
| 16 | 10.666 | 10.667 | -0.1 |
| 50 % Phenyl Column (SPB50) | 3 | 37.777 | 37.770 | 0.4 |
| 5 | 25.642 | 25.653 | -0.7 |
| 12 | 13.537 | 13.542 | -0.3 |
| 20 | 9.565 | 9.555 | 0.6 |
| 8 | 18.101 | 18.113 | -0.7 |
| 10 | 15.405 | 15.415 | -0.6 |
| 16 | 11.099 | 11.097 | 0.1 |
| Wax Column (Supelco Wax) | 3 | 42.413 | 42.410 | 0.2 |
| 5 | 28.357 | 28.358 | -0.1 |
| 12 | 14.548 | 14.548 | 0.0 |
| 20 | 10.082 | 10.082 | 0.0 |
| 8 | 19.721 | 19.725 | -0.2 |
| 10 | 16.667 | 16.662 | 0.3 |
| 16 | 11.801 | 11.802 | 0.0 |
| 2- dodecanone | 5 % Phenyl Column (SLB5ms) | 3 | 33.761 | 33.757 | 0.3 |
| 5 | 23.053 | 23.057 | -0.2 |
| 12 | 12.268 | 12.268 | 0.0 |
| 20 | 8.700 | 8.697 | 0.2 |
| 8 | 16.350 | 16.352 | -0.1 |
| 10 | 13.942 | 13.943 | -0.1 |
| 16 | 10.080 | 10.078 | 0.1 |
| 50 % Phenyl Column (SPB50) | 3 | 35.056 | 35.047 | 0.6 |
| 5 | 23.982 | 23.992 | -0.6 |
| 12 | 12.827 | 12.832 | -0.3 |
| 20 | 9.133 | 9.125 | 0.5 |
| 8 | 17.048 | 17.060 | -0.7 |
| 10 | 14.557 | 14.567 | -0.6 |
| 16 | 10.562 | 10.560 | 0.1 |
| Wax Column (Supelco Wax) | 3 | 33.366 | 33.365 | 0.1 |
| 5 | 22.936 | 22.935 | 0.1 |
| 12 | 12.304 | 12.303 | 0.0 |
| 20 | 8.745 | 8.747 | -0.1 |
| 8 | 16.342 | 16.343 | -0.1 |
| 10 | 13.967 | 13.962 | 0.3 |
| 16 | 10.123 | 10.125 | -0.1 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
| Table 3.   |   | 5 % Phenyl Column |   | Wax Column |
|   | Estimation Method | Estimated ΔH(To)(kJ·Mol-1) | Estimated ΔS(To)(J·K-1·Mol-1) | Estimated ΔCp (J·K-1·Mol-1) |   | Estimated ΔH(To)(kJ·Mol-1) | Estimated ΔS(To)(J·K-1·Mol-1) | Estimated ΔCp (J·K-1·Mol-1) |
| undecane | isothermal  | -47.34 | -73.41 | 83.80 |   | -36.71 | -56.75 | 75.94 |
|   | temperature programmed  | -47.30 | -74.11 | 81.41 |  | -37.80 | -61.81 | 70.33 |
|   | relative error | 0.1 | -1.0 | 2.9 |   | -3.0 | -8.9 | 7.4 |
|   |  |  |  |  |  |  |  |   |
| dodecane | isothermal  | -51.87 | -80.03 | 92.58 |   | -40.40 | -61.92 | 81.59 |
|   | temperature programmed  | -51.57 | -80.08 | 87.49 |  | -42.24 | -68.93 | 36.09 |
|   | relative error | 0.6 | -0.1 | 5.5 |   | -4.5 | -11.3 | 55.8 |
|   |  |  |  |  |  |  |  |   |
| tridecane | isothermal  | -56.18 | -86.12 | 98.56 |   | -44.10 | -67.10 | 87.42 |
|   | temperature programmed  | -55.73 | -85.77 | 91.90 |  | -45.41 | -72.46 | 31.92 |
|   | relative error | 0.8 | 0.4 | 6.8 |   | -3.0 | -8.0 | 63.5 |
|   |  |  |  |  |  |  |  |   |
| tetradecane | isothermal  | -60.42 | -92.08 | 104.00 |   | -47.78 | -72.27 | 92.83 |
|   | temperature programmed  | -59.31 | -90.33 | 101.77 |  | -48.48 | -75.89 | 63.92 |
|   | relative error | 1.8 | 1.9 | 2.1 |   | -1.5 | -5.0 | 31.1 |
|   |  |  |  |  |  |  |  |   |
| undecanone | isothermal  | -55.28 | -84.20 | 94.33 |   | -52.27 | -75.03 | 83.26 |
|   | temperature programmed  | -55.24 | -84.87 | 99.80 |  | -51.62 | -74.60 | 41.83 |
|   | relative error | 0.1 | -0.8 | -5.8 |   | 1.2 | 0.6 | 49.8 |
|   |  |  |  |  |  |  |  |   |
| dodecanone | isothermal  | -59.55 | -90.18 | 100.07 |   | -55.82 | -79.86 | 86.90 |
|   | temperature programmed  | -59.36 | -90.08 | 83.62 |  | -54.88 | -78.69 | 53.75 |
|   | relative error | 0.3 | 0.1 | 16.4 |   | 1.7 | 1.5 | 38.2 |
|   |  |  |  |  |  |  |  |   |
| tridecanone | isothermal  | -63.76 | -96.06 | 105.30 |   | -59.29 | -84.56 | 91.65 |
|   | temperature programmed  | -63.63 | -96.55 | 110.93 |  | -57.77 | -81.87 | 54.84 |
|   | relative error | 0.2 | -0.5 | -5.3 |   | 2.6 | 3.2 | 40.2 |
|   |  |  |  |  |  |  |  |   |
| undecanol | isothermal  | -58.70 | -89.04 | 98.38 |   | -64.33 | -95.05 | 110.57 |
|   | temperature programmed  | -59.05 | -90.73 | 108.95 |  | -62.01 | -90.38 | 62.92 |
|   | relative error | -0.6 | -1.9 | -10.7 |   | 3.6 | 4.9 | 43.1 |
|   |  |  |  |  |  |  |  |   |
| dodecanol | isothermal  | -62.94 | -94.95 | 103.67 |   | -67.81 | -99.73 | 114.57 |
|   | temperature programmed  | -63.45 | -97.09 | 118.34 |  | -65.41 | -94.94 | 74.06 |
|   | relative error | -0.8 | -2.3 | -14.1 |   | 3.5 | 4.8 | 35.4 |
|   |  |  |  |  |  |  |  |   |
| tridecanol | isothermal  | -67.31 | -101.03 | 110.92 |   | -71.20 | -104.60 | 119.20 |
|   | temperature programmed  | -68.22 | -104.32 | 133.31 |  | -68.62 | -99.03 | 80.96 |
|   | relative error | -1.4 | -3.3 | -20.2 |   | 3.6 | 5.3 | 32.1 |
|   |  |  |  |  |  |  |  |   |
| tetradecanol | isothermal  |   |   |   |   | -75.42 | -110.49 | 130.14 |
|   | temperature programmed  | -71.94 | -109.01 | 130.32 |  | -71.90 | -103.36 | 88.75 |
|   | relative error |   |   |   |   | 4.7 | 6.5 | 31.8 |

Table 4.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Temperature Ramp°C·min-1 | Compound | Primary Retention Time (s) | Estimated Retention Time (s) | Difference (s) | Secondary Retention Time (s) | Estimated Retention Time (s) | Difference (s) |
| 3 | Undecane | 943.5 | 933.2 | -10.3 | 1.0 | 1.0 | 0.0 |
| Dodecane | 1219.5 | 1215.2 | -4.3 | 1.0 | 1.0 | 0.0 |
| Tridecane | 1486.5 | 1488.4 | 1.9 | 1.1 | 1.0 | 0.0 |
| Tetradecane | 1740.0 | 1744.8 | 4.8 | 1.1 | 1.1 | 0.0 |
| Undecanone | 1473.0 | 1466.5 | -6.5 | 4.1 | 4.1 | 0.0 |
| Dodecanone | 1729.5 | 1728.1 | -1.4 | 4.0 | 3.9 | -0.1 |
| Tridecanone | 1972.5 | 1975.4 | 2.9 | 3.8 | 3.8 | 0.0 |
| Undecanol | 1681.5 | 1678.3 | -3.2 | 9.5 | 9.4 | -0.1 |
| Dodecanol | 1924.5 | 1929.3 | 4.8 | 8.6 | 8.4 | -0.2 |
| Tridecanol | 2157.0 | 2171.6 | 14.6 | 7.8 | 7.5 | -0.3 |
| Tetradenol | 2376.0 | 2394.5 | 18.5 | 7.2 | 6.9 | -0.3 |
| 5 | Undecane | 709.5 | 701.2 | -8.3 | 0.8 | 0.8 | 0.0 |
| Dodecane | 880.5 | 876.3 | -4.2 | 0.8 | 0.8 | 0.0 |
| Tridecane | 1044.0 | 1044.0 | 0.0 | 0.8 | 0.8 | 0.0 |
| Tetradecane | 1198.5 | 1201.0 | 2.5 | 0.8 | 0.8 | 0.0 |
| Undecanone | 1036.5 | 1030.9 | -5.6 | 2.7 | 2.7 | 0.0 |
| Dodecanone | 1192.5 | 1190.8 | -1.7 | 2.6 | 2.6 | 0.0 |
| Tridecanone | 1339.5 | 1341.3 | 1.8 | 2.6 | 2.5 | -0.1 |
| Undecanol | 1161.0 | 1159.6 | -1.4 | 5.7 | 5.7 | 0.0 |
| Dodecanol | 1309.5 | 1312.4 | 2.9 | 5.2 | 5.1 | -0.1 |
| Tridecanol | 1452.0 | 1459.7 | 7.7 | 4.8 | 4.6 | -0.2 |
| Tetradenol | 1584.0 | 1595.6 | 11.6 | 4.5 | 4.3 | -0.2 |
| 8 | Undecane | 543.0 | 537.0 | -6.0 | 0.7 | 0.7 | 0.0 |
| Dodecane | 652.5 | 649.3 | -3.2 | 0.7 | 0.7 | 0.0 |
| Tridecane | 756.0 | 756.0 | 0.0 | 0.7 | 0.7 | 0.0 |
| Tetradecane | 855.0 | 855.9 | 0.9 | 0.7 | 0.7 | 0.0 |
| Undecanone | 751.5 | 748.0 | -3.5 | 1.9 | 1.9 | 0.0 |
| Dodecanone | 850.5 | 849.6 | -0.9 | 1.8 | 1.8 | 0.0 |
| Tridecanone | 945.0 | 944.9 | -0.1 | 1.8 | 1.8 | 0.0 |
| Undecanol | 831.0 | 829.3 | -1.7 | 3.6 | 3.6 | 0.0 |
| Dodecanol | 925.5 | 926.2 | 0.7 | 3.3 | 3.3 | 0.0 |
| Tridecanol | 1015.5 | 1019.5 | 4.0 | 3.0 | 3.0 | 0.0 |
| Tetradenol | 1099.5 | 1105.6 | 6.1 | 2.9 | 2.8 | -0.1 |
| 10 | Undecane | 478.5 | 473.4 | -5.1 | 0.6 | 0.6 | 0.0 |
| Dodecane | 567.0 | 564.3 | -2.7 | 0.6 | 0.6 | 0.0 |
| Tridecane | 651.0 | 650.4 | -0.6 | 0.6 | 0.6 | 0.0 |
| Tetradecane | 730.5 | 730.9 | 0.4 | 0.6 | 0.6 | 0.0 |
| Undecanone | 648.0 | 644.1 | -3.9 | 1.6 | 1.6 | 0.0 |
| Dodecanone | 729.0 | 726.0 | -3.0 | 1.5 | 1.5 | 0.0 |
| Tridecanone | 804.0 | 802.7 | -1.3 | 1.5 | 1.5 | 0.0 |
| Undecanol | 711.0 | 709.5 | -1.5 | 2.9 | 2.9 | 0.0 |
| Dodecanol | 787.5 | 787.5 | 0.0 | 2.6 | 2.6 | 0.0 |
| Tridecanol | 859.5 | 862.6 | 3.1 | 2.4 | 2.4 | 0.0 |
| Tetradenol | 927.0 | 932.0 | 5.0 | 2.3 | 2.3 | 0.0 |
| 12 | Undecane | 432.0 | 427.5 | -4.5 | 0.6 | 0.6 | 0.0 |
| Dodecane | 507.0 | 503.9 | -3.1 | 0.6 | 0.6 | 0.0 |
| Tridecane | 577.5 | 576.2 | -1.3 | 0.6 | 0.6 | 0.0 |
| Tetradecane | 643.5 | 643.7 | 0.2 | 0.6 | 0.6 | 0.0 |
| Undecanone | 574.5 | 571.0 | -3.5 | 1.4 | 1.4 | 0.0 |
| Dodecanone | 640.5 | 639.7 | -0.8 | 1.3 | 1.3 | 0.0 |
| Tridecanone | 705.0 | 704.0 | -1.0 | 1.3 | 1.3 | 0.0 |
| Undecanol | 627.0 | 625.7 | -1.3 | 2.4 | 2.4 | 0.0 |
| Dodecanol | 691.5 | 691.1 | -0.4 | 2.2 | 2.2 | 0.0 |
| Tridecanol | 751.5 | 754.1 | 2.6 | 2.1 | 2.1 | 0.0 |
| Tetradenol | 808.5 | 812.2 | 3.7 | 1.9 | 1.9 | 0.0 |
| 16 | Undecane | 369.0 | 365.2 | -3.8 | 0.5 | 0.5 | 0.0 |
| Dodecane | 426.0 | 423.2 | -2.8 | 0.5 | 0.5 | 0.0 |
| Tridecane | 480.0 | 478.0 | -2.0 | 0.5 | 0.5 | 0.0 |
| Tetradecane | 529.5 | 529.0 | -0.5 | 0.5 | 0.6 | 0.0 |
| Undecanone | 477.0 | 474.2 | -2.8 | 1.1 | 1.1 | 0.0 |
| Dodecanone | 528.0 | 526.2 | -1.8 | 1.1 | 1.1 | 0.0 |
| Tridecanone | 576.0 | 574.8 | -1.2 | 1.0 | 1.1 | 0.0 |
| Undecanol | 517.5 | 515.5 | -2.0 | 1.8 | 1.8 | 0.1 |
| Dodecanol | 565.5 | 565.0 | -0.5 | 1.7 | 1.7 | 0.0 |
| Tridecanol | 612.0 | 612.7 | 0.7 | 1.5 | 1.6 | 0.0 |
| Tetradenol | 654.0 | 656.6 | 2.6 | 1.5 | 1.5 | 0.0 |
| 20 | Undecane | 327.0 | 324.2 | -2.8 | 0.5 | 0.5 | 0.0 |
| Dodecane | 373.5 | 371.2 | -2.3 | 0.5 | 0.5 | 0.0 |
| Tridecane | 417.0 | 415.3 | -1.7 | 0.5 | 0.5 | 0.0 |
| Tetradecane | 457.5 | 456.4 | -1.1 | 0.5 | 0.5 | 0.0 |
| Undecanone | 415.5 | 412.4 | -3.1 | 0.9 | 1.0 | 0.0 |
| Dodecanone | 456.0 | 454.3 | -1.7 | 0.9 | 0.9 | 0.0 |
| Tridecanone | 495.0 | 493.5 | -1.5 | 0.9 | 0.9 | 0.1 |
| Undecanol | 447.0 | 445.6 | -1.4 | 1.4 | 1.5 | 0.1 |
| Dodecanol | 486.0 | 485.5 | -0.5 | 1.3 | 1.4 | 0.0 |
| Tridecanol | 523.5 | 523.9 | 0.4 | 1.3 | 1.3 | 0.1 |
| Tetradenol | 558.0 | 559.3 | 1.3 | 1.2 | 1.2 | 0.0 |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |

Figure 1.



Figure 2.



Figure 3.



Figure 4.



1. [] F. Aldaeus, Y. Thewalim. A. Colmsjö. *Anal. Bioanal. Chem*. 389 (2007) 941 [↑](#endnote-ref-1)
2. [] Y.F. Guan, Z. Peng, L.M. Zhou. *J. High Res. Chromatogr.* Vol. 15 (1992) p. 18-23 [↑](#endnote-ref-2)
3. [] J. Harynuk, T. Gorecki. *American Laboratory*. Vol. 39, Issue 4 (2007) p. 36-39 [↑](#endnote-ref-3)
4. [] J. Dalluge, et. al. *J. Chromatogr. A*. 974. (2002) p. 169-184 [↑](#endnote-ref-4)
5. [] J. Beens, R. Tijssen, J. Blomberg. *J. Chromatogr. A*. 822 (1998) 233-251 [↑](#endnote-ref-5)
6. [] R.J. Western, P.J. Marriott. *J. Sep. Sci*. 25 (2002) 832–838 [↑](#endnote-ref-6)
7. [] C. Vendeuvre, F. Bertoncini, D. Thiebaut, M. Martin, M. Hennion. *J. Sep. Sci*. 28 (2005) 1129-1136 [↑](#endnote-ref-7)
8. [] T Pang , S Zhu, X Lu, G.W. Xu (2007) J Sep Sci 30:868–874 [↑](#endnote-ref-8)
9. [] J.S. Arey, R.K. Nelson, L. Xu, C.M. Reddy. *Anal. Chem*. 77 (2005) 7172-7182 [↑](#endnote-ref-9)
10. [] J.V. Seeley, E.M. Libby, K.A. Hill Edwards, S.K. Seeley. *J. Chromatogr. A*. 1216 (2009) 1650-1657 [↑](#endnote-ref-10)
11. [] S. Bieri, P.J. Marriott. *Anal. Chem.* 80 (2008) 760-768 [↑](#endnote-ref-11)
12. [] J. Dimandja, T. Leavell, F.L. Dorman, D.W. Armstrong, *Characterization of GC×GC column sets with bidimensional retention normalization* Presented at Pacifichem 2010, International Chemical Congress of Pacific Basin Societies, Honolulu, HI, United States, December 15-20, 2010 (2010), ANYL-142. [↑](#endnote-ref-12)
13. [] J.V. Seeley, S.K. Seeley. *J. Chromatogr. A*. 1172 (2007) 72-83 [↑](#endnote-ref-13)
14. [] Y.P. Zhao, J. Zhang, B. Wang, S. Ho Kim, A. Fang, B. Bogdanov, Z. Zhou, C. McClain, X. Zhang. *J. Chromatogr. A* 1218 (2011) 2577-2583 [↑](#endnote-ref-14)
15. [] C. von Muehlen, P.J. Marriott. *Anal. Bioanal. Chem.* 401 (2011) 2351-2360 [↑](#endnote-ref-15)
16. [] S. Zhu, X. Lu, Y. Qiu, T. Pang, H. Kong, C. Wu, G. Xu. J. Chromatogr. A. 1150 (2007) 28-36 [↑](#endnote-ref-16)
17. [] X. Lu, H. Kong, H. Li, C. Ma, J. Tian, G. Xu. J. Chromatogr. A. 1086 (2005) 175-184 [↑](#endnote-ref-17)
18. [] Y. Thewalim, I.Sadiktsis, A Colmsjö *J. Chromatogr. A.* 1218 (2011) 5305-5310 [↑](#endnote-ref-18)
19. [] F.L. Dorman, P.D. Schettler, L.A. Vogt, J.W. Cochran. *J. Chromatogr. A*. 1186 (2008) 196-201 [↑](#endnote-ref-19)
20. [] S. Zhu, S. He, D.R. Worton, A.H. Goldstein. *J. Chromatogr. A.* 1233 (2012) 147-151 [↑](#endnote-ref-20)
21. [] R.C. Castells, E.L. Arancibia, A.M. Nardillo. *J. Chromatogr.* 504 (1990) 45-53 [↑](#endnote-ref-21)
22. [] F.R. Gonzalez. AM Nardillo. *J. Chromatogr. A.* 842 (1999) 29-49 [↑](#endnote-ref-22)
23. [] T.M. McGinitie, J.J. Harynuk. *J. Chromatogr. A.* 1255 (2012) 184-189 [↑](#endnote-ref-23)
24. [] T.M. McGinitie, J.J. Harynuk. *J. Sep. Sci.* 35 (2012) 2228-2232 [↑](#endnote-ref-24)
25. [] B. Karolat, J.J. Harynuk. *J. Chromatogr. A* 1217(2010) 4862-4867 [↑](#endnote-ref-25)
26. [] M. Gorgenyi and K. Heberger. *J. Chromatogr. Sci.,* 37 (1999) 11-16 [↑](#endnote-ref-26)
27. [] K. Heberger and M. Gorgenyi. *J. Chromatogr. Sci.*, 39 (2001) 113-120 [↑](#endnote-ref-27)
28. [] K. Heberger, M. Gorgenyi and T. Kowalska. *J. Chromatogr. A*, 973 (2002) 135-142 [↑](#endnote-ref-28)
29. [] M. Gorgenyi, K. Heberger. *J. Chromatogr. A*, 985 (2003) 11-19

[30] H. Snijders, H.G. Janssen, C. Cramers, J. Chromatogr. A 718 (1995) 339.

[31] J.C. Lagarias, J.A. Reeds, M.H. Wright, P.E. Wright, Convergence properties of the

Nelder–Mead simplex method in low dimensions, SIAM J. Optim. 9 (1) (1998)

112.

[32] Comprehensive Chemometrics, Vol.1, p. 555.

[33] N.J. Micyus, S.K. Seeley, J.V. Seeley, J. Chromatogr. A 1086 (2005) 171 [↑](#endnote-ref-29)