A Standardized Method for the Calibration of Thermodynamic Data for the Prediction of Gas Chromatographic Retention Times

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**Abstract**

A new method for normalizing thermodynamic data to be used in the prediction of analyte retention times is presented. The method allows thermodynamic data collected on one column to be used in making predictions across columns of the same stationary phase but with varying geometries. This normalization is essential as slight variances in the column inner diameter and stationary phase film thickness between columns or as a column ages will adversely affect the accuracy of predictions. The normalization technique uses a Grob standard mixture along with a Nelder-Mead simplex algorithm and a previously developed model of GC retention times based on a three-parameter thermodynamic model to estimate both inner diameter and stationary phase film thickness. The normalization method is highly successful with the predicted retention time for a set of alkanes, ketones and alcohols having an average error of 1.6 seconds across three columns.

**1. Introduction**

Predictive modelling of gas chromatographic separations is valuable both for the optimization of separation conditions [[[1]](#endnote-1)] and in the determination of unknown peaks in chromatograms [[[2]](#endnote-2)]. The increased interest in comprehensive multidimensional gas chromatography (GC×GC) creates a need for improved tools to aid in optimization and peak identification.

Tools for computer-based optimization of GC×GC separations are required because the true optimization of these separations across the multitude of possible stationary phase and geometry combinations available is time consuming for even experienced users. This arises from the interdependence of the separation conditions in the two dimensions of the GC×GC experiment. Any 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)]. Accurate predictive modelling tools would prove extremely useful for the rapid development of both GC×GC, and to a lesser extent GC methods.

Predictive modelling also aids in the determination of unknown peaks within chromatographic separations, particularly when used in conjunction with mass spectrometry. Retention data adds another layer of information and confidence to compound identification, particularly for compounds such as structural isomers that would otherwise be difficult or outright impossible to distinguish by mass spectrometry alone. The use of retention data as supplemental information for compound identification has already been demonstrated through the use of linear retention indices to improve the accuracy of NIST library hit tables [[[4]](#endnote-4)]. Retention indices (RI) form a popular basis for retention modelling techniques due to the ease with which data can be collected and used [[[5]](#endnote-5)]. Linear retention index (LRI) [[[6]](#endnote-6)], a variation of the Kovats retention index is one of the more popular forms of retention index as data can be collected in a single temperature-programmed run. As such the LRI is often offered as supporting data when identifying unknown compounds, with the current version of the NIST mass spectral library offering RI values for ~71,000 compounds. A recent review by Zellner et. al. [[[7]](#endnote-7)] highlights the widespread usage of LRI.

While RI data are fast and easy to use, RI values have a dependence on the experimental conditions which leads to variations in the reported RI values for both inter- and intra-laboratory studies [4]. For the roughly 71,000 compounds listed as having RI values in the NIST database there are ~350,000 RI values listed for those compounds, the bulk of which are for standard non-polar stationary phases (100% polydimethylsiloxane or poly(95%dimethyl- 5%diphenylsiloxane)). If retention data are used to assist the determination of structurally similar compounds any variation in RI values could lead to inconclusive results or prove useful only for a select set of experimental conditions.

Within the context of the GC×GC experiment, the application of RI is relatively straightforward for the first separation dimension (1D), but it is not so for the second dimension (2D). Isovolatility curves can be generated from a series of alkanes to estimate 2RI (second-dimension retention index), but this is technically difficult on commercial instruments and can be time consuming [[[8]](#endnote-8)]. It has also been suggested that alkanes are not an appropriate series of standard molecules for second dimension of a GC×GC experiment [[[9]](#endnote-9)]. Nevertheless, RI-based approaches remain popular with several new studies conducted within the last few years [[[10]](#endnote-10), [[11]](#endnote-11)] and a recent review by von Muehlen and Marriott [5].

Our research has focused on exploiting predictive models based upon thermodynamic data. This approach has a significant advantage over RI methods, namely accuracy is maintained over a range of instrumental conditions [[[12]](#endnote-12)], and the errors when converted to RI units are typically a fraction of an RI unit [12]. Various studies have been conducted on the use of thermodynamic models for a variety of analytes [[[13]](#endnote-13)-,[[14]](#endnote-14),[[15]](#endnote-15),[[16]](#endnote-16),[[17]](#endnote-17),[[18]](#endnote-18)]. Additionally, for GC×GC methods, thermodynamic models perform equally well in the first and second dimensions [[[19]](#endnote-19)]. Thus, unlike the RI, they are inherently suitable for the prediction of GC×GC separations.

The two downsides to the thermodynamic approach have historically been the time required to collect the data and a method to account for variability in column geometry. These two hurdles have kept thermodynamic approaches academically interesting but of little practical value. Recent work in our laboratory [[[20]](#endnote-20)] has changed this. Our algorithm has allowed us to reduce the instrument time required to obtain thermodynamic data for a set of ten compounds from 41.6 hours to 2.0 hours and thus set the stage for the development of a library of thermodynamic data that can be used for predictive models, much like those in place for RI. Briefly, nonlinear fitting techniques are used 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* directly from experimental data from a series of temperature-programmed experiments.

To apply the approach, the column’s length, film thickness, and inner diameter are required, bringing the second challenge for applying thermodynamic tools in GC. The vendor-supplied nominal values for column geometry are not precise enough to permit the translation of thermodynamic parameters measured on one column to another column. Small variations in the actual film thickness and column inner diameter result in large errors between the predicted and experimental retention times.

A method to normalize thermodynamic data and account for variation in column geometry in order to obtain accurate predictions across multiple columns is required. To be practically useful, the method must fulfill several requirements: the experimentation required to normalize the column must be rapid and compatible with standard commercial GC equipment. The chemicals required should also be both universally available and inexpensive. Herein, we introduce and validate an approach that meets the above criteria and enables the reliable use of thermodynamic data across multiple columns.

**2. Experimental**

***2.1 Chemicals***

A Grob mix (Sigma-Aldrich #47304; Oakville, Ontario) consisting of 2,3-butanediol, decane, dicyclohexlamine, 2,6-dimethylaniline, 2,6-dimethylphenol, 2-ethylhexanoic acid, methyl decanoate, methyl laurate, methyl undecanoate, nonanal, 1-octanol, and undecane was used to normalize the column geometry. The compounds are of varying concentration ranging from 290 – 530 µg/mL (Sigma-Aldrich).

A second mixture comprised of alkanes, alcohols and ketones was used for the validation of the normalization procedure. 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 1-undecanol, 1-dodecanol and 1-tridecanol 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 Bruker 461 GC (Bruker, Milton, ON) equipped with a split/splitless injector and flame ionization detector was used for all experiments. 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 100 Hz. 99.999 % Helium (Praxair, Edmonton, AB) was used as a carrier gas. All columns used for the study were of a 5 % phenyl substituted polydimethylsiloxane stationary phase, specifically SLB5ms (Supleco, Bellefonte, PA). The dimensions of each column used are listed in Table 1.

Except where mentioned, all separations were performed under constant flow conditions. For all 0.25 mm ID columns, the carrier gas flow was set to 1.0 mL·min-1 and for the 0.1 mm ID column, the carrier gas flow rate was set at 0.29 mL·min-1. The separations were initialized at 50 °C, with the oven temperature programmed at ramp rates of 5, 8, 10, 12, 16, and 20 °C·min-1 to 250 °C. The column inner diameter, column film thickness, thermodynamic estimations, and GC retention time predictions were calculated using custom scripts written in MATLAB 7.10.0 (The Mathworks, Natick, MA).

**3. Results and Discussion**

**3.1 *Normalization Techniques***

Normalization of the column is carried out in three steps; first the column length must be determined, followed by the determination of the column inner diameter, and finally the estimation for the stationary phase film thickness. A 30 m × 0.25 mm; 0.25 µm film column was chosen to serve as a reference column for this study. This column was chosen as the reference column due to historical usage of this size of column within our thermodynamic studies and because these dimensions are among the most popular commercially.

*3.1.1 Column Length*

To determine column length, the reference column was unwound from the column cage and measured down to the nearest cm. This was done to ensure a highly accurate measurement of the internal diameter as the calculation of internal diameter is dependent upon the column length. Subsequent column lengths were estimated by measuring the diameter of the column coil and counting loops on the column cage. This estimation if performed on a well-wound column is typically able to provide estimates with an error of ±10 cm. If greater precision is required, then a new column can be unwound and measured directly.

*3.1.2 Estimation of Inner Diameter*

The column inner diameter is estimated based on fluid dynamics equations for a compressible fluid where the radius of the column, *r* (cm) is given by Equation 1 [[[21]](#endnote-21)].

 (1)

Where is the experimental average carrier gas velocity in cm·s-1 determined by the taking the length of the column *L* and dividing by the retention time of methane, *η* is the viscosity in poise (g·cm-1·s-1) of the carrier gas at the experimental temperature T, in Kelvin (K) (Equation 2 for He and Equation 3 for H2) [[[22]](#endnote-22)]. *Pi* and *Po* are the pressures in dynes (g·cm·s-1) at the column inlet and outlet, respectively.

 (2)

 (3)

The column radius was estimated based on triplicate injections of methane at each of three temperatures: 50 °C, 100 °C, and 150 °C. For each temperature the instrument flow was set to an average linear velocity of ~30 cm·s-1. The average result from these nine estimates of inner diameter was then used as the actual internal diameter for this column.

*3.1.3 Stationary Phase Film Thickness*

Obtaining an accurate value for the stationary phase film thickness is difficult to accomplish experimentally. The physical thickness of the stationary phase can be measured via scanning electron microscopy; however, even the best-manufactured column is subject to non-uniformity in the film thickness along its length. Often the film thickness will change even a few cm along the column, and in a given segment of column, the thickness can vary depending on the position around the cross section of the column [[[23]](#endnote-23)]. Thus estimation of the film thickness by SEM requires multiple measurements along the length of the column and thus the ultimate destruction of the column. Obviously the need to sacrifice a column and the extensive time required to perform SEM measurements makes this a poor method to determine the stationary phase film thickness in practice.

In this approach, a series of probe molecules is used to compare the film thickness of a new column to a ‘reference column’. While this technique does not result in the true physical dimension of the film thickness of a particular column, it provides a relative comparison that permits normalization of thermodynamic data between columns. A similar concept which compared the elution temperatures of a probe molecule to determine the film thickness of different columns was originally proposed by Grob [[[24]](#endnote-24)]. It is fitting then that the probe molecules chosen here for calibrating the film thickness are the Grob Mix compounds. They are widely available as a ready-made, inexpensive mixture covering a range of chemistries, and thus should perform well across a range of column chemistries.

To determine the film thickness, a series of temperature-programmed separations with ramp rates of 5, 8, 10, 12, 16 and 20 °C·min-1 were performed using the Grob standard. 2,3-butanediol, 2-Ethylhexanoic acid, and dicyclohexylamine were omitted from subsequent calculations due to their poor chromatographic performance on the 5% phenyl stationary phase. The identities of all compounds were verified via mass spectrometry. The thermodynamic parameters for all components of the Grob Mix on the reference column were obtained using the non-linear optimization techniques described previously [20]. In these thermodynamic calculations the length and inner diameter of the column were determined as per the above protocols while the nominal value was assumed for the stationary phase film thickness. The resulting thermodynamic estimations for the nine test compounds are shown in Table 2.

Subsequent determinations of the stationary phase film thickness for a particular column rely on the thermodynamic values determined for the Grob Mix using the ‘reference column’. To determine the film thickness of the three other columns, the Grob Mix was run on the remaining three columns using the same set of temperature programs as the reference column and the absolute retention times for each analyte were collected.

The retention data for the Grob Mix on the new column are then used in conjunction with the previously estimated thermodynamic parameters for the compounds on the ‘reference column’ and the chromatographic conditions to calculate the average effective film thickness the column. This is performed by a custom-written script in Matlab that relies on a Neadler-Mead simplex algorithm to estimate a value for the film thickness that is consistent with both the collected experimental data and the previously estimated thermodynamic parameters.

The script begins by using the nominal value for the film thickness and the estimated thermodynamic values to predict the retention time for each analyte under every temperature ramp using a time summation model developed previously [19]. The algorithm proceeds to change the film thickness to minimize the error between the predicted and experimental retention times for all compounds simultaneously, thus providing an estimate for the column stationary phase film thickness.

The columns for the study were chosen to span a range of geometries and demonstrate that the normalization method was effective regardless of the geometry or age of the column. A new, unused 30 m × 0.25 mm; 0.25 μm film column was chosen as the reference column to avoid effects due to column degradation. A column of nominal length 30 m × 0.25 mm; 0.5 μm film was chosen to evaluate the effect of film thickness on the normalization and another new 15 m × 0.1 mm; 0.1 μm film column was used to investigate if normalization would be effective for a column of radically different dimensions but of the same stationary phase. Finally a column of the same stationary phase and dimensions as the reference column (30 m × 0.25 mm; 0.25 µm film) that had been used extensively over a period of four years was used to investigate the use of the normalization method to recalibrate an aged, partially degraded column.

Each column was normalized to the reference column using the method described above. The experimentally determined column diameter and film thicknesses for each column are listed in Table 1. The experimentally determined column inner diameters agree closely with the nominal values with an average error of 2.0 %. The stationary phase film thickness shows a larger discrepancy between the nominal and experimentally determined values with an average error of 11.8 %; however, both the error in the column inner diameter and film thickness are typical of the variation observed when using SEM to observe the column directly [23, [[25]](#endnote-25)].

To validate the results of the normalization, a test mixture of alkanes, ketones and alcohols was prepared and the thermodynamic parameters *ΔH(T0)*, *ΔS(T0)*, and *ΔCp*were gathered for each analyte based on experimental data obtained using the reference column. Subsequently, the test mixture was separated on each of the other columns using temperature programs of 5, 8, 10, 12, 16, and 20 °C·min-1. The retention times for each analyte were predicted using the thermodynamic prediction model described previously [20] and the predicted and experimental results compared. Table 3 presents the absolute error between the predicted and experimental results of each test compound across all four columns. The retention times for all compounds were predicted on the reference column to compare the relative success of the normalization on the other columns. The largest absolute error for the reference column was 1.49 s while the average absolute error for all compounds on the reference column was 0.36 s. In comparison the, 30 m × 0.25 mm; 0.5 μm film column had an average error of 2.1 s, the 15 m × 0.1 mm; 0.1 μm film column 1.5 s, and the old 30 m × 0.25 mm; 0.25 μm film column had an average error of 1.1 s. The largest error across all compounds and columns was for tridecanol on the 15 m column at 6.4 s.

Using undecanone as an example we can compare these results to those found using LRI, the LRI value reported for undecanone using flavornet is 1296 [[[26]](#endnote-26)], however other sources place the LRI value at 1294 [[[27]](#endnote-27)]. This variation is typical when using LRI and so for this comparison we will assume that a ‘true’ LRI value any experimental value would optimistically fall within ±2 LRI units of the measured value. Furthermore between our 5°C·min-1 and 20°C·min-1 experiments we found a difference of 3 RI units (1293-1296). If we convert each LRI unit into a measure of time, the associated error for all columns given ± 2 RI values would be ± 3.2 s, an order of magnitude larger than the error than our reference column, and larger than any of the errors observed for this molecule across all of the columns in the study.

To demonstrate the need for normalization, the retention time predictions were also made using the nominal column inner diameters and film thicknesses. Without the normalization the average error for the each column (30 m, 15 m, and 30 m old) increased to 34.1, 9.9, and 7.9 s, respectively. The large increase in errors when using the nominal dimensions highlights the importance of column normalization if attempting to make retention time predictions based on thermodynamic models.

**4. Conclusions**

We have demonstrated an approach to column normalization which permits thermodynamic-based models of retention to account for changes in column inner diameter and film thickness, including variability during the manufacturing process and degradation of stationary phase that occurs as a column ages. Thus, thermodynamic parameters collected on one column may be translated to another column of the same stationary phase chemistry and used to produce accurate predictions of retention time.

The calibration of a new column is reasonably fast, and requires inexpensive calibration standards. Work is currently underway to validate our previously presented method for obtaining thermodynamic parameters and this method for column normalization across multiple laboratories with multiple column chemistries and a more extensive list of analytes.

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**6. References:**

Table Captions

Table 1. Measured values for column length, and experimentally determined column inner diameter and the calculated film thickness for all columns used.

Table 2. Estimated values for *ΔH(T0)*, *ΔS(T0)*, and *ΔCp* for the Grob test mixture compounds used in the normalization procedure.

Table 3. Average absolute error between the predicted and actual retention time for each test analyte across all temperature ramps, on each column used in the study.

Table 1.

|  |  |  |  |
| --- | --- | --- | --- |
| Column  | Determined Length (m) | Determined Inner Diameter (mm) | Estimated Average Film Thickness (µm) |
|   |  |  |   |
| 30m × 0.25 mm × 0.25 µm (reference) | 29.99 | 0.248 | 0.250 |
|   |  |  |   |
| 30m × 0.25 mm × 0.50 µm | 31.66 | 0.244 | 0.567 |
|   |  |  |   |
| 15m × 0.1 mm × 0.1 µm | 16.40 | 0.103 | 0.121 |
|   |  |  |   |
| 30m × 0.25 mm × 0.25 µm (>4 years of use) | 29.10 | 0.254 | 0.253 |

Table 2.

|  |  |  |  |
| --- | --- | --- | --- |
| Compound Name | Estimated ΔH(To)(kJ·Mol-1) | Estimated ΔS(To)(J·K-1·Mol-1) | Estimated ΔCP (J·K-1·Mol-1) |
| Decane | -43.94 | -69.57 | 11.51 |
| 1-Octanol | -47.69 | -75.66 | 31.99 |
| Undecane | -48.02 | -74.90 | 26.22 |
| Nonanal | -47.69 | -73.70 | 23.39 |
| 2,6-Dimethylphenol | -47.53 | -73.17 | 109.60 |
| 2-Ethylhexanoic acid | -49.83 | -79.17 | 5.97 |
| 2,6-Dimethylaniline | -47.40 | -69.35 | 39.46 |
| C10 acid methyl ester | -57.35 | -87.61 | 58.77 |
| Dicyclohexylamine | -56.09 | -79.39 | 45.16 |
| C11 acid methyl ester | -59.97 | -89.28 | 41.88 |
| C12 acid methyl ester | -65.36 | -98.18 | 74.80 |

Table 3.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound Name | Average Absolute Error (s) (reference column) | Average Absolute Error (s) (30 × 0.25 × 0.5 ) | Average Absolute Error (s) (15 × 0.10 × 0.10 ) | Average Absolute Error (s) (30 × 0.25 × 0.25 ) |
| undecane | 0.4 | 2.0 | 1.2 | 1.1 |
| dodecane | 0.4 | 2.3 | 1.3 | 1.1 |
| tridecane | 0.6 | 2.3 | 1.1 | 1.2 |
| tetradecane | 0.2 | 2.0 | 0.8 | 1.1 |
| 2-undecanone | 0.2 | 2.2 | 0.8 | 1.2 |
| 2-dodecanone | 0.2 | 2.1 | 0.6 | 1.1 |
| 2-tridecanone | 0.3 | 2.0 | 2.4 | 1.1 |
| 1-undecanol | 0.8 | 2.3 | 0.4 | 1.0 |
| 1-dodecanol | 0.3 | 2.0 | 2.1 | 1.1 |
| 1-tridecanol | 0.2 | 1.6 | 4.7 | 1.2 |

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