

Application for Validation of Compound Identification in GC×GC Using Retention Index Based

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INTRODUCTION & AIM

Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful technique for separating, identifying, and quantifying volatile and semi-volatile compounds in complex samples. Typically, mass spectrometry (MS) is used for peak identification in GC×GC, but relying solely on MS library comparison can have limitations, especially for isomers with similar mass spectra. Additionally, optimizing the separation conditions for improved resolution in GC×GC can be challenging.

To enhance the peak identification, GC retention database such as that obtained from Gibbs energy additivity [4], linear solvation energy relationship (LSER) [2] and Kovats and van den Dool relationship [5] could be taken into account. A desirable goal is to establish approach for simulation of retention times in first and second dimensional separations (1t_R and 2t_R) for a compound of interest in GC×GC result in order to confirm the peak identity obtained from the MS library match. 1t_R and 2t_R are related to properties of each compound leading to different interactions, e.g., dispersity-related, dipolarity-type, hydrogen bond and dispersion/cavity formation, with stationary phase. However, prediction of t_R from the thermodynamic constants has not been widely applied due to the limited amount of database and the complexity in database construction (e.g., prediction of 10 compounds on 10 types of columns under a certain condition requiring up to 100 sets of the thermodynamic constants), LSER method is thus more suitable for bulk analysis systems. Apart from these, Kovats and van den Dool relationship were used for retention index calculation which has been the most widely used database for comparison of retention order within among different research groups and to support peak identification with MS library.

This research will illustrate the capability of computational program to predict peak positions (1t_R and 2t_R) and peak intensity from I and improve identification and experimental design of GC×GC with gradient temperature elution.

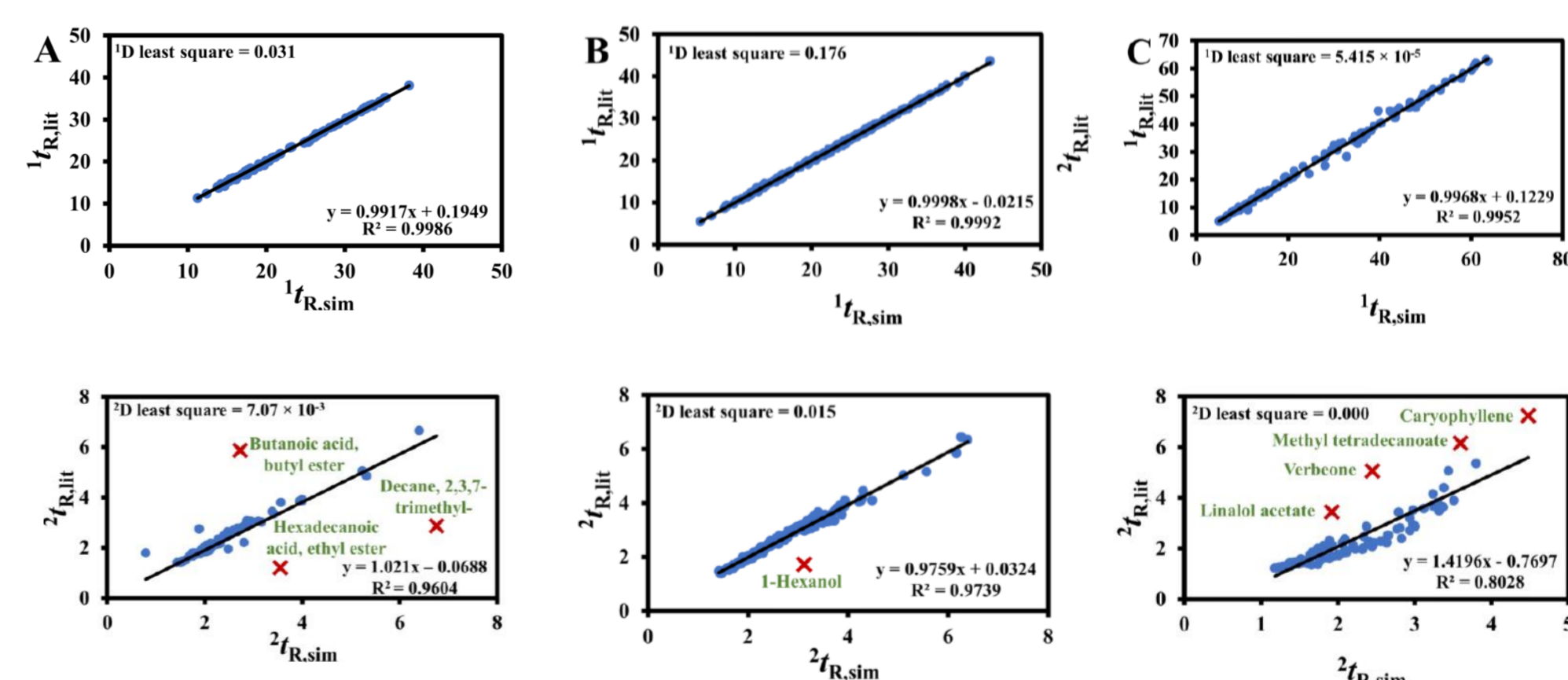
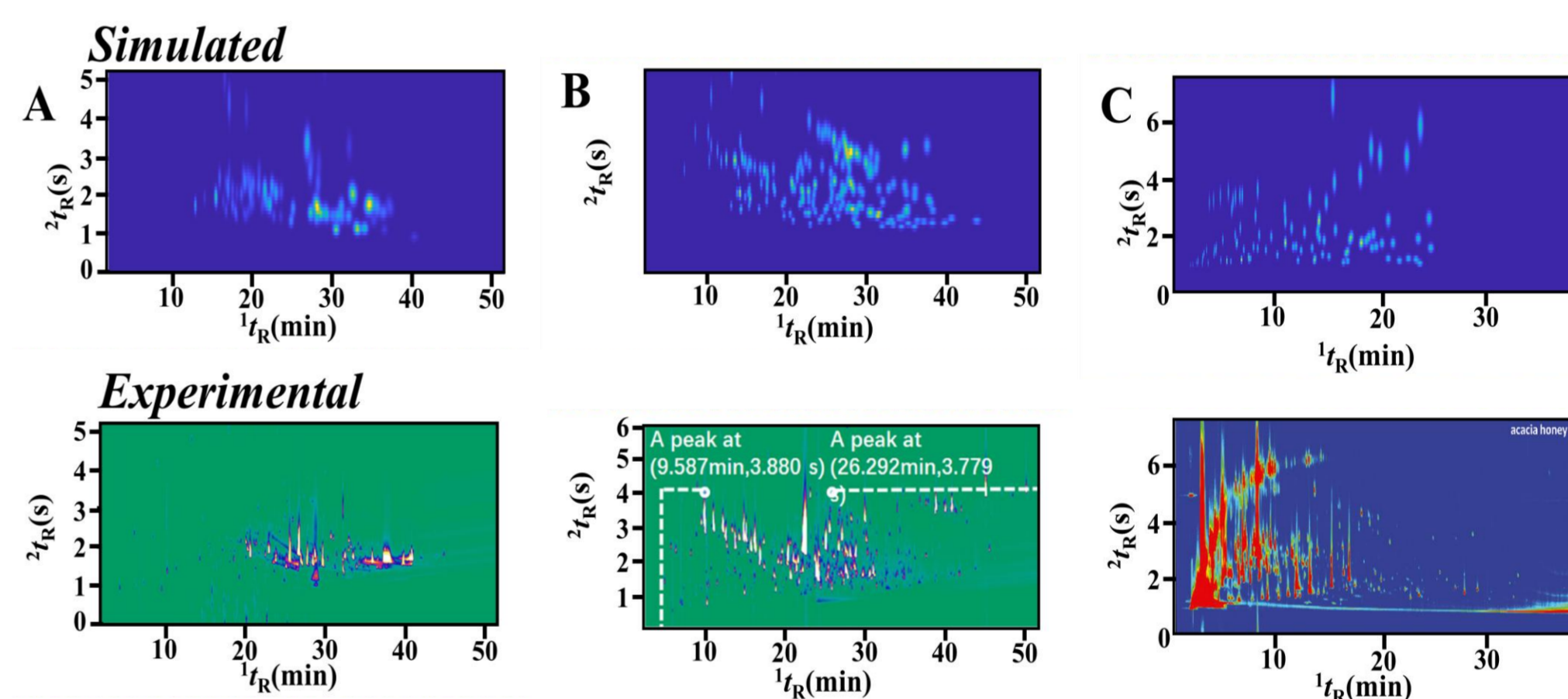
METHOD

Overall process for simulation of peak position (step 1-7), σ (step 8-9) and peak intensity (step 10-11).

STEP	Equation	Function	Output
1	-	Collect $^1t_{R,lit}$, $^2t_{R,lit}$, $^1I_{lit}$, $^2I_{lit}$, and compound names from paper	-
2	$^1I_{fitting,i} = 100n + 100 \left(\frac{^1t_{R(train,i)} - ^1t_{R(n)}}{^1t_{R(n+1)} - ^1t_{R(n)}} \right)$ (1) $^1t_{R,sim,i} = \frac{^1I_{lit,i} - 100n}{100} (^1t_{R(n+1)} - ^1t_{R(n)}) + ^1t_{R(n)}$ (2)	Generate $^1I_{fitting}$, $^1t_{R(n)}$ and $^1t_{R,sim,i}$ formula by using equation 30.	-
3	$^1I_{fitting,i} = 100n + 100 \left(\frac{^1t_{R(train,i)} - ^1t_{R(n)}}{^1t_{R(n+1)} - ^1t_{R(n)}} \right)$ (1)	Substitute $^1t_{R,lit}$ into equation 1 and vary $^1t_{R(n)}$ and $^1t_{R(n+1)}$ to calculate $^1I_{fitting}$. ($^1t_{R(n)}$ and $^1t_{R(n+1)}$ are varied until $ ^1I_{fitting} - ^1I_{lit} \approx 0$)	$^1t_{R(n)}$ $^1I_{fitting}$
4	$^1t_{R,sim,i} = \frac{^1I_{lit,i} - 100n}{100} (^1t_{R(n+1)} - ^1t_{R(n)}) + ^1t_{R(n)}$ (2)	Input $^1t_{R(n)}$ and $^1t_{R(n)}$ into equation 2, and vary $^1t_{R,sim,i}$ to calculate $^1I_{fitting}$. ($^1t_{R,sim,i}$ is varied until $ ^1I_{fitting} - ^1I_{lit} = 0$)	$^1t_{R,sim,i}$
5	$^2t_{R(n)} = \exp(\exp(p_1 \times ^2T_e + p_2) \times n + \exp(p_3 + ^2T_e + p_4) + p_5)$ (3) $^2I_{fitting,i} = 100n + 100 \left(\frac{\log ^2t_{R(train,i)} - \log ^2t_{R(n)}}{\log ^2t_{R(n+1)} - \log ^2t_{R(n)}} \right)$ (4)	Generate $^2I_{fitting}$, $^2t_{R(n)}$ and $^2t_{R,sim,i}$ formula by substitute equation 4 into equation 3.	-
6	$^2t_{R(n)} = \exp(\exp(p_1 \times ^2T_e + p_2) \times n + \exp(p_3 + ^2T_e + p_4) + p_5)$ (3) $^2I_{fitting,i} = 100n + 100 \left(\frac{\log ^2t_{R(train,i)} - \log ^2t_{R(n)}}{\log ^2t_{R(n+1)} - \log ^2t_{R(n)}} \right)$ (4)	Substitute $^2t_{R,lit}$ into equation 4, and vary p_1 - p_5 to calculate $^2t_{R(n)}$, $^2t_{R(n+1)}$ and $^2I_{fitting}$ in the same time.	p_1 - p_5 $^2t_{R(n)}$ $^2I_{fitting}$

STEP	Equation	Function	Output
7	$^2t_{R,sim,i} = 10 \left(\frac{^2I_{lit,i} - 100n}{100} (\log ^2t_{R(n+1)} - \log ^2t_{R(n)}) + \log ^2t_{R(n)} \right)$ (5)	Input $^2t_{R(n)}$ and $^2t_{R(n)}$ into equation 5, and vary $^2t_{R,sim,i}$ to calculate $^2I_{fitting}$ using Solver. ($^2t_{R,sim,i}$ is varied until $ ^2I_{fitting} - ^2I_{lit} = 0$)	$^2t_{R,sim,i}$
8	$\sigma = \sqrt{\frac{Ht_R^2}{L}}$ (6)	Generate σ formula by using equation 6.	-
9	$\sigma = \sqrt{\frac{Ht_R^2}{L}}$ (6)	Input $^1t_{R,sim,i}$ and $^2t_{R,sim,i}$ into equation 6 to calculate $^1\sigma$ and $^2\sigma$, respectively	$^1\sigma$ $^2\sigma$
10	$f(x, y) = A \exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2} - \frac{(y-y_0)^2}{2\sigma_y^2}\right)$ (7)	Generate peak intensity formula by using equation 7.	-
11	$f(x, y) = A \exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2} - \frac{(y-y_0)^2}{2\sigma_y^2}\right)$ (7)	Input $^1t_{R,sim,i}$, $^2t_{R,sim,i}$, $^1\sigma$ and $^2\sigma$ into equation 7 to calculate peak intensity.	Peak intensity

RESULTS & DISCUSSION



CONCLUSION

Applications for confirmation of compound identification for different samples reported from the literature were demonstrated via their 2t_R correlation plots. Solver has been found to be a useful tool to vary p_1 - p_5 minimizing the difference between $^2I_{lit}$ and $^2I_{fitting}$ leading to simulation of the results based on the assumption that the compound identities reported from the literature were mostly correct. Thus, the observation of some compounds being out of the correlation trendline (mismatching between $^2I_{lit}$ and $^2I_{fitting}$) suggests that there is an error for the compound identification.

FUTURE WORK / REFERENCES

Thus, the developed approach can provide more reliable compound identification results in diverse samples. However, this application requires the training from the specialist before use, or the established application need to simplify especially for reducing complexity of the approach to be more user friendly in the future.

Reference

P. Kakanopas, P. Janta, S. Vimolmangkang, F. Hermatasia, C. Kulsing, Journal of Chromatography A 1679 (2022) 463394.