



Review

High-speed gas chromatography: The importance of instrumentation optimization and the elimination of extra-column band broadening

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ARTICLE INFO

Article history:

Received 11 April 2008

Accepted 11 May 2008

Available online 21 May 2008

Keywords:

Gas chromatography

High-speed

Gas chromatographic theory

Optimal linear flow velocity

Instrumentation advancements

Chemical separations

ABSTRACT

This review provides a summary of chromatographic theory as it applies to high-speed gas chromatography. A novel method for determining the optimal linear flow velocity, \bar{u}_{opt} , from specific experimental parameters, is discussed. An in-depth theoretical understanding of \bar{u}_{opt} and its relation to experimental parameters is presented, in the absence of extra-column band broadening, as a means of method evaluation and optimization. Recent developments in high-speed GC are discussed, in the context of the theory presented within this review, to ascertain the influence of extra-column band broadening. The theory presented herein can be used as a means of evaluating the various areas of GC instrumentation (injection, separation, detection, etc.) that need further development to further minimize the effects of extra-column band broadening. The theoretical framework provided in this review, can be, and is, readily used to evaluate high-speed GC results presented in the literature, and thus, the general practitioner may more readily select a specific capillary length and/or internal diameter for a given application. For example, it is theoretically shown, and prior work cited, that demonstrates a peak width of ~ 1 ms is readily achievable in GC, when extra-column band broadening is eliminated.

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Contents

1. Introduction	703
2. Theory	705
2.1. Review of separation thermodynamics	705
2.2. Band broadening in gas chromatography	706
2.3. Deriving \bar{u}_{opt} from experimental parameters	706
2.4. Fundamental GC parameters governing theoretical simulations	707
3. Chromatographic theory and its implications for the present and future of high-speed gas chromatography	708
3.1. Optimizing experimental parameters in the context of chromatographic theory	708
3.2. Practical implementation of high-speed GC in the context of theory	710
References	716

1. Introduction

Fundamental gas chromatographic theory and the general practice of gas chromatography (GC) have been developed over the past several decades [1–7]. Much of the theoretical focus has been on the thermodynamic relationships governing chromatographic separations and the origins of band broadening in chromatographic separations. There have been numerous metrics developed

(i.e., separation efficiency (N), plate height (H), peak capacity (n_c), resolution (R_s), etc.) to gauge the quality of a particular chromatographic instrument or a specific chromatographic separation [3,8–12]. While these metrics determine whether or not there is room for improvement with respect to the theoretical optimum for a particular instrument or separation, they can also be used to compare one instrumental configuration to another.

In order to design a highly efficient high-speed GC instrument, all the experimental parameters (i.e., column length, capillary inner diameter, stationary phase composition, uniformity and thickness, inlet pressure, oven temperature and temperature programming rate) need to be properly selected and experimentally optimized. In addition, the individual components of the high-speed

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Nomenclature

B	longitudinal diffusion (cm^2/s)
B_o	column permeability (cm^2)
C_G	mass transfer in mobile (gas) phase (s)
C_L	mass transfer in the stationary (liquid) phase (s)
d_c	capillary inner diameter (cm)
d_f	stationary phase film thickness (cm)
D_G	gas diffusion coefficient (cm^2/s)
$D_{G,o}$	gas phase diffusion coefficient at the column outlet (cm^2/s)
D_L	stationary phase diffusion coefficient (cm^2/s)
F_c	flow rate at end of column (cm^3/s)
f	gas compressibility factor, Giddings
ΔG°	Gibbs free energy (kJ/mol)
H	plate height (cm)
H_{\min}	minimum plate height (cm)
ΔH°	enthalpy (kJ/mol)
j	gas compressibility factor, James–Martin
K	analyte (compound) distribution constant
k	retention factor
L	column length (cm)
N	efficiency
N_{opt}	efficiency at average optimal linear flow velocity
P	reduced pressure
$P_{\text{@opt}}$	reduced pressure at \bar{u}_{opt}
P_i	absolute head pressure (Pa)
P_o	pressure at the column outlet (Pa)
R	ideal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
R_s	resolution
ΔS°	entropy (kJ/mol)
T	separation temperature (K)
t_M	mobile phase hold-up time (s)
t_R	analyte (compound) retention time (s)
u	linear flow velocity (cm/s)
\bar{u}	average linear flow velocity (cm/s)
\bar{u}_{opt}	optimum average linear flow velocity (cm/s)
V_G	volume of the mobile (gas) phase (cm^3)
V_M	retention volume of an unretained analyte (cm^3)
V_M°	retention volume of an unretained analyte corrected for gas compression (cm^3)
V_R°	retention volume of a retained analyte corrected for gas compression (cm^3)
V_R	analyte retention volume (cm^3)
V_S	volume of stationary phase (cm^3)
w_b	peak width at the base (s)
$w_{b@opt}$	peak width at the base at average optimal linear flow velocity (s)

Greek letters

α	selectivity
β	phase ratio
η	gas viscosity (Pa s)

high carrier gas velocities with relatively short capillary columns lengths [15–20]. The optimum linear velocity, \bar{u}_{opt} , is the average on-column velocity at which the plate height, H , has a minimum value, resulting in a maximum of the separation efficiency, N . The use of a high carrier gas velocity, above \bar{u}_{opt} , results in a decrease in the resolution between chromatographic peaks and a reduction in N [17,21]. One of the most difficult parameters to optimize is the carrier gas velocity since it depends on all the previously mentioned experimental parameters. The dependence of \bar{u}_{opt} on specific experimental parameters is unclear based on the current expressions for \bar{u}_{opt} . In order to more fully understand how \bar{u}_{opt} depends upon the various experimental parameters, specifically column length and inner diameter, a new method for determining \bar{u}_{opt} must be derived. A more full understanding of these issues is a key focus of this review. An in depth theoretical understanding of the \bar{u}_{opt} and its relation to experimental parameters, in the absence of extra-column band broadening, should provide a more comprehensive method for optimization. Then, experimental data could be readily compared to the theoretical expectations, to ascertain the influence of extra-column band broadening. Ultimately, the process presented in this review should lead researchers toward a better understanding of the true potential and challenges in optimizing high-speed GC instrumentation for general practice.

Thus, one of the primary goals of this review is to provide readers with a summary of chromatographic theory as it applies to high-speed GC. This review is a compilation of previously developed fundamental chromatographic theory combined with a new theoretical approach toward the optimization of current chromatographic systems. This review will also relate these theoretical chromatographic relationships to recently reported high-speed GC developments. Chromatographic theory will also be used as a means for determining which areas of GC instrumentation need further development in order to eliminate, or at least minimize, extra-column band broadening. For more rigorous discussions of the theory behind separation science readers should see texts by Giddings [10], Karger et al. [11], and Purnell [9]. Additionally, a comprehensive study of many of the important theoretical aspects relating to fast capillary GC by Blumberg has been published as a four part series [22–25]. The first part of the series focused on the development of an equation for the plate height, assuming that the gas compressibility is constant, for separations occurring at high pressure drop [22]. The second part of the series involved the derivation of expressions for speed-optimized hold-up time and a comparison of the theoretical hold-up time to the hold-up time of efficiency-optimized columns [23]. In the third part of the series Blumberg examined the difference between speed-optimized carrier gas velocity and speed-optimized flow rate and how they relate to the plate height [24]. The final part of the study determined the effects of stationary phase thickness on column performance [25].

The novel approach utilized to theoretically relate \bar{u}_{opt} to key experimental parameters presented in the review herein, cast in the context of column length and inner column diameter, provides a simplified and succinct method for determining \bar{u}_{opt} . The theoretically calculated \bar{u}_{opt} values can be used as a means of evaluating experimental chromatographic data to ascertain the presence, and impact, of extra-column band broadening. Essentially, a comparison could be made between the theoretically predicted and the experimentally obtained values of \bar{u}_{opt} . Another important aspect of the novel approach to determine and evaluate the theoretical \bar{u}_{opt} utilized in this review is that there have not been any mathematical assumptions that could lead to a discrepancy between the actual and theoretically predicted values of \bar{u}_{opt} . Consequently, any differences between the theoretical and experimental \bar{u}_{opt} are likely the result of extra-column band broadening, i.e., non-ideal experimental influences. Finally, the theoretical framework utilized in this

GC instrument need to be designed to eliminate sources of extra-column band broadening [3,10,13,14]. Common sources of extra-column band broadening include, but are not limited to, large injection volumes, non-uniform oven temperatures and/or temperature programs and dead volumes at column connections and/or at the detector [14,15]. Once, the experimental parameters mentioned above have been selected and are implemented, separation efficiency, N , depends largely on the carrier gas velocity, u . The most direct route to high-speed GC separations is the use of

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