Specific transport efficiency – a universal metric of a column structural quality in liquid and gas chromatography

Leonid M. Blumberg(1,*), Gert Desmet(2)

(1) Advachrom, P.O. Box 1243, Wilmington, DE 19801, USA.
(2) Vrije Universiteit Brussel, Department of Chemical Engineering, Pleinlaan 2, 1050 Brussels, Belgium.

(*)Corresponding author leon@advachrom.com.

HIGHLIGHTS

Specific Transport Efficiency (STE) is a metric of tradeoff between time and separation
The larger is a column STE the larger is its peak capacity in the same time and at the same pressure
STE, effective diameter and nominal diffusivity are the core set of column parameters
Use of the core parameters for evaluation of several metrics of column performance demonstrated
Specific transport efficiency – a universal metric of a column structural quality in liquid and gas chromatography

Leonid M. Blumberg\textsuperscript{(1,*)}, Gert Desmet\textsuperscript{(2)}

(1) Advachrom, P.O. Box 1243, Wilmington, DE 19801, USA.

(2) Vrije Universiteit Brussel, Department of Chemical Engineering, Pleinlaan 2, 1050 Brussels, Belgium.

(*)Corresponding author leon@advachrom.com.

Keywords: effective diameter; transport efficiency; specific transport efficiency; universal plate height; nominal diffusivity

ABSTRACT

A metric of structural quality of a column in liquid and gas chromatography – the column specific transport efficiency ($e_s$) – is proposed. Measurable by identical rules for all column types (open-tubular, packed, monolithic, pillar-array, etc., regardless of retention mechanism), $e_s$ supersedes such quality metrics as dimensionless plate height ($h$), Bristow-Knox separation impedance (SI), Golay specific performance index (SPI) and others. Peak capacity, and other separation performance measures of a chromatographic system are proportional to $e_s$. To theoretically predict the separation-time performance of a column with known $e_s$, two measurable parameters – a column effective diameter ($d_{\text{eff}}$) and nominal diffusivity ($D_n$) were introduced. Quantities $e_s$ and $D_n$ represent the properties of classes of self-similar columns while $d_{\text{eff}}$ represents a particular column. The use of parameters $d_{\text{eff}}$, $e_s$ and $D_n$ for evaluation of relations between efficiency and void time ($t_{\text{v}}$) in columns of several types has been demonstrated. It is always more time-efficient to use maximum available instrumental pressure ($\Delta p_{\text{max}}$) for obtaining a predetermined column efficiency even if that efficiency is
relatively low so that operation at $\Delta p_{\text{max}}$ requires non-optimal flow. It has been also demonstrated that reducing characteristics cross-sectional dimension ($d_{\text{eff}}$, particle size of a packed column, internal diameter of and open-tubular column, etc.) of a column operating at the same $\Delta p_{\text{max}}$ reduces the column efficiency with the benefit of disproportionally faster analysis.

1. Introduction

The key issue for this report is to identify a core set of measurable properties of LC and GC columns that is sufficient for the prediction of a column general separation performance, analysis time and the tradeoff between them.

Two types of properties of chromatographic columns – the transport properties and the selectivity – can be distinguished. The latter represents a column ability to transport different solutes in different times and to effect by that a column specific separation performance – the separation of particular peak pairs. On the other hand, the transport properties are concerned with transporting each single solute or, in the case of transporting a solute mixture, the transport properties describe the similarities rather than differences in transporting different solutes. Peak capacity ($n_c$), column plate number ($N$) and plate height ($H$) are examples of metrics of a column transport properties representing its general separation performance (briefly, separation performance). Among other transport properties are void time ($t_M$) and loadability (sample capacity). The former affects the analysis time while the latter represents the largest amount of sample that can be transported through the column without distorting other transport properties. While recognizing the importance of loadability, we only mention but do not evaluate its effect and only evaluate the relations between the separation performance and the analysis time.
The interdependence of a column separation performance and analysis time has been recognized since the early days of chromatography, and it enjoys significant attention in contemporary studies [1-15]. Golay was the first to recognize the interdependence in 1957 [1] together with being also the first to recognize that the tradeoff between the two is constrained by the available column pressure: “the pressure drop, is what you might call the price paid for a certain column performance” [1], “the performance index is … a measure of … [efficiency] with which a given column design achieves a certain resolution with a given pressure differential and a given time” [3].

The separation-time tradeoff substantially depends on a column structure. Golay demonstrated [1, 2] that, in GC, an open-tubular column (OTC) yields the same separation performance in shorter time and/or at lower pressure than a packed column does.

Several metrics of column performance are known in chromatography. In addition to earlier mentioned \( n, N \) and \( H \), they include a column dimensionless plate height \( (h) \), Golay’s specific performance index (SPI) for GC columns [2], Bristow-Knox separation impedance (SI) for LC columns [8], and others. With so many metrics, the question of choice arises.

A metrics of choice in this report should be measurable by objective external measurement of a column as a whole. The objectivity means that the measurement of a particular metric should be conceptually identical for all columns and techniques. Thus, because a peak retention time \( (t) \) and standard deviation \( (\sigma) \) are externally measurable (briefly, measurable) quantities, a column plate number:

\[
N = \left( \frac{t}{\sigma} \right)^2, \quad \text{(static)}
\]  

(1)

in static chromatography [16, 17] (isothermal isobaric GC, isocratic isothermal isobaric LC, etc.) is a measurable quantity. Also measurable is a column plate height:

\[
H = \frac{L}{N} = L \left( \frac{\sigma}{t} \right)^2
\]  

(2)
where a column length ($L$) is measurable not only because it can be measured by a ruler, but also because it can be found (Supplement) from measuring a column operational parameters (without “opening a column compartment” in the instrument).

An example of unmeasurable (subjective) property in the context of this report is a packed column particle size ($d_p$) which cannot be found from the measurement of parameters of a column as a whole.

There are additional difficulties with identifying $d_p$ for monolithic [18, 19], pillar-array [20, 21], and other columns where the subjectivity arises from the need to compare intrinsically incomparable spherical and non-spherical support structures. In all such cases, $d_p$ is typically defined on the basis of subjective considerations [14]. As a result, the dimensionless plate height of a packed column [22, 23]:

$$h = \frac{H}{d_p}, \quad \text{(packed column)}$$

is also a subjective quantity. Additionally, the dimensionless plate height in an OTC is typically defined as [24, 25]:

$$h = \frac{H}{d_c}, \quad \text{(OTC)}$$

where $d_c$ is internal diameter of a column tubing. Replacing the normalizing characteristic cross-sectional dimension $d_p$ in Eq. (3) with $d_c$ in Eq. (4) is also subjective.

We identified below a core set of three intensive transport properties of chromatographic columns and a corresponding core set of three measurable parameters that are sufficient for evaluating other transport properties. One of the core parameters – the dimensionless specific transport efficiency ($e_s$) – supersedes the earlier mentioned parameters $h$, SI, SPI as the metrics of a column structural quality.

Because the standard deviation ($\sigma$) is the only known measurable peak width metric that can be theoretically predicted from column properties and operational conditions [26], it is the only peak width metric in this report. This approach makes the result of the study applicable to all peak shapes.

The terms peak standard deviation and peak width are treated below as synonyms. As another
convention, the term retention factor \((k)\) is synonymous in this report with what is also known as the \textit{phase retention factors} \((k')\) [14, 27].

To eliminate from this study the \textit{extra-column} factors [28] such as insufficiently sharp sample introduction and limits to ability of data analysis subsystem to \textit{resolve} (identify and quantify) closely spaced peaks, we assume that the sample introduction is sufficiently \textbf{sharp} for a negligible effect on a column performance, and we do not consider the specifics of the peak measurement and identification. Additional assumptions introduced below are typed in the \textbf{boldface} type.

\section{Theory}

\subsection{Transport efficiency}

To identify the core set of intensive properties of a chromatographic column that affect its performance, we first consider a broader picture.

The key purpose of chromatography is the \textit{separation}. Other parameters of chromatographic analysis like the \textit{analysis time} and a column \textit{loadability} are subordinate to the separation performance and can be viewed as its price. It is important, therefore, to use the performance metrics that most transparently and intuitively relate to the separation performance.

Several layers of general separation performance of a chromatographic system can be recognized [29]. On the top is the largest statistically expected number \((m)\) of peaks that the system can \textit{resolve}. This can be viewed as the ultimate performance metric. Below \(m\) is the \textit{peak capacity} \((n_c)\) [23, 30] – the largest number of resolvable peaks that can be packed in the separation space of analysis. According to peak overlap statistics [23, 31], \(m\) is proportional to \(n_c \; (m \sim n_c)\). Thus, when all peaks are identical, \(m = n_c/(2e) \approx 0.184n_c\) [23, 29, 31]. The next layer down is the column \textit{separation capacity} \((s)\) [29, 32] – the number of \(\sigma\)-\textit{slots} \((\sigma\)-wide segments) along a chromatogram. Quantities \(n_c\) and \(s\) relate
as \( n_c = s/\Delta s_{\text{req}} \) where \( \Delta s_{\text{req}} \) is the smallest number of \( \sigma \)-slots between two peaks that the data analysis subsystem requires for resolving them [29]. One has: \( m \sim n_c \sim s \). The next layer down is a column plate number (\( N \)), Eq. (1). In static and dynamic (temperature-programmed GC, gradient LC, etc.) chromatography, quantities \( m, n_c \) and \( s \) are proportional to \( \sqrt{N} \) (the same is true for not considered here peak resolution, \( R_s \) [33], and separation, \( \Delta s \) [29]). The fact that \( N \) is not proportional to the key metrics of separation performance is a source of substantial disruption in the system of metrics and of frequently exaggerated significance of the values of \( N \): “\( N \) is an) awkward measure, as the resolving power is only proportional to the square root of the plate number” (Poppe [11]). Similar frustrations with \( N \) as a performance metric were expressed by other workers [34, 35].”

There are also questions about physical meaning of quantity \( N \). Defined by widely known and IUPAC recommended [33] expression \( N = (t/\sigma)^2 \), Eq. (1), quantity \( N \) can be different from the actual number, \( L/H_{\text{loc}} \), of local plate height (\( H_{\text{loc}} \)) units along a column. For example, due to the carrier gas compressibility, this is always the case in GC [26, 36]. Similarly, \( N \neq L/H_{\text{loc}} \) in LC with non-uniform columns [37, 38], etc. A question inevitably arises: What is a rationale for parameter \( N \) that can be different from its declared physical meaning, and that is calculated as \((t/\sigma)^2\) in order to be followed by calculation of \( \sqrt{(t/\sigma)^2} \) in evaluations of all known parameters of separation performance? The answer seems to be: a historically established tradition, but not a scientific reason.

Instead of \( N \), a column transport efficiency, \( E = \sqrt{N} \) [15, 17, 29, 39] (separation power [32, 40]), can be used. Due to Eqs. (1) and (2), quantities \( E \) and \( H \) can be defined as:

\[
E = \frac{t}{\sigma} \quad (5)
\]

\[
H = \frac{L}{E^2} \quad (6)
\]
The following observations illustrate an important aspect of proportionality of $s$ and, therefore, of $n_c$ and $m$ to $E$.

**Characteristic thermal constant** ($\theta_{\text{char}}$) in GC [26, 39, 41, 42], and **characteristic strength constant** ($\Phi_{\text{char}}$) in LC [15, 17, 43] play important role in these techniques. They can be estimated as

$$
\theta_{\text{char}} \approx 30 \, ^\circ\text{C}, \quad \Phi_{\text{char}} \approx 0.1 \text{ (or 10\%)} \text{ in RPLC (reverse phase LC) of small molecules and } \Phi_{\text{char}} \approx \sqrt{3/M}
$$

of large molecules having $M > 300$ ($M$ is molecular weight). Increasing GC column temperature by $\theta_{\text{char}}$ or increasing the solvent strength in LC by $\Phi_{\text{char}}$ reduces $\ln k$ by 1. Quantity $E$ relates to $\theta_{\text{char}}$ and $\Phi_{\text{char}}$ in the following straightforward way. In temperature-programmed GC, the incremental separation capacity ($\Delta s$) of each $\theta_{\text{char}}$-wide temperature span is equal to $E$ at slow heating rate and to $0.8E$ at optimal heating rate [44]. Similarly, in gradient LC, $\Delta s$ of each $\Phi_{\text{char}}$-wide solvent strength span is equal to $E$ [17] at slow solvent strength programming, and to $0.8E$ at optimal solvent strength increasing rate [45]. In other words, there are straightforward relationships between $E$ and the number of $\sigma$-slots in characteristic segments of the separation space in temperature-programmed GC and gradient LC. For example, In RPLC analysis of small molecules ($\Phi_{\text{char}} \approx 10\%$) at optimal solvent strength programming rate, there are approximately $0.8E$ $\sigma$-slots in each time segment corresponding to 10% solvent composition change. This implies that, if a $4\sigma$-separation is required for resolving two peaks then the incremental peak capacity ($\Delta n_c$) of each 10% solvent composition span can be estimated as $\Delta n_c \approx 0.8E/4 = 0.2E$, and the maximum peak capacity ($n_{c,\text{max}}$) of optimal programming from 0 to 100% of stronger solvent is $n_{c,\text{max}} \approx 2E$.

Using in column performance evaluations $E$ instead of $N$, extends the chain of proportionalities,

$$
m \sim n_c \sim s \sim E
$$

(7)
Generally, the lower is the level of performance property the smaller is the number of factors affecting it. Thus, metrics $m$ and $n_c$ in the upper level depend on the column and on ability of data analysis subsystem to resolve closely spaced peaks. Metrics $s$ and $E$ in the next two lower levels only depend on a column and its operational conditions, but, unlike $m$ and $n_c$, do not depend on the subsystems (like the data analysis subsystem) that do not control the column operation. And among metrics $s$ and $E$, only the former strongly depends on the analysis time while time has no direct effect on $E$. All metrics in Eq. (7) represent a column extensive properties as all depend on the column length, and all but $E$ depend on analysis time. Our next goal is to identify a lower level intensive metric that can be added to the chain in Eq. (7).

2.2 Operational conditions

The basic definitions in this report apply to linear (no column overloading) LC and GC based on packed columns (conventional, monolithic [18, 19], pillar-array [20, 21], etc.) with totally or partially porous packing, and on open-tubular columns (OTC) – WCOT (wall-coated open tubular), PLOT (porous layer open-tubular), etc. with incompressible solvent in LC and ideal carrier gas in GC.

2.3 Transport permeability

Let $p_i$, $p_o$ and $\Delta p = p_i - p_o$ be a column inlet pressure, outlet pressure and pressure drop, respectively. In a $L$-long column with fluid viscosity $\eta$, the void time ($t_M$) – the average time of transporting the mobile phase molecules from column inlet to outlet – can be found as [14, 26, 46]:

\[ t_M = \frac{L^2 \eta}{K_v \Delta p_{\text{eff}}} \]  

(8)

where $K_v$ is a column transport permeability (chromatographic permeability [8, 47], permeability based on mean velocity of unretained solute [14], $u_o$-based permeability [48]), and $(\Delta p_{\text{eff}})$ is the effective pressure (virtual pressure [26]) defined as:
\[ \Delta P_{\text{eff}} = \begin{cases} \Delta P, & \text{incompressible fluid} \\ j_H \Delta P, & \text{ideal gas} \end{cases} \]  

(9)

where:

\[ j_H = \frac{3(p_i + p_o)^2}{4(p_i^2 + p_i p_o + p_o^2)} \]  

(10)

is the *Halász-Hartmann-Heine compressibility factor* \([26, 49]\). As parameters \(L\), \(\Delta P_{\text{eff}}\), \(t_M\) and \(\eta\) are measurable quantities, Eq. (8) defines quantity \(K_v\) measurable for incompressible fluid and ideal gas as:

\[ K_v = \frac{L^2 \eta}{\Delta P_{\text{eff}} t_M} \]  

(11)

In forthcoming numerical examples, we will use theoretically predicted values of measurable parameters. Thus, according to *Poiseuille law* \([26, 50]\), \(K_v\) in an open circular tube of internal diameter \(d\) and in a packed column can be estimate as \([6, 8, 14, 20, 47, 48, 51-53]\):

\[ K_v = \frac{d^2}{32}, \quad (\text{open circular tube}) \]  

(12)

\[ K_v = \frac{d_p^2}{\phi}, \quad (\text{packed column}) \]  

(13)

where \(\phi\) is the *transport resistance factor (flow parameter)* \([6]\), *flow resistance factor* \([51, 52]\), *dimensionless flow resistance parameter* \([8]\), *column resistance factor* \([47]\), *flow resistance* \([14, 20]\).

It can be noticed that, being defined in Eq. (13) through unmeasurable quantity \(d_p\), quantity \(\phi\) is also unmeasurable. It is known, however, that, for a column packed with identical non-porous spherical particles of diameter \(d_p\), quantity \(\phi\) can be estimated as \([20, 47, 48, 53]\):

\[ \phi \approx 400, \quad (\text{regular spherical packing}) \]  

(14)

This estimate is used in all forthcoming numerical evaluations.
2.4 Effective diameter

The effective transport diameter (briefly, effective diameter), \( d_{\text{eff}} \), of a \( L \)-long column (with compressible or incompressible fluid) is the internal diameter (\( d \)) of equally long open uniform inert circular reference tube with incompressible fluid that yields the same void time (\( t_M \)) as does the column when \( \Delta p \) and \( \eta \) are the same in both cases.

Eqs. (8), (9) and (12) yield:

\[
t_M = \frac{32 \eta L^2}{d^2 \Delta p}, \quad \text{(reference tube)} \quad (15)
\]

The definition of \( d_{\text{eff}} \) suggests that \( d_{\text{eff}} \) is the solution of this equation for \( d \):

\[
d_{\text{eff}} = L \sqrt{\frac{32 \eta}{t_M \Delta p}} \quad (16)
\]

As all parameters in the right hand side of this definition are measurable quantities, \( d_{\text{eff}} \) is also a measurable quantity. Combining the last equation with Eqs. (8) and (9), one can also express \( d_{\text{eff}} \) as:

\[
d_{\text{eff}} = \sqrt{\frac{32 K_v \Delta p_{\text{eff}}}{\Delta p}} = \sqrt{\frac{32 K_v}{j_H}}, \quad \text{LC \{1\}, GC \{1\}} \quad (17)
\]

It might be also convenient to replace the ratio \( 32 \eta / \Delta p \) in some expressions with its time-equivalent:

\[
t_p = \frac{32 \eta}{\Delta p} \quad (18)
\]

For example, in LC with 50/50 (\( V/V \)) water/acetonitrile solvent at 25 °C, \( \eta \approx 0.81 \) cP [54]. At \( \Delta p = 1200 \) bars (close to the highest commercially available pressure), Eq. (18) yields \( t_p \approx 0.22 \) ns.

What should be the \( \Delta p \) in GC to obtain the same \( t_p \)? For hydrogen (the fastest carrier gas [26, 39]) at 150 °C (approximately the middle of GC temperature range), \( \eta \approx 0.0113 \) cP [26]. Eq. (18) yields:

\( \Delta p = 16.8 \) bars. Known commercial GC instruments do not supply this pressure, but mostly because there is no practical need for that as the dominant performance limit for GC WCOT columns is not
pressure, but detection limit [39]. Assuming that, if necessary, 20 bars and higher pressure could be
available in GC, quantity:

\[ t_p = 0.2 \text{ ns} \] \hspace{1cm} (19)

is used in all forthcoming numerical examples (GC and LC) as the lowest (the best) practically
available \( t_p \).

With notation \( t_p \), Eq. (16) becomes:

\[ d_{\text{eff}} = L \sqrt{\frac{t_p}{t_M}} \] \hspace{1cm} (20)

It follows from Eq. (17) that \( d_{\text{eff}} \) depends on the column structure and cross-sectional dimensions
(both represented by parameter \( K_v \)). In GC, \( d_{\text{eff}} \) also depends via parameter \( j_{\text{H}} \), Eq. (10), on the column
inlet and outlet pressure \((p_i \text{ and } p_o)\). While expressing \( K_v \) in the form of effective diameter \( (d_{\text{eff}}) \) seems
natural, defining \( d_{\text{eff}} \) as being dependent on the column operational conditions \((p_i \text{ and } p_o)\) can be
questioned. Alternatively, \( d_{\text{eff}} \) could have been defined as being independent of pressure by, e.g., using
in Eq. (16) \( \Delta p_{\text{eff}} \) instead of \( \Delta p \). However, the alternative choices would spill over to other concepts
introduced below either complicating them or complicating their relations.

2.5 Separation impedance and universal plate height

Let \( t \) and

\[ k = \frac{t}{t_M} - 1 \] \hspace{1cm} (21)

be a solute retention time and retention factor, respectively, in static analysis. The separation
impedance (SI),

\[ \text{SI} = \frac{\Delta pt}{E^4 \eta (1 + k)} \] \hspace{1cm} (22)
was introduced by Bristow and Knox [8] as a dimensionless performance measure of packed LC columns (quantity $N^2$ instead of $E^4$ was used in the source). All parameters in this definition are measurable quantities, and nothing prevents its extension to GC and LC with both, OTC and packed columns. Due to Eqs. (6), (20) and (21), SI in Eq. (22) can be expressed as:

$$\text{SI} = \frac{\Delta \rho t_M}{E^4 \eta} = \frac{32 t_M}{E^4 t_p}$$  \hspace{1cm} (23)$$

$$\text{SI} = 32 h_U^2$$  \hspace{1cm} (24)$$
where dimensionless quantity $h_U$, defined as:

$$h_U = \frac{H}{d_{\text{eff}}}$$  \hspace{1cm} (25)

can be called as the universal plate height – universal because a column characteristic cross-sectional dimension, $d_{\text{eff}}$ (the normalization factor in the definition of $h_U$) is measured in the same way, Eq. (16), for all columns. Eqs. (17), (23), (24) and (25) allow one to express SI and $t_M$ as:

$$\text{SI} = \frac{H^2 \Delta \rho}{K_v \Delta \rho_{\text{eff}}} = \frac{H^2}{K_v} \left[ \frac{1}{1/\sqrt{J_H}}, \quad \text{GC} \right]$$

$$t_M = \frac{E^4 t_p}{32} = h_U^2 E^4 t_p$$  \hspace{1cm} (27)$$

Eq. (24) indicates that SI and $h_U$ are equivalent to each other – a value of one uniquely determines the other. Furthermore, comparison of Eq. (24) with the definitions, Eqs. (3), (4) and (25), of $h$ and $h_U$ suggests that SI is nothing but a differently normalized $h^2$, and that there is no conceptual difference between metrics SI and $h_U$ on the one hand, and conventional dimensionless plate height ($h$) on the other. However, although the difference between $h_U$ and $h$ is not conceptual, it is essential. The characteristic cross-sectional dimensions ($d_p$ and $d$) in the definitions, Eqs. (3) and (4), of $h$ are different from each other. On top of that, $d_p$ is unmeasurable and, in some cases (monolithic columns, pillar-array columns), its values is chosen arbitrarily. As a result, $h$ is unsuitable for comparison of
columns of different type (packed and open-tubular, packed conventional and pillar-array, etc.). On the other hand, the consistent measurement of $d_{\text{eff}}$ as a column characteristic cross-sectional dimension offers a single and objective measurable value ($d_{\text{eff}}$) enabling the comparison of different column types.

Thus, according to Eq. (27),

*any two columns operating at the same ratio $\eta/\Delta p$ and yielding the same transport efficiency ($E$)*

*require the same $t_M$ as long as both have the same $h_U$.*

To a certain degree, the choice of $d_{\text{eff}}$ as characteristic cross-sectional dimension for all columns is the essence of the treatment in this report.

How do the metrics SI and $h_U$ relate to Golay’s SPI (specific performance index) [2] for GC columns – the earliest known metric of separation-time tradeoff and the prototype for Bristow-Knox SI [8]? As shown in Supplement,

$$\text{SPI} = \frac{\text{SI}}{\text{SI}_{\text{WCOT, thin, min}}} = \left( \frac{h_U}{h_{U,\text{WCOT, thin, min}}} \right)^2 \quad (28)$$

indicating that, like $h_U$ and SI, the SPI is just another differently normalized and/or differently powered dimensionless plate height. However, as quantities $\text{SI}_{\text{WCOT, thin, min}}$ and $h_{U,\text{WCOT, thin, min}}$ depends on a solute retention factor in a reference thin film WCOT column, SPI is not equivalent to mutually equivalent metrics $h_U$ and SI.

2.6 Specific transport efficiency

Both metrics, SI and $h_U$, represent intensive properties of a column separation performance. As they are equivalent to each other, either one could be a candidate for a set of a column core parameters. However, neither is proportional (nor inversely proportional) to mutually proportional higher level metrics in Eq. (7) as, according to Eqs. (6), (24) and (25): $h_U \sim 1/E^2$, $\text{SI} \sim 1/E^4$. 
To avoid these shortcomings, we propose a column *specific transport efficiency* (briefly, *specific efficiency*) defined as:

\[ e_s = \sqrt{\frac{d_{\text{eff}}}{H}} \]  

(29)

It follows from Eqs. (6), (7), (24) and (25) that \( e_s \) is proportional to \( E \) and, therefore,

\[ m \sim n_e \sim s \sim E \sim e_s \]  

(30)

While satisfying this proportionality chain, \( e_s \) is equivalent to \( h_U \) and SI relating to them as:

\[ e_s = \frac{1}{\sqrt{h_U}} = 2 \left( \frac{2}{\text{SI}} \right)^{1/4} \]  

(31)

Due to Eqs. (5), (6), (18), (20) and (29), \( e_s \) can be expressed as a functions of directly measurable parameters \( \Delta p, t, t_M, \eta \) and \( \sigma \):

\[ e_s = E \sqrt{\frac{d_{\text{eff}}}{L}} = t \left( \frac{t_p}{t_M} \right)^{1/4} = \frac{t}{\sigma} \left( \frac{32\eta}{\Delta pt_M} \right)^{1/4} \]  

(32)

One can use the right hand side of this expression to plot a function \( e_s(u) \) where \( u = L/t_M \). It follows from the definition of \( e_s \) in Eq. (29) that \( e_s(u) \) has a maximum \( (e_{s,\text{max}}) \) at \( u_{\text{opt}} \) corresponding to \( H_{\text{min}} \).

Using \( e_s \), Eq. (27) can be expressed as:

\[ t_M = \left( \frac{E}{e_s} \right)^{4} t_p, \quad \text{or} \quad \frac{t_M}{t_p} = \left( \frac{E}{e_s} \right)^{4} \]  

(33)

implying that \( E \) and, therefore, other metrics in Eq. (30) are proportional to \( e_s \) when \( \Delta p \) and \( t_M \) are fixed. The last equation also indicates that \( e_s \) is the transport efficiency \( (E) \) per unit of \( (t_M/t_p)^{1/4} \) justifying naming \( e_s \) as the *specific* transport efficiency. Being a monotonically declining function of \( H \), Eq. (29), quantity \( e_s \) has the maximum \( (e_{s,\text{max}}) \) at optimal flow rate \( (F_{\text{opt}}) \) where \( H \) has the minimum.

The optimal \( t_M \) and \( E \) corresponding to \( F_{\text{opt}} \) are denoted here as \( t_{M,\text{Opt}} \) and \( E_{\text{Opt}} \) where the purpose of the
capital “O” in the subscript “Opt” is to distinguish the fact that quantities $t_{M,\text{Opt}}$ and $E_{\text{Opt}}$ correspond to two conditions: optimal flow rate ($F_{\text{opt}}$) and fixed pressure drop ($\Delta p$).

The properties in Eq. (30) are arranged in the order of decreasing their level from left to right. An improvement in performance on some level improves the performance on all higher levels. As $e_{s,\text{max}}$ is the metric of the lowest level in the chain, its improvement improves the performance metrics on all other levels. Thus, increasing $e_s$ by, say, a factor of two, increases $E$ at a fixed $\Delta p$ and $t_M$ as well as all other metrics in Eq. (30) by the same factor of two. If raising $e_s$ is not dictated by the need to increase all other performance metrics then, according to Eq. (33), the larger $e_s$ at fixed $\Delta p$ and $E$ can be used for reducing the analysis time in inverse proportions to $e_s^4$. Thus, doubling $e_s$ without changing $\Delta p$ and $E$ makes $t_M$ 16 times shorter. As it depends on a column structure, and as it effects all other performance metrics of a column, quantity $e_{s,\text{max}}$ can be viewed as a measure of structural transport quality of a column design – representing relative sharpness of chromatographic peaks that different column designs can deliver under comparable conditions. The larger is $e_{s,\text{max}}$ the better is the quality and the better are all other performance metrics under otherwise identical conditions.

Quantity $e_{s,\text{max}}$ can be used for comparison of the separation-time performance of columns of different structures (conventional packed, monolithic, pillar-array, PLOT, etc.), different ways of raising column loadability (by, say, raising porosity of support structure, or by increasing a column tubing diameter without changing the support structure [55]), different orientation of internal pores (say, random or radial [56]), etc.

2.7 Attainable performance

Parameter $e_s$ quantifies the tradeoff between the column transport efficiency ($E$) and the void time ($t_M$). However, it does not say what actually a given column can deliver. Can it deliver, e.g., $E = 1000$? Under what conditions? Some of these issues were addressed in the literature separately for GC [39]
and LC [45]. Here they are evaluated from a single perspective. Recognizing that other extensive 
properties in Eq. (30) are proportional to $E$ and that the analysis time is proportional to $t_M$, we only 
evaluate below $E$ and $t_M$.

Let $u$ and $u_{opt}$ be, respectively, the velocity of transporting mobile phase molecules along the column 
and its optimum corresponding to the minimum ($H_{min}$) in $H$ and, therefore, to the minima in $h_U$ and SI 
and to the maximum ($e_{s,max}$) in $e_s$. How $u_{opt}$ can be predicted from a column measurable parameters? 

Quantity $u_{opt}$ strongly depends on a column characteristic cross-sectional dimension being, in 
general, inversely proportional to it [17]. As a result, the product $d_{eff}u_{opt}$ for a given solute, mobile 
phase and conditions is more or less independent of $d_{eff}$. To formalize these observations, we extend 
the concept of *self-similar* packed LC columns [14, 15] to arbitrary LC and GC ones. Extending the 
GC *method translation* concept [26, 57] to LC, we define that two columns are *translations* of each 
other if retention factor of any solute is the same in both columns. A column plate height can be 
described [15, 26, 39] as a function of the ratio $u/u_{opt}$. For example, it can be verified by direct 
substitution of parameters in Eq. (35) into Eq. (34) that van Deemter equation $H = A + B/u + Cu$ for a 
packed LC column can be expressed as a function of its optimal parameters $u_{opt}$ and $H_{min}$:

$$H = H_{min} \left( a + \frac{1}{2} \left( \frac{u_{opt}}{u} + \frac{u}{u_{opt}} \right) \right)$$  \hspace{1cm} (34)$$

$$H_{min} = A + 2\sqrt{BC}, \hspace{0.5cm} a = \frac{A}{H_{min}}, \hspace{0.5cm} u_{opt} = \frac{B}{\sqrt{C}}$$  \hspace{1cm} (35)$$

Eq. (34) also applies to thin film WCOT GC columns [26, 39] for which $a = 0$. Two columns are said 
to be *self-similar* [15] if they are translations of each other, and if for any solute under identical 
conditions in both columns:

- the product $d_{eff}u_{opt}$ is the same
\( h_u \) (and, therefore, \( e_s \)) is the same when the ratio \( u/u_{\text{opt}} \) is the same

Mutual translatability of two columns is the key requirement for a practical method transfer, as it preserves the relative retention of all peaks. If two mutually translatable columns are not self-similar, different transport efficiency might be required for obtaining a necessary separation of the target peak pairs. The efficiency can be adjusted by choosing a proper column length in each case [26, 57].

Returning to column parameters affecting \( u_{\text{opt}} \), let’s define two quantities:

\[
D_{np} = \frac{d_{\text{eff}}u_{\text{opt}}}{2} 
\]  
(36)

\[
D_n = D_{np} \cdot \begin{cases} 
1, & \text{LC} \\
1/p_{\text{p/st}}, & \text{GC} 
\end{cases} 
\]  
(37)

where \( p_{\text{p/st}} = 1 \text{ atm (standard pressure)} \). Both quantities are measured in units of diffusivity (length\(^2\)/time). We will call \( D_n \) as the \textit{nominal diffusivity} (of a given solute in a given column and the mobile phase). There is no difference between \( D_{np} \) and \( D_n \) in LC. In GC, \( D_{np} \) is measured at the same pressure as is \( u_{\text{opt}} \) while \( D_n \) is \( D_{np} \) rescaled to 1 atm. As \( D_n \) for a given solute and mobile phase is the same for all self-similar columns, it can be used for evaluation of \( u_{\text{opt}} \) in a column with particular \( d_{\text{eff}} \).

As \( u_{\text{opt}} \) is approximately proportional to a solute molecular diffusivity \( (D_m) \), quantities \( D_{np} \) and \( D_n \) are also approximately proportional to \( D_m \). For example, in a thin film WCOT column, \( u_{\text{opt}} \approx 5.5D_m/d \) at \( k = 2 \) [26]. From Eqs. (10), (12), (13) (14), (17) and (37), one can find that \( D_n \) in GC-MS can be estimated as \( D_n \approx 2.4D_{m,\text{st}} \) where \( D_{m,\text{st}} \) is \( D_m \) at 1 atm. For a solute eluting with \( k = 2 \) from a typical column with hydrogen at 150 °C, this yields \( D_n \approx 1.3 \text{cm}^2/\text{s} \) [26]. For LC columns with spherical packing, \( u_{\text{opt}} \) can be estimated as [48, 58] \( u_{\text{opt}} \approx 10D_m/d_p \) leading to \( D_n \approx 1.4D_m \). For small molecules in LC, \( D_m \) can be approximated as \( D_m = 10^{-5} \text{cm}^2/\text{s} \) [58, 59] leading to \( D_n \approx 1.4 \times 10^{-5} \text{cm}^2/\text{s} \). The values:

17
are used in forthcoming numerical examples.

Since $D_m$ is a function of a solute molecular size [60, 61], it covers a relatively wide range especially in LC. The same is true for $D_n$, approximately proportional to $D_m$. As a result, $D_n$ in a given column is a solute-dependent parameter and cannot be treated as a column parameter. When $D_n$ of two columns is compared in this report, the same solute is always assumed.

On the other hand, the proportionality of $D_n$ to $D_m$ in a given class of self-similar columns suggests that their ratio $D_n/D_m$ might represent a solute-independent property of the class. The dimensionless mobile phase velocity, $v = ud_p/D_m$ introduced by Giddings [22, 62] for packed columns might serve as a prototype for the metric of that property. The reason for not directly using $v$ as such metric is that, being a function $d_p$, quantity $v$ is not a measurable parameter. This problem is avoided in dimensionless quantity:

$$v_U = \frac{d_{eff}u}{2D_m}$$

which can be interpreted as the universal mobile phase velocity – universal because parameter $d_{eff}$ in it is measured the same way for all columns. Let $v_{U,opt}$ be $v_U$ at $u = u_{opt}$. Comparison of Eqs. (36), (37) and (39) yields:

$$v_{U,opt} = \begin{cases} 
D_n/D_m, & \text{LC} \\
D_n/D_{m,\text{st}}, & \text{GC}
\end{cases}$$

indicating that the optimal universal mobile phase velocity ($v_{U,opt}$) of a given solute in a given column is the ratio of its molecular and nominal diffusivities in the column. More experimental data is needed to find out how well a single value of $v_{U,opt}$ for a column class can represent that class.
Due to carrier gas compressibility in GC, $u_{\text{opt}}$ can be different at different locations along a column. This complicates the whole concept of $u_{\text{opt}}$ and its measurement in GC. For an ideal gas, the product $pu$ of pressure ($p$) and $u$ is the same at any location [26, 36, 63]. Thus:

$$pu = p_o u_o, \quad pu_{\text{opt}} = p_o u_{o,\text{opt}}, \quad \text{(ideal gas)}$$ (41)

where $u_o$ and $u_{o,\text{opt}}$ are $u$ and $u_{\text{opt}}$ at the column outlet. Quantity $pu$ can be further transformed into a measurable volumetric flow rate ($F$) measured in GC at predetermined pressure (typically 1 atm) and temperature (typically 25 ºC) [26, 39, 64]. For a given column:

$$\frac{u}{u_{\text{opt}}} = \frac{F}{F_{\text{opt}}}$$ (42)

where $F_{\text{opt}}$ is the optimal $F$ corresponding to $u_{\text{opt}}$. Being a function of $H$, Eq. (29), quantity $e_s$, is a function of $u/u_{\text{opt}}$, i.e. the notation $e_s$ is an abbreviated notation for the functions $e_s(u/u_{\text{opt}})$ and $e_s(F/F_{\text{opt}})$, i.e. $e_s = e_s(u/u_{\text{opt}}) = e_s(F/F_{\text{opt}})$ – the same way as $H$ actually stands for $H(u/u_{\text{opt}})$.

So far, we identified a column intensive properties represented by parameters $d_{\text{eff}}$, $e_s$ and $D_n$. The extensive properties represented by parameters $E$, $t_M$ and $L$ of a particular column relate to quantities $d_{\text{eff}}$, $e_s$ and $D_n$ as [15, 39] (Supplement):

$$E = \frac{d_{\text{eff}}}{\sqrt{2D_n j_{\text{st}} t_p}} \left( e_s \sqrt{\frac{F_{\text{opt}}}{F}} \right)$$ (43)

$$t_M = \frac{d_{\text{eff}}^4}{4D_n^2 j_{\text{st}}^2 t_p^2} \left( \frac{F_{\text{opt}}}{F} \right)^2$$ (44)

$$L = \frac{1}{2D_n j_{\text{st}} t_p} \frac{F_{\text{opt}}}{F}$$ (45)

In these expressions:

$$j_{\text{st}} = \begin{cases} 1, & \text{LC} \\ \frac{p_{\text{st}} f_i}{p_o}, & \text{GC} \end{cases} \quad j_{\text{st}} = \begin{cases} 1, & \text{LC} \\ \frac{3p_{\text{st}}(p_i + p_o)}{2(p_i^2 + p_i p_o + p_o^2)}, & \text{GC} \end{cases}$$ (46)
where \( j \) is the *James-Martin compressibility factor* [26, 65]. Eqs. (43), (44) and (45) express parameters \( t_M, E \) and \( L \) of a particular column at a fixed instrumental pressure (represented by parameter \( t_p \)) as functions of:

- parameters \( e_s \) and \( D_n \) of a class of self-similar columns to which the column belongs
- parameter \( d_{\text{eff}} \) of a particular column
- variable \( F/F_{\text{opt}} \) — the *relative* flow rate in the column

The remaining parameter, \( j_{\text{st}} \) in the expressions represents a separation technique (GC with strong or weak gas decompression along the column, or LC with incompressible solvent) rather than operational conditions in a technique.

As \( e_s \) is a function of \( F/F_{\text{opt}} \), the combination \( (e_s \sqrt{F/F_{\text{opt}}}) \) in Eq. (43) represents a net functions of \( F/F_{\text{opt}} \). The same is true for similar combinations in other equations. When \( F/F_{\text{opt}} \) is fixed, \( e_s \) is fixed even if \( F \) and/or \( F_{\text{opt}} \) vary. Eqs. (43), (44) and (45) allow one to evaluate the effect of parameters \( d_{\text{eff}}, e_s \) and \( D_n \) at a fixed \( F/F_{\text{opt}} \) (e.g. when \( F = F_{\text{opt}} \)). Eq. (45) shows that [15, 39]:

In order to keep the ratio \( F/F_{\text{opt}} \) fixed for all self-similar columns with different effective diameters and lengths operating under the same pressure, the ratio \( L/d_{\text{eff}}^3 \) must be fixed.

According to Eqs. (43) and (44), the following relations of proportionality for self-similar columns exist:

\[
E \sim d_{\text{eff}} \quad t_M \sim d_{\text{eff}}^4 \quad \text{(fixed } t_p \text{ and } F/F_{\text{opt}} \text{)}
\]

Also, together with Eqs. (45) and (46), Eqs. (43) and (44) describe the dependencies of \( E, t_M \) and \( L \) on \( t_p \) and, therefore, on the column pressure. In GC with weak gas decompression along a column
(|Δp|<<p_o) and in LC, quantity j_{st} is fixed (j_{st} = 1 in LC, j_{st} = p_{st}/p_o in GC with |Δp|<<p_o). As a result, Eqs. (44), (43) and (45) provide a complete picture of dependencies of $E$, $t_M$ and $L$ on $Δp$ ($t_M$ and $L$ are proportional to $Δp$ while $E$ is proportional to $\sqrt{Δp}$). This is different in GC with significant gas decompression along the column where presence of the pressure-dependent parameter $j_{st}$ in Eqs. (43), (44) and (45) affects these dependencies on $Δp$. In the extreme case of GC-MS where $p_o = 0$ and $p_t = Δp$, the dependencies become simpler. Eq. (46) yields:

$$j_{st} = \frac{3p_{st}}{2Δp}, \quad (\text{GC-MS})$$

which, together with Eq. (18) allows one to express Eqs. (43), (44) and (45) as:

$$E = \frac{d_{eff} Δp}{\sqrt{96D_{n}p_{st} η}} \left( e_{s} \frac{F_{opt}}{F} \right), \quad (\text{GC-MS})$$

$$t_M = \frac{d_{eff}^4 Δp^3}{288D_{n}^2 p_{st}^3 η} \left( \frac{F_{opt}}{F} \right)^2, \quad (\text{GC-MS})$$

$$\frac{L}{d_{eff}^3} = \frac{Δp^2}{96D_{n}p_{st} η} \frac{F_{opt}}{F}, \quad (\text{GC-MS})$$

indicating that, in order to maintain a fixed ratio $F/F_{opt}$ in self-similar columns with the same $d_{eff}$ in GC-MS, $L$ should increase in proportion to $Δp^2$ causing an increase in $E$ and $t_M$ in proportion to $Δp$ and $Δp^3$, respectively.

Also instructive is the relationship between $t_M$ and $E$ in a column operating below the instrumental pressure limit where the $t_p$ value is not a consideration. Exclusion of $t_p$ from Eqs. (43) and (44) yields:

$$t_M = \frac{E^2 d_{eff}^2}{2D_{n}j_{st}} \left( \frac{F_{opt}}{e_{s}^2 F} \right), \quad (\text{GC-MS})$$
This equation is valid for LC and for GC with any degree of gas decompression along a column.

However, similar to Eqs. (43), (44) and (45), quantity $j_{st}$ in Eq. (52) is fixed only in the case of GC with weak gas decompression along a column and in LC. In these cases, Eq. (52) can be expressed as:

$$t_M = \frac{E^2 d_{eff}^2}{2D_n} \left( \frac{F_{opt}}{e^2 F} \right) \begin{cases} 1, & \text{LC} \\ p_{st}/p_o, & \text{GC at } |\Delta p| << p_o \end{cases} \tag{53}$$

In GC with significant gas decompression, the presence of the pressure-dependent parameter $j_{st}$ in Eq. (52) complicates the relationship between $d_{eff}$, $E$ and $t_M$. The relationship becomes simple in GC-MS. Excluding $\Delta p$ from Eqs. (49) and (50). One has:

$$t_M = d_{eff} E^3 \sqrt{\frac{32\eta}{3D_n p_{st}}} \left( \frac{1}{e^2} \right) \sqrt{\frac{F_{opt}}{F}}, \quad \text{(GC-MS)} \tag{54}$$

Eqs. (52), (54), (33) and (51) represent the following relations of proportionality for self-similar columns operating at fixed $F/F_{opt}$ [15, 26, 39, 45, 66]:

$$t_M \sim E^2, \quad \text{(fixed } d_{eff} \text{ in GC at } \Delta p << p_o \text{ and in LC at } \Delta p < \Delta p_{\text{max}}) \tag{55}$$

$$t_M \sim E^3, \quad \text{(fixed } d_{eff} \text{ in GC at } p_o << \Delta p < \Delta p_{\text{max}}) \tag{56}$$

$$t_M \sim E^4 \quad \text{(fixed } \Delta p \text{ and } \eta) \tag{57}$$

indicating that, if the ratio $F/F_{opt}$ does not change, then the time “price” for increasing the separation performance is the lowest in a column operating below instrumental pressure limit ($\Delta p_{\text{max}}$) if, on top of that, the gas decompression in GC column is weak ($\Delta p << p_o$). On the other hand, the “price” for the separation performance is the highest in a column operating at $\Delta p = \Delta p_{\text{max}}$. Thus, doubling $E$ requires 4 times longer $t_M$ in the least “expensive” case, and 16 times longer $t_M$ in the most “expensive” one. In the intermediate case of GC-MS operating below $\Delta p_{\text{max}}$, doubling $E$ requires 8 times longer $t_M$.

From Eqs. (49), (50) and (51), one can also obtain complete dependencies $t_M(L)$ and $E(L)$ (Supplement) not considered here.
The analysis developed here suggests that there are two essential differences between transport properties of GC and LC, and between kinetics of the techniques in general.

- The mobile phase is compressible in GC and essentially incompressible in LC. This difference leads to the unique for GC third power dependence, $t_M \sim E^3$, Eq. (56), of $t_M$ on $E$, and more generally, to the third power dependence of analysis time on column separation performance.

- Molecular diffusivity ($D_m$) in LC is several orders of magnitude lower than that in GC. It follows from Eq. (44) where the product $D_n j_{st}$ is of the same order of magnitude as $D_m$ that, in order to maintain equal $t_M$ (and, therefore, comparable analysis times) in both techniques, $d_{eff}$ in LC should be substantially smaller than that in GC which causes substantially smaller loadability of an OTC LC column compared to that in GC. This, in turn, is the key reason for using the multi-path (packed, monolithic, pillar-array, etc.) columns in LC with all consequences of such columns.

Other differences between transport properties of the two techniques are less consequential. For example, liquids have much higher viscosity compared to gases. However, liquids can also sustain much higher pressure than gases. As shown in the comments to Eq. (18), the time-equivalents ($t_p$), Eq. (18), of the two factors are comparable in both techniques causing no significant external difference in their performance.

### 3. Discussion

The forthcoming discussion demonstrates how the metric $e_s$ affects the separation-time tradeoff, and how all three core metrics ($e_s$, $D_n$ and $d_{eff}$) can be used for choosing a suitable column and its optimization.

The key feature of metrics in this report is that they can be measured experimentally. However, their numerical values in the discussion are based in several cases on theoretical evaluations. It is assumed
in all numerical examples and illustrations that a WCOT column has thin stationary phase film (film thickness has negligible effect on plate height), and a packed column is packed with spherical particles of the same size. Parameters of several column types and/or specific columns together with their operational conditions are compiled in Error! Reference source not found..

Quantity $H_{min}$ and related parameters in Error! Reference source not found. substantially depend on retention factor ($k$). In Error! Reference source not found., the entries for WCOT columns correspond to $k = 0$ and $k = 2$. The choice of $k = 2$ is not accidental and can be recommended for column comparison. In temperature-programmed GC at optimal heating rate [13, 39, 44], and in gradient LC with optimal mixing rate [15, 17, 45, 66], all solutes elute with $k \approx 2$. As a result, parameters statically measured at $k \approx 2$ also represent elution parameters in optimal dynamic analyses. The $k$-values for other columns in Error! Reference source not found. were taken from published experimental results. The data available for $k$ closest to $k \approx 2$ were chosen where possible. The relationships between $t_M$ and $E$, Eq. (33), for the data with $k > 0$ in Error! Reference source not found. are illustrated in Figure 1.

3.1 Attainable column performance

Eq. (33) and Figure 1 describe and illustrate the dependence of relationship between $E$ and $t_M$ on $e_s$. However, they don’t say what actual $E$ or $t_M$ can be obtained from actually available columns. These values can be found for LC and GC under all operational conditions from Eqs. (43) and (44) which, for specifics of GC-MS were reduced to Eqs. (49) and (50). The optimal values $E_{Opt}$, $t_{M,Opt}$ and $e_{s,max}$ of quantities $E$, $t_M$ and $e_s$ for the column with $k > 0$ in Error! Reference source not found. are compiled in Error! Reference source not found..

Speaking of attainable performance, we do not attempt to identify specific performance limits for practically available columns of each evaluated type. Instead, we consider this discussion as an
illustration of how these issues can be addressed using parameters \( e_s, D_n \) and \( d_{\text{eff}} \). For that purpose, we treat the column cross-sectional dimensions in Error! Reference source not found. and Error! Reference source not found. as the smallest that can be currently manufactured and assume that larger dimensions are available. The dependencies of \( E_{\text{opt}} \) and \( t_{M,\text{opt}} \) on \( d_{\text{eff}} \) are shown in Figure 2 where the markers correspond to \( d_{\text{eff}} \)-values in Error! Reference source not found.. The thinner lines to the left of the markers represent the operations that are assumed to be currently impossible as they require smaller than currently available \( d_{\text{eff}} \).

Suppose that, in analyses of small molecules, \( t_M \) larger than 10 min (about 1 hour long analysis at optimal mixing rate [15, 45, 66]) are unacceptable. Figure 2b and the listing of \( t_{M,\text{opt}} \) (the shortest \( t_M \) for a given \( E \) in each column type) in Error! Reference source not found. show that only GC-MS WCOT and LC packed columns satisfy this requirement. Interestingly, the two packed columns (the only two practically useful LC columns at \( \Delta p = 1200 \) bars) have the lowest (the worse) \( e_{s,\text{max}} \) (Error! Reference source not found. and Error! Reference source not found.) of all columns in Error! Reference source not found. and Error! Reference source not found.. This is not a contradiction because \( e_{s,\text{max}} \) is a metric of the tradeoff between \( E \) and \( t_M \) for a given column type, but not a measure of \( E \) and \( t_M \) actually obtainable from a particular column.

The effective diameters found by solving Eqs. (44) and (50) for \( d_{\text{eff}} \) at \( t_M = 10 \) min and \( F = F_{\text{opt}} \), as well as other cross-sectional dimensions of the column types in Error! Reference source not found. that yield \( t_{M,\text{opt}} = 10 \) min are listed in Error! Reference source not found. together with corresponding \( E_{\text{opt}} \). Also listed in Error! Reference source not found. are \( e_{s,\text{max}} \) for each column type (copied from Error! Reference source not found.). Using the data in Error! Reference source not found., one can observe that, since all columns yield the same \( t_{M,\text{opt}} \), a column with larger \( e_{s,\text{max}} \) yields
proportionally larger $E_{\text{Opt}}$. And, of course, as their $e_{s,\text{max}}$ are the lowest, the two packed LC columns have the lowest $E_{\text{Opt}}$.

The data in Error! Reference source not found. also show that, in order to yield a reasonable void time at high $\Delta p$ (10 min and 1200 bar in Error! Reference source not found.), the $d_{\text{eff}}$ of a LC column should be in vicinity of 1 µm, and internal diameters ($d$) of an OTC (WCOT, PLOT) in LC should be close to that. With so small internal diameter, a reasonably fast LC OTC has very low loadability. For that reason, no LC OTC is included in further evaluations. Also excluded are the WCOT GC columns typical for GC. Their separation-time tradeoffs are practically limited not by the maximum available pressure, but by the loadability [39].

Among the remaining pillar-array and conventional packed columns (core-shell and totally porous), the pillar-array ones ($e_{s,\text{max}} = 0.643$) appear to have 56% to 93% better transport quality compared to the packed columns ($e_{s,\text{max}} = 0$.Error! Reference source not found. and Error! Reference source not found.). Thus, the pillar-array column in Error! Reference source not found. delivers 56% to 93% larger $E$, respectively, than the other two deliver with the same $t_{M,\text{Opt}}$. However, in order to realize their structural advantage and obtain their higher available $E$ in a practically reasonable $t_{M,\text{Opt}}$, the pillar dimensions should be reduced by about a factor of 2 – from the ones in Error! Reference source not found. to those in Error! Reference source not found.. Without that, the pillar-array columns can compete with conventional packed ones only in the instruments that cannot supply high pressure.

3.2 Sub-optimal LC operations

So far, the changes in column dimensions were evaluated at fixed ratio $F/F_{\text{opt}}$ with possible changes in $F$ and $F_{\text{opt}}$. The fixed $F/F_{\text{opt}}$ case includes the flow-optimized case of $F = F_{\text{opt}}$. As shown below, allowing for the ratio $F/F_{\text{opt}}$ to change and for the column to operate at sub-optimal conditions ($F \neq F_{\text{opt}}$) can be beneficial in some cases.
Let $E_{\text{Opt}}$ and $t_{M,\text{Opt}}$ be the transport efficiency and the void time, respectively, in a column having effective diameter $d_{\text{eff}}$ and flow-optimized at the instrumental pressure limit ($\Delta p_{\text{max}}$). Suppose that $E_{\text{Opt}}$ is substantially different from a required target $E$ ($E_{\text{targ}}$). Three ways of obtaining $E_{\text{targ}}$ are considered below.

(a) Ideally, one would prefer another self-similar column, the target one, that has its own effective diameter $d_{\text{eff,targ}}$ and optimal flow ($F_{\text{opt,targ}}$) so that, at $F = F_{\text{opt,targ}}$ and $\Delta p_{\text{max}}$, its optimal $E$ is $E_{\text{targ}}$.

Due to proportionality $E \sim d_{\text{eff}}$, Eq. (47), one has:

$$\frac{d_{\text{eff,targ}}}{d_{\text{eff}}} = \frac{E_{\text{targ}}}{E_{\text{Opt}}}$$  \hspace{1cm} (58)

(b) If $E_{\text{targ}} < E_{\text{Opt}}$ then $E_{\text{targ}}$ can be obtained at $F = F_{\text{opt}}$ and $\Delta p < \Delta p_{\text{max}}$ in a shorter column.

(c) $E_{\text{targ}}$ can be also obtained at $\Delta p_{\text{max}}$ by changing the column length ($L$) without changing $d_{\text{eff}}$ \cite{11, 14, 58} and allowing for $F \neq F_{\text{opt}}$.

Different conditions lead to different $t_{M}$, Figure 3, at the same $E_{\text{targ}}$. It follows from Eqs. (55) and (57) that the ratio $t_{M}/t_{M,\text{Opt}}$ is proportional to $(E_{\text{targ}}/E_{\text{Opt}})^{4}$ in case (a) and to $(E_{\text{targ}}/E_{\text{Opt}})^{2}$ in case (b). The relations in case (c) are more complex and depend on specifics of dependency of $H$ (and, therefore, $e_{s}$) on $F/F_{\text{opt}}$. Shown in Figure 3 are the graphs based on Eq. (34) with several values of parameter $a$ defined in Eq. (34). The mathematics are described in the Supplement.

Figure 3 confirms that, as expected, the target column having effective diameter $d_{\text{eff,targ}}$ and operating at $F = F_{\text{opt,targ}}$, case (a), provides the most time-efficient way of obtaining $E_{\text{targ}}$, i.e. the shortest $t_{M}$ at $E_{\text{targ}}$ regardless of the difference between $E_{\text{targ}}$ and $E_{\text{Opt}}$, or, from another perspective \cite{58}, regardless of the difference between the required effective diameter ($d_{\text{eff,targ}}$) and the available one ($d_{\text{eff}}$). Suppose that $E_{\text{targ}} < E_{\text{Opt}}$, but $d_{\text{eff}}$ cannot be reduced. The time saving due to reduction in $E$ without changing $d_{\text{eff}}$ can be obtained by reducing the column length ($L$). Two ways of doing so are illustrated in Figure 3. In
case (b), a shorter column can be flow-optimized at $\Delta p < \Delta p_{\text{max}}$. In case (c), the column length is reduced without reducing $\Delta p$, i.e. keeping $\Delta p = \Delta p_{\text{max}}$ and, therefore, using non-optimal flow $F > F_{\text{opt}}$.

Figure 3 shows that (b) is the least time-efficient case – it requires the longest $t_M$ for obtaining the same $E_{\text{targ}}$. One can conclude that,

The most time-efficient way of obtaining a required $E$ ($E_{\text{targ}}$) is by using a target column having target effective diameter ($d_{\text{eff,targ}}$) that optimizes the column at maximum instrumental pressure ($\Delta p_{\text{max}}$).

However, if $E_{\text{targ}} < E_{\text{Opt}}$ but a column with smaller $d_{\text{eff}}$ is not available, it is always more time-efficient to obtain $E_{\text{targ}}$ at $\Delta p_{\text{max}}$ using non-optimal flow rather than using optimal flow at $\Delta p < \Delta p_{\text{max}}$.

Figure 3 at $E_{\text{targ}}/E_{\text{Opt}} > 1$ also shows that it is possible to raise $E$ above $E_{\text{Opt}}$ by using sub-optimal conditions ($L > L_{\text{Opt}}$ and, therefore, $F < F_{\text{opt}}$) in a column with a given $d_{\text{eff}}$ operating at $\Delta p_{\text{max}}$, case (c).

However, although it is a possibility, this way of raising $E$ is less time-efficient than the case (a) and its highest available $E$ is limited. As shown in the Supplement, in a column with $H$ in Eq. (34), $E$ at $\Delta p_{\text{max}}$ cannot exceed $\sqrt{2/(1-a)}E_{\text{Opt}}$.

Figure 3 also shows that the purpose of reducing a column characteristic cross-sectional dimensions ($d_{\text{eff}}, d_p$, etc.) without changing $\Delta p$ is to reduce the efficiency with the purpose of disproportionally greater reduction in analysis time.

4. Conclusions

Three measurable parameters (metrics) – effective diameter ($d_{\text{eff}}$), specific efficiency ($e_s$) and nominal diffusivity ($D_n$), representing three core intensive properties of GC and LC columns – are
sufficient for objective comparison of the column separation-time performance. Quantities $e_s$ and $D_n$ represent the properties of classes of self-similar columns while $d_{\text{eff}}$ represent a particular column. The largest number of peaks that a chromatographic system can resolve in a fixed time is proportional to $e_s$ giving rise to interpreting $e_s$ as a measure of column transport quality, or more precisely as the ability of a particular column design to transport and elute the solutes with a minimum of peak broadening and pressure losses. The higher is $e_s$ the shorter (the better) is the analysis time required for resolving the same number of peaks. Quantity $e_s$ is equivalent to, introduced here, universal plate height ($h_U$) and to separation impedance (SI) introduced by Bristow and Knox for packed LC columns and extended here to all LC and GC columns. All three ($e_s$, $h_U$ and SI) are nothing but differently normalized and differently powered familiar dimensionless plate heights. The advantage of the quantity $e_s$ over the others is that it is proportional to the number of components that can be resolved with a given column which is the ultimate performance measure for any chromatographic column.

The time of chromatographic analysis is proportional to void time ($t_M$) while the largest number of peaks that a column can resolve is proportional to the column transport efficiency ($E$) which, in turn, is proportional to $e_s$. It has been shown that the core set of parameters ($d_{\text{eff}}$, $e_s$ and $D_n$) is sufficient for describing the relations between $E$, $t_M$, and other specific parameters of a column and its operation (column length ($L$), flow rate ($F$), pressure drop ($\Delta p$), etc.). The relationships between $d_{\text{eff}}$, $e_s$, and $D_n$ on the one hand and parameters $E$, $t_M$, $\Delta p$, $L$ and $F$ on the other have been established. Some implications of these relations are:

In a column operating below instrumental pressure limit, reduction in $d_{\text{eff}}$ can be used for making larger $E$, or shorter $t_M$, or for obtaining both improvements. Reducing $d_{\text{eff}}$ increases required $\Delta p$. Once the instrumental pressure limit is reached, the effect of further reduction in $d_{\text{eff}}$ changes. If a fixed ratio
\( F/F_{\text{opt}} \) is maintained at any \( d_{\text{eff}} \) and fixed \( \Delta p \) then the reduction in \( d_{\text{eff}} \) reduces \( t_M \) in proportion with the 4th power of reduction in \( d_{\text{eff}} \) at the expense of reducing \( E \) in proportion with the reduction in \( d_{\text{eff}} \).

To keep the ratio \( F/F_{\text{opt}} \) fixed when \( d_{\text{eff}} \) changes and \( \Delta p \) does not, the change should be accompanied by changing \( L \) in a way that keeps the ratio \( L/d_{\text{eff}}^3 \) fixed.

The most time-efficient way of obtaining a required (target) \( E \) \( (E_{\text{targ}}) \) is by using a target column having target effective diameter \( (d_{\text{eff,targ}}) \) that optimizes the column at maximum instrumental pressure \( (\Delta p_{\text{max}}) \). However, even if a column with \( d_{\text{eff,targ}} \) is not available, it is always more time-efficient to obtain \( E_{\text{targ}} \) at \( \Delta p_{\text{max}} \) using sub-optimal conditions rather than using optimal conditions at \( \Delta p < \Delta p_{\text{max}} \).

Although only LC and GC are considered, the study in this report suggests that the same approach can be extended to other techniques where the concepts similar to those of void time and maximum available pressure can be identified.

5. Nomenclature

Abbreviations:

OTC – open-tubular column
PLOT – porous layer open tubular
SI – separation impedance
SPI – specific performance index
WCOT – wall-coated open-tubular

Subscripts:

max – maximum
min – minimum
opt – optimum at $H_{\text{min}}$

Opt – optimum at lowest $H_{\text{min}}$ and fixed $\Delta \rho$
## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$</td>
<td>internal diameter of open space in OTC</td>
</tr>
<tr>
<td>$d_c$</td>
<td>internal diameter of column tubing</td>
</tr>
<tr>
<td>$d_{eff}$</td>
<td>effective diameter, Eq. (16)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>particle size</td>
</tr>
<tr>
<td>$D_m$</td>
<td>solute diffusivity in mobile phase</td>
</tr>
<tr>
<td>$D_{m, st}$</td>
<td>$D_m$ at 1 atm</td>
</tr>
<tr>
<td>$D_n$</td>
<td>nominal diffusivity, Eq. (37)</td>
</tr>
<tr>
<td>$D_{op}$</td>
<td>$D_n$ rescaled to pressure $p$, Eq. (36)</td>
</tr>
<tr>
<td>$E$</td>
<td>transport efficiency, Eq. (5)</td>
</tr>
<tr>
<td>$e_s$</td>
<td>specific transport efficiency, Eq. (29)</td>
</tr>
<tr>
<td>$F$</td>
<td>mobile phase volumetric flow rate</td>
</tr>
<tr>
<td>$H$</td>
<td>(apparent) plate height, Eqs. (2) and (6)</td>
</tr>
<tr>
<td>$h$</td>
<td>dimensionless plate height, Eqs. (3) and (4)</td>
</tr>
<tr>
<td>$h_U$</td>
<td>universal plate height, Eq. (25)</td>
</tr>
<tr>
<td>$j_H$</td>
<td>Halász-Hartmann-Heine compressibility factor, Eq. (10)</td>
</tr>
<tr>
<td>$j_{st}$</td>
<td>Eq. (46)</td>
</tr>
<tr>
<td>$k$</td>
<td>retention factor (the same as $k'$)</td>
</tr>
<tr>
<td>$K_v$</td>
<td>transport permeability, Eq. (8)</td>
</tr>
<tr>
<td>$L$</td>
<td>column length</td>
</tr>
<tr>
<td>$m$</td>
<td>statistically expected number of resolved peaks</td>
</tr>
<tr>
<td>$n_c$</td>
<td>peak capacity</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
</tr>
<tr>
<td>$p_i$</td>
<td>inlet pressure</td>
</tr>
<tr>
<td>$p_o$</td>
<td>outlet pressure</td>
</tr>
<tr>
<td>$p_{st}$</td>
<td>standard pressure, $p_{st} = 1$ atm</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>pressure drop</td>
</tr>
<tr>
<td>$\Delta p_{eff}$</td>
<td>effective pressure, Eq. (9)</td>
</tr>
<tr>
<td>$s$</td>
<td>separation capacity</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
</tbody>
</table>
\( t_M \)  void time

\( t_p \)  time-equivalent of pressure and viscosity, Eq. (18)

\( u \)  mobile phase velocity

\( u_o \)  mobile phase outlet velocity

\( \eta \)  mobile phase viscosity

\( \sigma \)  peak standard deviation (width)

\( \phi \)  transport resistance factor, Eq. (13)

6. References


acetonitrile–water mixtures at pressures up to 3500 bar using a novel capillary time-of-flight

Chromatography Columns with Inner Diameters from 20 to 50 µm, Anal. Chem. 61 (1989) 1128-
1135.

[56] S. Deridder, M. Catani, A. Cavazzini, G. Desmet, A theoretical study on the advantage of core-

[57] L. M. Blumberg, M. S. Klee, Method Translation and Retention Time Locking in Partition GC,


[59] H. Song, Y. Vanderheyden, E. Adams, G. Desmet, D. Cabooter, Extensive database of liquid
phase diffusion coefficients of some frequently used test molecules in reversed-phase liquid
chromatography and hydrophilic interaction liquid chromatography, J. Chromatogr. A 1455
(2016) 102-112.

[60] E. N. Fuller, J. C. Giddings, A Comparison of Methods for Predicting Gaseous Diffusion

[61] C. R. Wilke, P. Chang, Correlation of diffusion coefficients in dilute solutions, AIChE J. 1
(1955) 264-270.

[62] J. C. Giddings, Reduced Plate Height Equation: A Common Link between Chromatographic
Methods, J. Chromatogr. 13 (1964) 301-304.


Figure Captions

Figure 1. Void time ($t_M$) vs. efficiency ($E$), Eq. (33), at maximum specific efficiency ($e_{s,max}$), Table 1, for each column type operating at $t_p = 0.2$ ns – nearly the lowest (the best) practical $t_p$, Eq. (19). In each column type, $E$ at the same $t_M$ is proportional to its $e_{s,max}$, while $t_M$ at a the same $E$ is inversely proportional to $e_{s,max}$.

Figure 2. Optimal transport efficiency and void time ($E_{Opt}$ and $t_{M,Opt}$), Eqs. (43), (44), (49) and (50), vs. effective diameters ($d_{eff}$) in Table 2 for the columns operating at $t_p = 0.2$ ns. All other conventions and conditions are the same as in Figure 1. The $t_{M,Opt}$ marker for LC WCOT in (b) falls far above the graph.

Figure 3. Void time ($t_M$) at the same target efficiency ($E_{targ}$) in several columns and conditions as explained in the main text. Due to Eq. (58), the graphs can be interpreted as functions of the ratio $E_{targ}/E_{Opt}$ or $[58]$ of the ratio $d_{eff,targ}/d_{eff}$. The dash-dot line for $\Delta p \leq \Delta p_{max}$, case (b), only exists at $E_{targ} \leq E_{Opt}$, i.e., equivalently, at $d_{eff,targ} \leq d_{eff}$.
Figure

- packed LC, total pores
- packed LC, core-shell
- pillar-array LC
- PLOT LC
- WCOT GC, $\Delta p \gg p_0$
- WCOT LC
\[ \frac{d_{\text{eff}, \text{targ}}}{d_{\text{eff}}} = \frac{E_{\text{targ}}}{E_{\text{Opt}}} \]

- \( \Delta p = \Delta p_{\text{max}}, F = F_{\text{opt,targ}} \)
- \( \Delta p \leq \Delta p_{\text{max}}, F = F_{\text{opt}} \)
- all others: \( \Delta p = \Delta p_{\text{max}}, F \neq F_{\text{opt}} \)
Table 1. Column parameters and experimental conditions.

<table>
<thead>
<tr>
<th>Column</th>
<th>Conditions</th>
<th>$K_v$</th>
<th>$d_{\text{eff}}$ Eq. (17)</th>
<th>$H_{\text{min}}$</th>
<th>$e_{\text{s,max}}$ Eq. (29)</th>
<th>$h_{U,\text{min}}$ Eq. (25)</th>
<th>$SI_{\text{min}}$ Eq. (24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCOT [26]</td>
<td>$k = 0$ GC at $</td>
<td>\Delta p</td>
<td>&lt;&lt; p_o$, LC</td>
<td>$d^2/32$</td>
<td>$d$</td>
<td>0.289$d$</td>
<td>1.861</td>
</tr>
<tr>
<td></td>
<td>GC-MS</td>
<td></td>
<td>0.866$d$</td>
<td>0.325$d$</td>
<td>1.633</td>
<td>0.375</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>$k = 2$ GC at $</td>
<td>\Delta p</td>
<td>&lt;&lt; p_o$, LC</td>
<td>$d$</td>
<td>0.726$d$</td>
<td>1.173</td>
<td>0.726</td>
</tr>
<tr>
<td></td>
<td>GC-MS</td>
<td></td>
<td>0.866$d$</td>
<td>0.817$d$</td>
<td>1.029</td>
<td>0.944</td>
<td>28.5</td>
</tr>
<tr>
<td>PLOT [67]</td>
<td>$k = 1.42$ LC</td>
<td>$d^2/39.2$</td>
<td>0.903$d$</td>
<td>5.24 $\mu$m</td>
<td>0.874</td>
<td>1.31</td>
<td>54.7</td>
</tr>
<tr>
<td>Pillar-array [21]</td>
<td>$k = 2.3$</td>
<td>$0.27 \mu m^2$</td>
<td>2.94 $\mu$m</td>
<td>7.1 $\mu$m</td>
<td>0.643</td>
<td>2.41</td>
<td>186</td>
</tr>
<tr>
<td>Packed CS [68]</td>
<td>$k = 6$, $\varphi_p = 1/6$</td>
<td>$d_p^2/569$</td>
<td>0.237$d_p$</td>
<td>1.4$d_p$</td>
<td>0.412</td>
<td>5.9</td>
<td>1115</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_p = 0.4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed TP [68]</td>
<td>$\varphi_p = 1/2$</td>
<td>$d_p^2/640$</td>
<td>0.224$d_p$</td>
<td>2$d_p$</td>
<td>0.334</td>
<td>8.94</td>
<td>2560</td>
</tr>
</tbody>
</table>

Notes:
The columns are listed in the order of decreasing (worsening) $e_{\text{s,max}}$.
Quantities $H_{\text{min}}$, $e_{\text{s,max}}$, $h_{U,\text{min}}$ and $SI_{\text{min}}$ are $H$, $e_s$, $h_U$ and SI, respectively, at $F = F_{\text{opt}}$.
Highlighted are only the values of $e_{\text{s,max}}$ at $k > 0$.
CS = core-shell, TP = total porosity, $\varepsilon_p$ = porosity of packing material, $\varphi_p = d_S/d_p$ ($d_S$ = shell thickness).
Table 2. Performance ($E_{\text{Opt}}$, $t_{M,\text{Opt}}$) of several column types at $t_p = \eta/\Delta p = 0.2$ ns, Eq. (19).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Column</th>
<th>$D_n/(\text{cm}^2/\text{s})$, source</th>
<th>$d_{\text{cx}}$</th>
<th>$d_{\text{cx}}/\mu\text{m}$</th>
<th>$d_{\text{eff}}/\mu\text{m}$</th>
<th>$e_{s,\text{max}}$</th>
<th>$E_{\text{Opt}}$, Eqs. (44), (50)</th>
<th>$t_{M,\text{Opt}}$/min, Eqs. (45), (51)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-MS</td>
<td>WCOT</td>
<td>1.3, Eq. (38)</td>
<td>$d$</td>
<td>100</td>
<td>86.6</td>
<td>1.029</td>
<td>1349</td>
<td>9.83</td>
</tr>
<tr>
<td>LC</td>
<td>WCOT</td>
<td>0.000004, estimate</td>
<td>$d$</td>
<td>100</td>
<td>100</td>
<td>1.173</td>
<td>92726</td>
<td>$1.3\times10^8$</td>
</tr>
<tr>
<td>PLOT [67]</td>
<td>0.0000088</td>
<td></td>
<td>$d$</td>
<td>4.59</td>
<td>4.15</td>
<td>0.874</td>
<td>6084</td>
<td>7813</td>
</tr>
<tr>
<td>Pillar-array [21]</td>
<td>0.000031</td>
<td>($d_{\text{pil}}, \Delta y$)</td>
<td>(5, 2.5)</td>
<td>2.94</td>
<td>0.643</td>
<td>1702</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>packed CS</td>
<td>0.000014, Eq. (38)</td>
<td>$d_p$</td>
<td>2</td>
<td>0.474</td>
<td>0.412</td>
<td>260</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>packed TP</td>
<td>0.000014, Eq. (38)</td>
<td>$d_p$</td>
<td>2</td>
<td>0.447</td>
<td>0.334</td>
<td>199</td>
<td>0.417</td>
<td></td>
</tr>
</tbody>
</table>

Notes:

$D_n$ values in LC represent small molecules only.

$d_{\text{pil}}$ and $\Delta y$ are pillar diameter and inter-pillar distance, respectively [21].

$d_{\text{cx}}$ is a symbol for cross-sectional dimensions $d, d_{\text{pil}}, \Delta y, d_p$ of different columns

Other conventions are as in Table 1
Table 3. Cross-sectional dimensions \(d_{\text{eff}}, d_{\text{cx}}\) and optimal efficiency \(E_{\text{Opt}}\) for the columns in Table 2 at \(t_p = \eta/\Delta p = 0.2\) ns and \(t_{M,\text{Opt}} = 10\) min.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Column</th>
<th>(d_{\text{cx}})</th>
<th>(d_{\text{cx}}/\mu m)</th>
<th>(d_{\text{eff}}/\mu m) Eqs. (45), (51)</th>
<th>(e_{\text{s, max}})</th>
<th>(E_{\text{Opt}}) Eqs. (44), (50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-MS</td>
<td>WCOT</td>
<td>(d)</td>
<td>100.4</td>
<td>87</td>
<td>1.029</td>
<td>1355</td>
</tr>
<tr>
<td>LC</td>
<td>WCOT</td>
<td>(d)</td>
<td>1.67</td>
<td>1.67</td>
<td>1.173</td>
<td>1544</td>
</tr>
<tr>
<td></td>
<td>PLOT</td>
<td>(d)</td>
<td>0.868</td>
<td>0.784</td>
<td>0.874</td>
<td>1151</td>
</tr>
<tr>
<td></td>
<td>Pillar</td>
<td>((d_{\text{pit}}, \Delta y))</td>
<td>(2.49, 1.24)</td>
<td>1.46</td>
<td>0.643</td>
<td>847</td>
</tr>
<tr>
<td></td>
<td>packed CS</td>
<td>(d_p)</td>
<td>4.17</td>
<td>0.99</td>
<td>0.412</td>
<td>541</td>
</tr>
<tr>
<td></td>
<td>packed TP</td>
<td>(d_p)</td>
<td>4.43</td>
<td>0.99</td>
<td>0.334</td>
<td>440</td>
</tr>
</tbody>
</table>

Notes: \(d_{\text{cx}}\) values were found by rescaling their counterparts in Table 2 in proportion with changes in their \(d_{\text{eff}}\) values.
Click here to download Electronic Supplementary Material (online publication only): Transport properties - Supplement.docx