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THE NOMENCLATURE OF CHROMATOGRAPHY

II. LIQUID CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

This paper is the second in a three-part series, the purpose of which is to help unification of the nomenclature, terms, symbols and definitions used in chromatography. Part I[1] gave a general introduction to the subject and dealt in detail with questions related to gas chromatography (GC). The subject of this paper, Part II, is liquid chromatography (LC).

The situation in LC is different to that in GC. Gas chromatography, in the modern sense, developed very quickly, within less than a decade, and generally the people involved in it represented a fairly close-knit group, meeting frequently. Although their professional backgrounds were different, they considered their involvement in GC as their main activity: they were "chromatographers" by both activity and devotion. As a logical consequence of this, they had from the beginning a natural desire to unify and standardize and we should not underestimate this attitude. We should add that in the evolution of GC theoretical treatments and calculations played

an important role, and here one must agree on clearly distinguishable definitions and symbols. This automatically leads to standardization.

The evolution of liquid chromatography was different. This variant of chromatography is much older than the others and it developed more or less empirically, by trial and error. As pointed out earlier[2], until the early 1940s "it remained an art based only on a body of empirical observations and an intuitive use of the underlying physico-chemical phenomena". Also, the scientists involved in its development did not consider chromatography as their main activity: they were primarily biochemists or organic chemists for whom chromatography was only a tool in their main research field. Also, there was very little theory and therefore there was really not much to standardize in terms, symbols and definitions. Only after the evolution of the modern approach involving higher inlet pressures, smaller particles and conditions optimized according to theoretical approaches did the need for a standardized approach to the nomenclature become evident.

A further problem in liquid chromatography is that while gas chromatography has always been a single technique, this is not true of liquid chromatography. Its variants have often been handled as separate techniques, sometimes even with the term "chromatography" missing from their name, and, to some extent, this is true even today. The fact that within the American Society for Testing and Materials (ASTM) the nomenclature on liquid-exclusion (gel-permeation) chromatography is under the jurisdiction of Committee D-20 on Plastics while the other chromatography nomenclatures are handled by a special group (Committee E-19) devoted solely to chromatography, and that the proposal of the International Union of Pure and Applied Chemistry (IUPAC) for a nomenclature on ion exchange does not have the word "chromatography" in its title, are good illustrations of this plurality. Hence the efforts of IUPAC to create a unified approach to the nomenclature of chromatography and to have one group handling the various chromatography techniques is even more commendable.

2. THE VARIANTS OF CHROMATOGRAPHY

In Part I[1] we gave the definition of chromatography according to the generalized IUPAC nomenclature[3]. Gas chromatography is a relatively simple technique where further subdivision is usually made only on the basis of the mechanism of separation, using the terms adsorption and partition chromatography. However, the situation is more complicated in liquid chromatography, where further subdivision based on a number of principles is possible. Hence, we have to deal with this question here.

In general, chromatography can be subdivided on the basis of a number of principles. Five such subdivisions are widely used in practice and are also included, at least in principle, in the general nomenclatures. These are based on the following principles:

(a) the physical form of the chromatographic bed;
(b) the way in which the sample is fed into the chromatographic bed and whether an eluent is used or not;
(c) the physical state of the two phases;
(d) the mechanism of separation; and
(e) the relative polarity of the two phases.

According to the first classification we distinguish between *column chromatography* and *planar* (or *plane*) *chromatography*. In the former, the stationary phase is contained in a cylindrical tube (the *column*), while in the latter it is present as or on a plane. *Paper* (PC) and *thin-layer chromatography* (TLC) belong to planar chromatography. Gas chromatography automatically refers to column chromatography while liquid chromatography can be carried out in either way. In addition to the difference in the physical form, column and planar chromatography usually also differ in the way the separated fractions appear: in planar chromatography the separated fractions appear as spots behind the mobile phase front on the paper or layer, while in present-day column chromatography the sample components elute from the column at different times. The term "planar" or "plane" chromatography is a very useful term and thus should be universally adopted.

Considering the method of sample introduction and the presence or absence of a mobile phase, we can distinguish between *frontal*, *displacement* and *elution chromatography*. These represent the basic subgroups of all chromatographic techniques[4], well defined in every textbook and in the standard nomenclatures. Practically all of our present-day methods represent elution chromatography where a mobile phase is used.

Considering the physical state of the mobile phase, we can distinguish between *gas chromatography*, where it is a gas, and *liquid chromatography*, where it is a liquid. Concerning the stationary phase, it can be a liquid or a solid, or a liquid chemically bonded to a solid.

Based on the mechanism of the separation, we can distinguish between six techniques. Four of these are recognized in the standard nomenclatures: these are *partition chromatography*, where the separation is based on differences in the solubilities of the sample components in the mobile and stationary phases, *adsorption chromatography*, where the separation is based on the different adsorption affinities of the sample components toward the surface of an active solid, *ion-exchange chromatography*, where the separation is based on differences in the ion-exchange affinities of the sample components, and *exclusion chromatography*, where the size of the molecules plays the dominant role in the separation.

In addition to these four, two other variants became important relatively recently. The first is *ion-pair chromatography*, sometimes also called extraction chromatography, paired-ion chromatography, ion-pair extraction (or partition) chromatography, chromatography with a liquid ion exchanger or soap chromatography. This technique, in which ion-exchange and partition chromatography are combined, had been used earlier in classical liquid chromatography and liquid–liquid extraction; it was adapted to modern, high-resolution liquid chromatography by a number of researchers in 1973–1975[5a]. *Affinity chromatography*, the other new variant, exploits the unique biological specificity of the protein–ligand interaction and is used for the separation of proteins. The beginning of the technique can be related to the activities of Porath and co-workers[6,7] and of Cuatrecasas, Wilchek and Anfinsen[8].

Recently, the term *bonded-phase chromatography* has sometimes been applied to indicate partition chromatography with the liquid stationary phase chemically bonded to a solid; in fact, this term is even used in popular textbooks[5,9]. It is true that today, these column packings represent the most widely used materials and their recognition is therefore advisable. This is done in the ASTM liquid chromatography

nomenclature[10], which lists the term *bonded phase**, and this is the proper way to handle it. We see no reason for "bonded-phase chromatography" as a separate subgroup; after all, the separation mechanism is not different to those already well established by the existing terms.

Exclusion chromatography is a relatively new term to describe the technique in which the separation is based on the size of molecules. This variant of chromatography was originally introduced in 1959 by Porath and Flodin[11] as "gel filtration" (without "chromatography"), utilizing hydrophilic cross-linked polydextran gels, mainly for biochemical applications. The evolution of the technique increased significantly in the early 1960s after Moore introduced the hydrophobic polystyrene gels and described the application of the technique (he called it first "gel permeation chromatography" or GPC) for the determination of the molecular weight distribution of polymers[12,13]. As the technique spread, there were attempts to unify its name and, *e.g.*, Determann[14] proposed "gel chromatography" while the generalized IUPAC nomenclature[3] used "permeation" (or "gel permeation") chromatography, similarly to Moore. Recently, however, the term "size-exclusion chromatography" or simply "exclusion chromatography" has gained ground and has been accepted by ASTM Committees E-19 on Chromatography and D-20 on Plastics. Thus, the universal acceptance of this term is proposed.

It should be mentioned that the generalized IUPAC nomenclature[3] proposed to group exclusion chromatography and ion-exchange chromatography together, under the common term "liquid gel chromatography". This name is, however, not precise and therefore is misleading. After all, as mentioned above, "gel chromatography" has already been proposed by Determann as a joint name for "gel filtration" and "gel permeation" chromatography (however, without ion-exchange chromatography); furthermore, modern stationary phases used in exclusion chromatography are really not "gels". Hence we feel that this term should not be included in future revisions.

The last principle on which subdivision may be based is the relative polarity of the two phases. This distinction is particularly important in liquid chromatography. In GC, the mobile phase is always inert and thus the separation is based on the interaction between the sample molecules and the stationary phase; in other words, here we are concerned only with the polarity of *one* phase. This is not so, however, in liquid chromatography: here, the mobile phase represents an *additional* component influencing the separation mechanism. We may have two cases: in the first, the stationary phase is more polar than the mobile phase while in the second case the opposite is true. The first variant is called *normal-phase chromatography* and the second *reversed-phase chromatography*.

Reversed-phase chromatography was originally introduced in 1950 by Howard and Martin[15] and for some time was widely used in paper chromatography. However, at the start of modern (column) liquid chromatography, it fell in a temporary eclipse. This is the reason why the generalized IUPAC nomenclature[3] which was originally compiled about that time (its draft[16] was first published in 1972) calls reversed-phase chromatography a technique of only "historical interest". Since then the situation

* The IUPAC nomenclature[3] was compiled before these materials became important.

has changed and today reversed-phase chromatography is probably the most widely used variant of liquid chromatography.

It should be mentioned here that the name of the technique is often misspelled. As clearly stated by the standard nomenclatures[3,10] it should be reverse*d*-phase chromatography and not reverse-phase as used in some popular textbooks[5,9].

Finally, a few words are necessary concerning "liquid chromatography". When modern liquid chromatography, utilizing high inlet pressures and small-diameter particles, started to evolve, researchers coined the name *high-pressure liquid chromatography* and the acronym *HPLC* to characterize it, distinguishing it from the classical, gravity-flow techniques. Later "performance" was substituted for "pressure" in the name and *high-performance liquid chromatography* became the universal term to characterize modern column chromatography. ASTM, however, in the liquid chromatography nomenclature[10], discourages the use of this name or any derivative of it (*e.g.*, HPTLC for high-performance thin-layer chromatography).

It is difficult to predict whether this recommendation is going to be accepted or not. One may say that using such an adjective for the present technique implies that the pioneers in liquid chromatography could not achieve high performance, which obviously is not true; also, there is no need to use adjectives expressing the quality of separation in the name of universally used, well accepted techniques. On the other hand, proponents of such a term argue that the present-day liquid chromatography technique is different from the classical methods and some distinction is therefore advisable. We personally feel that the use of such a homeric adjective is entirely superfluous; after all, if one is referring to older work, the year in which it was performed automatically identifies whether the results were obtained using the older or newer techniques. If work was to be carried out today using the older methodology then that should rather be indicated by the expression *gravity-flow liquid chromatography*.

3. EXISTING NOMENCLATURES FOR LIQUID CHROMATOGRAPHY

At present, detailed nomenclatures exist for general liquid chromatography, ion-exchange and exclusion chromatography, issued by IUPAC and ASTM. We should add to these the very detailed proposals of Stahl[17] relating to planar chromatography, some terms of which being also included in the IUPAC and ASTM nomenclatures.

In Part I[1] we discussed in detail the activities of the Commission on Analytical Nomenclature, Analytical Chemistry Division of IUPAC. After finishing a thorough GC nomenclature[18] it has been engaged in proposing a unified nomenclature applicable to all forms of chromatography separation processes. The Committee, consisting of D. Ambrose, E. Bayer and O. Samuelson, first published its preliminary recommendations in 1972[16], which, in a somewhat modified form, were approved in 1973 and published in 1974[3]. This text compiles the definitions of the various chromatographic techniques and those terms and parameters which are applicable to all forms of chromatography.

In parallel with this work, O. Samuelson, in close association with E. Bayer and F. G. Helfferich, also prepared recommendations for an ion-exchange nomenclature which is harmonized with the other nomenclatures. This text was first pub-

lished as tentative recommendations in 1970[19] followed by the publication of the slightly modified final text in 1972[20]. These recommendations refer only to the terms and definitions characteristic of ion-exchange chromatography; concerning those common to all chromatographic processes, the text refers to the generalized IUPAC nomenclature[3].

In ASTM, Committee E-19 on Gas Chromatography, after changing its name in 1969 to Committee on Chromatography, started to consider the possibility of compiling a nomenclature which can be used in all forms of liquid chromatography and which is coordinated with the GC nomenclature. This work was carried out in parallel with the modification of the original ASTM GC nomenclature[21], the revised edition of which was published in 1977. The final text of the LC nomenclature was approved by the Committee on March 30, 1979, and published later that year[10]. This nomenclature also considered some of the terms used in planar and exclusion chromatography, so that it is fairly generally applicable.

As already mentioned, exclusion chromatography is handled within ASTM by another group, Committee D-20 on Plastics. Its Subcommittee on Analytical Methods prepared in the years around 1970 a nomenclature on gel-permeation chromatography (GPC) which was approved on January 6th, 1972[22]. Unfortunately, these recommendations were not coordinated with the then already existing GC nomenclatures, not even within ASTM. As a conclusion, identical terms were assigned different symbols. Probably the most blatant anomaly was to use N and n for the theoretical and effective plate numbers, respectively, while both the ASTM and IUPAC nomenclatures used the respective symbols in the opposite way, n for the theoretical and N for the effective plate numbers. In fact, there are discrepancies even within the standards approved by Committee D-20, *e.g.*, equations given for resolution are different in the GPC nomenclature and in two standard methods published by the same Committee in 1976[23] and 1977[24] for the determination of molecular weight averages and molecular weight distribution. The newest edition of D-3016[25], in which the name of the technique was finally changed to "liquid exclusion chromatography", eliminated a number of obsolete terms and reduced the number of discrepancies; unfortunately, however, some still remained.

Below, the recommendations of these nomenclatures are discussed in detail. First, we deal with the general liquid chromatography terms which are applicable to all or most liquid chromatography techniques; this is then followed by a discussion of the terms specific to the individual techniques. Prior to this discussion, however, we must first deal with the changing meaning of some terms during the evolution of liquid chromatography.

4. THE CHANGING MEANING OF SOME TERMS

Classical liquid chromatography has its origin in the work of Tswett, starting in 1903, and the technique evolved slowly in the subsequent decades, mostly in the 1930s, as a simple technique permitting the solution of complicated separation problems, particularly in organic and biochemistry. Until 1941, the media responsible for the separation consisted of adsorbents; at the end of 1941 Martin and Synge[26] introduced liquid–liquid partition chromatography, an achievement for which eleven years later, they received the Nobel Prize in Chemistry. Gas–liquid partition chro-

matography started in 1952[27] and within a few years revolutionized analytical chemistry. Also, gas chromatography represented the basis on which the theory of chromatography was developed in detail. Around the middle of the 1960s, based on their experiences in GC, researchers started to modernize liquid chromatography, thus creating the exponential evolution of the 1970s.

This very brief, and certainly superficial, historical summary* shows how liquid chromatography evolved from a simple, empirical technique into a sophisticated, universal separation method based on a sound theory. In this evolution the meaning of some terms changed, sometimes opening up the possibility of misunderstandings. There are particularly four common terms where such changes occurred: these are "liquid phase", "solvent", "carrier" and "chromatogram".

A. Liquid phase

In classical liquid chromatography, there were two phases: a solid, the adsorbent, and a liquid, the mobile phase. When Martin and Synge introduced liquid–liquid partition chromatography, they spoke about "two liquid phases", one stationary and the other mobile. In 1952, when first describing gas–liquid partition chromatography where the mobile phase is a gas, the term "liquid phase" was automatically applied to the stationary phase which indeed was a liquid, distributed on the support particles. As a conclusion of this, "liquid phase" is today automatically identified with the *stationary* phase by all those who became involved in chromatography via GC. However, this duality may create confusion when reading earlier LC literature, where "liquid phase" refers to the *mobile* phase. We should be aware of this. Also, in order to avoid any future misunderstanding, all the nomenclatures should make this clear.

B. Solvent

The second term where misunderstanding is possible is "solvent". In classical liquid chromatography this term was synonymous with the mobile phase (then the "liquid phase"), while in partition chromatography (be it gas–liquid or liquid–liquid), "solvent" refers to the stationary (liquid) phase. By tradition, the expression "solvent" is still often used in liquid chromatography for the mobile phase, *e.g.*, when giving its composition as the "solvent strength", although both general LC nomenclatures discourage its use either alone or in compound words such as "developing solvent", "eluting solvent" and "solvent front". The proper expression is always "mobile phase" and this should be clearly specified in the nomenclatures.

There are two other terms often used in lieu of "mobile phase": "eluent" and "developer". Again, there are historical reasons for their use: we have seen when discussing the variants of chromatography that "elution chromatography" is one of the basic variants of the technique. Similarly, in classical liquid chromatography and in planar (paper or thin-layer) chromatography where the separated compounds remain on the column or the plate, the expression "developing the separation" had been used. In our opinion, there is no reason to maintain these two terms in any

* For a detailed discussion of the history of the evolution of liquid chromatography, see Ettre[4].

nomenclature to express the mobile phase. However, the verbs "to elute" and "to develop" might be retained to express the basic difference between present-day column chromatography where the separated sample compounds *elute* from the column and planar chromatography where the separated sample components remain on the plate or paper and thus the separation is *developed* on it.

C. Carrier

The third term where different uses during the years can create misunderstandings is "carrier". In the past this term has been used in liquid chromatography to describe the solid on which the stationary phase is distributed or certain active groups or organic radicals involved in the separation process are bonded. However, owing to the similarity to the term "carrier gas", used as a synonym for the mobile phase in gas chromatography, the use of this expression is not recommended: *support* should be substituted for it.

D. Chromatogram

The last major term the meaning of which has changed is "chromatogram". Originally, in liquid chromatography, the sample was added to the top of the column and was then washed down the column with the solvent. In this process, the sample components separated formed colored rings along the column and the process was stopped before the first component emerged from the column. Thus, the column with the colored rings was the visual result of the analysis and it was called the *chromatogram*. Using Tswett's own words[28]:

"Like light rays in the spectrum, the different components of a pigment mixture, obeying a law, are resolved on the... column. I call such a preparation a chromatogram and the corresponding method the chromatographic method".

In the second part of the 1930s a new method started to gain acceptance, the so-called *Durchflusschromatogramm* (literally "flow-through chromatogram"), where the individual components are washed out of the column with the eluent and collected in individual fractions. As a logical extension of the original nomenclature, Zechmeister[29] called this a "liquid chromatogram". However, the name "chromatogram" remained in use for some time as a name for the column. For example, Martin and Synge[26], in their 1941 paper on partition chromatography, used this term and, obviously by habit, it was still used in 1952 by James and Martin in their first paper on gas chromatography[27] (example: "the chromatogram supported in the vapour jacket"). Soon, however, the use of the expression "column" became exclusive and the term "chromatogram" was transferred to describe the visual report of the analysis. As specified by the generalized IUPAC nomenclature[3] the chromatogram is "a graphical or other presentation of detector response, effluent concentration or other quantity used as a measure of effluent concentration, *versus* effluent volume or time". It should be emphasized, however, that in planar (paper and thin-layer) chromatography the term "chromatogram" is still applied to the paper or plate after separation has occurred. As specified by ASTM[10], in planar chromatography the chromatogram "is the paper or thin-layer media itself on which the solute mixture has been placed and separated", and Stahl[17] states this even shorter and clearer: "it is the layer with substances after separation".

5. GENERAL LIQUID CHROMATOGRAPHY NOMENCLATURES

As already mentioned, two nomenclatures deal with liquid chromatography in general: IUPAC's generalized nomenclature[3] and the liquid chromatography nomenclature[10] compiled by ASTM Committee E-19. We shall first discuss these in detail. Table 1 compares the symbols used in these nomenclatures while Table 2 lists the additional terms for which clear definitions are given.

As already pointed out in Part I[1], great care was taken in these nomenclatures to avoid any ambiguity. For example, capital letters are always used as subscripts to characterize the mobile (M) and stationary (S) phases; also, lower case l is never used because it can easily be mistaken for the numeral "one". Thus, the respective diffusion coefficients in the mobile and stationary phases are D_M and D_S and not D_m and D_s, as one often finds in publications. Similarly, great care was taken in the selection of lower-case and capital-letter symbols and their identification by the appropriate subscripts. For example, there is a difference between r and R (relative retention *vs.* fraction of the solute in the mobile phase), R and R_s (resolution) or r and r_c (inside column radius). Also, r is never used as a subscript; hence the subscript for retention is R (as in t_R and V_R) and retention temperature is T_R. Another intentional decision was never to use composite symbols or subscripts containing more letters unless absolutely necessary*. Superscripts are used only to distinguish the various retention time and volume values, such as t'_R and V'_R for the adjusted retention time and volume.

Of the two, the ASTM nomenclature is newer (it was finished in 1979) and, during its compilation, the IUPAC text was considered. Except a few places the two are very similar and, where they are not, the ASTM Committee deliberately did not follow the proposals of IUPAC.

Below, we comment on the points of disagreement and on some other important questions related to these nomenclatures. Also, we deal with those terms and symbols for which we disagree with either or both of the nomenclatures.

Capacity factor. In Part I[1] we discussed the divided opinions concerning the symbol for the capacity factor: both k and k' are used in the literature. As stated by ASTM[10], however, the use of k' is "the result of individuals' preferences and have never been officially endorsed by the IUPAC or ASTM". In other words, the proper symbol for the capacity factor is k and not k'.

A further problem related to this term is its name. It suggests that it has something to do with the sample capacity of a column, but this is not true: the capacity factor expresses the following ratio for a given solute at any point in the column at equilibrium:

$$k = \frac{\text{amount of solute in stationary phase}}{\text{amount of solute in mobile phase}} \tag{1}$$

and this has nothing to do with the "capacity" of the column. This discrepancy is well recognized. Still, however, as pointed out in Part I[1], terms, names and definitions are developed historically and there is no justification for a sudden change.

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* In many cases double letters in the literature are simply due to sloppy typing or copy-editing, not correcting the original typing error.

TABLE 1

GENERAL LIQUID CHROMATOGRAPHY SYMBOLS AND TERMS

Parameter	*ASTM*[10]	*IUPAC*[3]	*Notes*[a]
Capacity (partition) ratio; capacity factor; mass distribution ratio	k	D_m	$k = \frac{1 - R}{R}$
Column			
Cross-sectional area	A_c		
Interstitial volume	V_c	V_I	See Note 1
Inside diameter	d_c		
Length	L		
Phase ratio	β		See Note 2
Specific permeability	B_o		See Note 3
Stationary phase fraction		ε_s	See Note 4
Temperature	T_c		Degrees Kelvin
Volume		X	See Note 5
Hold-up volume (volume of mobile phase in column)	V_M		
Volume of stationary phase in column		V_s	See Note 6
Column packing			
Average diameter of solid particles	d_p		
Interparticle porosity	ε	ε_I	See Note 7
Pore radius	r_p		
Column efficiency			
Height equivalent to one effective plate, HEETP	H	H	$H = L/N$
Height equivalent to one theoretical plate, HETP	h	h	$h = L/n$
Number of effective plates; effective plate number	N	N	$N = 16(t'_R/w_b)^2 = 5.545(t'_R/w_h)^2$
Number of theoretical plates; theoretical plate number	n	n	$n = 16(t_R/w_b)^2 = 5.545(t_R/w_h)^2 = 4(t_R/w_i)^2$
Reduced plate height	h_r		$h_r = h/d_p$
Dead volume		V_d	See Note 8
Diffusion coefficient of solute in mobile phase	D_M		
Diffusion coefficient of solute in stationary phase	D_S		
Distribution of a solute			See Note 1
Distribution constant (partition coefficient)	K	K_D, D_c	
Distribution coefficients		D_g, D_c, D_s	
Fraction of a solute in the mobile phase		R	
Fraction of a solute in the stationary phase		$1 - R$	
Mobile phase			
Flow-rate at column outlet and ambient temperature	F_a		
Flow-rate at column outlet, corrected to column temperature	F_c	F_c	$F_c = F_a(T_c/T_a)$
Linear velocity	u	u	See Note 9
Nominal linear flow		F	See Note 10
Optimum linear velocity of the mobile phase	u_{opt}		See Note 11
Reduced mobile phase velocity	ν		$\nu = (ud_p)/D_M$
Viscosity	η		at column temperature

TABLE I *(continued)*

Parameter	*ASTM*[10]	*IUPAC*[3]	*Notes*[*]
Number of theoretical plates required for a given resolution of peaks 1 and 2	n_{req}		$n_{req} = 16R_s^2\left(\frac{\alpha}{\alpha-1}\right)^2\left(\frac{k_2+1}{k_2}\right)^2$ See Note 12
Number of effective plates required for a given resolution of peaks 1 and 2	N_{req}		$N_{req} = 16R_s^2\left(\frac{\alpha}{\alpha-1}\right)^2$ See Note 12
Peak area	A		
Peak width			
At base	w_b		See Note 13
At half-height	w_h		See Note 13
At inflection points	w_i		See Note 14
Pressure			
Column inlet pressure	P_i	p_i	
Column outlet pressure	P_o	p_o	
Pressure drop along the column	ΔP		$\Delta P = P_i - P_o$ See Note 15
Relative column pressure	P		$P = P_i/P_o$
Ambient (atmospheric) pressure	P_a		See Note 16
Relative retention	$r_{1,2}$		
Resolution	R_s		$R_s = \frac{2(t_{R2} - t_{R1})}{w_{b1} + w_{b2}}$ where $t_{R2} > t_{R1}$
Retention times			See Note 17
Adjusted retention time	t'_R	t'_R	$t'_R = t_R - t_M$
Mobile phase hold-up time	t_M	t_M	See Note 18
Net retention time		t_N	$t_N = V_N/F_c$ See Note 19
Retention time (total retention time)	t_R	t_R	See Note 20
Retention volumes			See Note 17
Adjusted retention volume	V'_R	V'_R	$V'_R = V_R - V_M = t'_R F_c$
Mobile phase hold-up volume	V_M	V_M	$V_M = t_M F_c$
Net retention volume		V_N	See Note 19
Retention volume (total retention volume)	V_R	V_R	See Note 20
Specific retention volume		V_g	See Note 21
Separation factor	α	$\alpha_{A/B}$	$\alpha = t'_{R2}/t'_{R1} = K_2/K_1 = k_2/k_1 \neq t_{R2}/t_{R1}$ where $t'_{R2} > t'_{R1}$ See Note 16
Temperature			
Ambient	T_a		
Of the column	T_c		See Note 22
Of the mobile phase	T		See Note 22

[*] *Notes:*

1. See discussion in text.
2. The phase ratio is defined as the volume of the mobile phase to that of the stationary phase in the column. Ideally, it is $\beta = V_I/V_S$. In practice, V_M is often used for the interstitial volume. The IUPAC nomenclature specifies this term without a symbol; it is not included in ASTM E 682 but this is an obvious oversight as it is included in the ASTM GC nomenclature.

(Continued on p. 40)

TABLE I *(continued)*

3. It is calculated for a packed column as
$$B_o = \frac{d_p^2 \varepsilon^3}{180(1-\varepsilon)^2}$$
Assuming $\varepsilon = 0.40$, $B_o = d_p^2/1000$.
4. It is defined as the volume of the stationary phase per the geometric volume of the column:
$$\varepsilon_s = V_s/X$$
5. The empty volume of that part of the tube which contains the packing. It is also called the "bed volume".
6. It is the volume of the stationary liquid phase or of the active solid or of the gel in the column. It does not include the volume of any solid support.
7. IUPAC uses the name "interstitial fraction"; it is equal to
$$\varepsilon_I = V_I/X$$
8. IUPAC defines it as the volume between the effective injection point and the effective detection point, less the column volume, X. This is, however, an ambiguous definition (see text).
9. IUPAC defines this as the "interstitial velocity". It is equivalent to the average linear velocity ($\bar{u}$) used in GC. It can be calculated as
$$u = L/t_M = F_c/\varepsilon A_c = F/\varepsilon$$
(because IUPAC's F is equal to F_c/A_c). IUPAC, in the generalized nomenclature, gives both u and $\bar{u}$ indicating that in GC, $\bar{u}$, the mean velocity, also includes the pressure correction factor:
$$\bar{u} = F_c j/\varepsilon_I A_c = L/t_M$$
and thus, in GC, u expresses the velocity at outlet pressure (u_o; see ref. 1). In other words, in GC, $\bar{u} = uj$ or $= u_o j$. Since in liquid chromatography, $j = 1$ can be assumed, here $u = u_o = \bar{u}$.
10. IUPAC defines this as F_c/A_c. In other words, it is the linear velocity in a part of the column not containing any packing.
11. The minimum of the HETP *vs.* u plot.
12. In the equation for n_{req} and N_{req}, $\alpha = t'_{R2}/t'_{R1}$, $k_2 = t'_{R2}/t_M$ and $t'_{R2} > t'_{R1}$.
13. IUPAC uses the respective terms without any specific symbol. In the IUPAC nomenclature "peak width" automatically refers to the peak width at base while if it is measured at 50% of the peak height at maximum, the name "peak width at half-height" should be used. We should always avoid the expression "half-width": it is not half of the width, as one would expect from this expression, but the full width at 50% of the maximum height. See also Fig. 1.
14. In the case of an ideal Gaussian peak, the inflection points are at 60.7% of the peak height at maximum (see Fig. 1).
15. There is a printing error in ASTM E 682: the delta is missing in the symbol.
16. The symbol α is used to designate the relative retention of two *consecutive* peaks. By agreement, $t'_{R2} \geq t'_{R1}$ and thus $\alpha \geq 1$. Relative retention in general is indicated by the symbol $r_{i,s}$ where i refers to the compound of interest and s to the standard. Depending on the relative position of the standard peak, the value of $r_{i,s}$ can be either larger or smaller than unity (or even equal to it).
17. The generalized IUPAC nomenclature only specifies retention volumes but indicates the existence of the corresponding retention times with the corresponding symbols.
18. Observed elution time of a non-retained substance.
19. In liquid chromatography, mobile phase compressibility is negligible and thus the pressure gradient correction factor (j) does not apply. For this reason, here the adjusted and net retention times are identical. The generalized IUPAC nomenclature lists this term because its nomenclature is applicable to both GC and LC.
20. In liquid chromatography, the total retention time might not be identical with the time elapsed between sample introduction into the column and the emergence of the peak maximum: it should be defined as the time between the start of the elution and the emergence of the peak maximum. This is pointed out by IUPAC: sometimes the column is washed with a liquid before the elution is started but after the application of the sample, to display components that are not retained. In such a case, the effluent obtained during the washing process (or the corresponding time) should not be included in the peak elution volume (time) unless the solutes are moving during washing. In such a case one should use the symbol $\bar{V}$ instead of V_R.
21. In general, the specific retention volume is equal to the ratio of the net retention volume to the amount of stationary liquid, active solid or solvent-free gel. In liquid chromatography, the compressibility of the mobile phase is usually negligible and, therefore, the adjusted and net retention volumes are identical; hence, the specific retention volume may be calculated by using the adjusted retention volume in the numerator.
22. ASTM distinguishes between the temperature of the mobile phase and column temperature. The symbol T always refers to absolute temperature (degrees Kelvin).

TABLE 2

GENERAL LIQUID CHROMATOGRAPHY TERMS (OTHER THAN THOSE IN TABLE 1) WHICH ARE DEFINED IN THE TWO LIQUID CHROMATOGRAPHY NOMENCLATURES

Term	*ASTM*[10]	*IUPAC*[3]	*Notes*[a]
Active solid		+	See Note 1
Adsorption chromatography		+	
Baseline	+	+	
Bonded phase	+		
Bulk property detector	+		
Bypass injector		+	
Chromatogram	+	+	
Chromatograph (noun)		+	
Chromatograph (verb)		+	
Chromatography	+	+	
Column	+	+	
Column chromatography	+	+	
Column packing (see also under Packing)	+	+	
Detection		+	
Detector	+		
Differential chromatogram	+		
Differential detector	+	+	
Displacement chromatography		+	
Dry-column chromatography	+		
Eluate		+	See Note 2
Eluent		+	See Note 2
Elute		+	See Note 2
Elution band		+	See Note 2
Elution chromatography		+	
Elution curve		+	See Note 2
Flow programming	+	+	See Note 3
Fraction collector	+		
Frontal chromatography		+	
Fronting		+	See Note 4
Gradient (elution)	+	+	See Note 5
Integral chromatogram	+		
Integral detector	+	+	
Interactive solid	+		See Note 1
Internal standard		+	
Isocratic (elution)	+		
Liquid chromatography	+	+	
Liquid–liquid chromatography	+	+	
Liquid phase	+		See Note 6
Liquid–solid chromatography	+	+	
Marker		+	See Note 7
Mobile phase	+	+	
Modified active solid		+	
Open tubular column		+	
Packed column		+	
Packing		+	
Partition chromatography		+	
Pellicular packing	+		
Peak	+	+	
Peak base	+	+	See Note 8

(Continued on p. 42)

TABLE 2 *(continued)*

Term	*ASTM*[10]	*IUPAC*[3]	*Notes**
Peak height (at maximum)	+	+	
Pneumatic pump	+		
Pump	+		
Reciprocating pump	+		
Reversed-phase chromatography	+	+	
Salting-out chromatography		+	See Note 9
Sample inlet system	+	+	Also sample injector
Selective elution		+	
Separation temperature		+	
Septum injector	+		
Septumless injector	+		
Solid support	+	+	
Solute	+		
Solute property detector	+		
Stationary phase	+	+	
Step	—	+	
Step height	+	+	
Stepwise elution		+	
Stopped-flow injection	+		
Syringe pump	+		
Tailing		+	See Note 4
Totally porous packing	+		
Valve injectors	+		
Zone		+	See Note 10

* *Notes:*

1. The ASTM definition of "interactive solid" is practically identical with the IUPAC definition of "active solid".
2. The IUPAC nomenclature maintains the various terms derived from "elute" mainly to eliminate the expressions of "develop" and "development". Thus, *elute* is proposed instead of "develop" and *elution* instead of "development"; *eluent* is synonymous with the mobile phase and *elution band* with the peak; *eluate* represents the effluent from the chromatographic bed (column or plate) and *elution curve* is a general expression for the chromatogram or a part of it in elution chromatography.
3. The IUPAC nomenclature lists it as *flow-programmed chromatography*.
4. *Fronting* is defined as peak asymmetry where the front (the ascending part of the peak) is less steep than the rear, and *tailing* refers to peak asymmetry where the rear (the descending part of the peak) is less steep than the front.
5. The term *gradient* specifies in general the technique where a deliberate change in the mobile phase operating conditions is made during the chromatographic procedure. The changes may be continuous or stepwise. *Flow programming* is, in essence, also a gradient technique. On the other hand, *gradient elution* specifically refers to the technique where the *composition* of the mobile phase is changed during a run.
6. In liquid chromatography one must be particularly careful in realizing that "liquid phase" does *not* refer to the mobile phase (which is also a liquid) but to the liquid *stationary* phase used in true liquid–liquid partition chromatography. See discussion in text.
7. IUPAC defines it as "a reference substance chromatographed with the sample to assist in identifying the components".
8. "Peak base" should not be confused with the peak width *at* base. See Fig. 1 and the discussion in the text.
9. IUPAC defines it as "a procedure in which a non-sorbable electrolyte is added to the eluent to modify the distribution equilibria of the components to be separated".
10. IUPAC defines it as "a region in a chromatographic column or layer where one or more components of the sample are located".

IUPAC, well aware of this controversy, proposed in the generalized nomenclature to change both the name and the symbol of this term. However, the proposed symbol, D_m, is very unfortunate because it is practically identical with the symbol universally used for the diffusion coefficient of the solute in the mobile phase (D_M, sometimes also written as D_m!): in fact, the use of D for the diffusion coefficient is actually specified by IUPAC in a very clear discussion[30] which we shall deal with in Part III[31].

Concerning the name of this term, we cannot question its ambiguity. Still, as pointed out in Part I[1], terms, names and definitions have been developed historically; thus, "capacity ratio" and "capacity factor" have been used in thousands of publications, and both are well understood. A sudden change would create much more confusion than maintaining the present name, even if it is not precise.

Distribution constants. Practically since the introduction of modern chromatography theory, the term "partition coefficient" or "distribution coefficient" has been used with the corresponding symbol K (or k if k' was used as the capacity factor). IUPAC, in the generalized nomenclature[3], proposed a complete change from this. As already pointed out in Part I[1], the symbols proposed by IUPAC for the distribution constants are very unfortunate, again because of the possible confusion with the diffusion coefficients (see above). In our opinion, there is absolutely no reason to change K. In fact, K has been specified by IUPAC's Division of Physical Chemistry as a general symbol for equilibrium constants (see Part III[31]), and therefore changing it to D would contradict IUPAC's own recommendations. However, the distinction between the individual variations of the distribution coefficients (or constants) is very appropriate and should be maintained. Thus, we propose the following final symbols for the terms defined by the right-hand sides of the equations:

$$K_c = k \cdot \frac{\text{volume of mobile phase in column}}{\text{volume of stationary phase}} \tag{2}$$

$$K_g = k \cdot \frac{\text{volume of mobile phase in column}}{\text{weight of dry stationary phase}} \tag{3}$$

$$K_v = k \cdot \frac{\text{volume of mobile phase in column}}{\text{volume of stationary bed}} \tag{4}$$

$$K_s = k \cdot \frac{\text{volume of mobile phase in column}}{\text{surface area of stationary phase}} \tag{5}$$

The definition of k has already been given in eqn. 1 and this definition is used in eqns. 2–4. In eqn. 5, the definition is slightly modified to

$$k \text{ (eqn. 5)} = \frac{\text{amount of solute adsorbed on the stationary phase}}{\text{amount of solute in the mobile phase}} \tag{1a}$$

K_c is both a general term and one applicable in partition chromatography*; K_g is applicable in ion-exchange and exclusion (gel) chromatography where swelling occurs, and in adsorption chromatography with adsorbents of unknown surface area;

* Since the fraction in the right-hand side of eqn. 2 is equal to the phase ratio (β), eqn. 2 is equal to the fundamental equation of chromatography:

$$K = k\beta \tag{6}$$

K_v is applicable when it is not practical to determine the weight of the solid stationary phase; and K_s is applicable in adsorption chromatography with a well characterized adsorbent of known surface area.

There are two additional ambiguities in the generalized IUPAC nomenclature related to the "distribution constants": both "constant" and "coefficient" are used and, in addition to D_c (K_c) there is another term, K_D, while D_c (K_c) actually has a different name, "concentration distribution ratio". Concerning the first problem, we propose to eliminate "coefficient" and, in accordance with the recommendations of IUPAC's Division of Physical Chemistry[30], use exclusively the term "constant". For the same reason, we do not believe that the special name for D_c (K_c) is justified: after all, it is also a *distribution constant*. However, the situation of K_D *vs.* K_c (D_c) needs some explanation.

The difference between K_D and K_c (D_c) lies in the definition of "solute" in the capacity factor, k: in K_D, it is defined as *the solute in a single definite form* while in K_c (D_c) it is simply defined as *the solute*. In most cases, the two are identical. However, as pointed out by IUPAC in the explanation of the terms, a solute may be present in more than one form, *i.e.*, associated or dissociated forms, and these forms are generally not specified and may even not be known. Hence it is generally more appropriate to disregard the restriction "in a single definite form" and define the distribution constant as given in eqn. 2 and subsequent equations.

R value. This value was originally introduced by LeRosen[32] as the ratio of zone velocity to mobile phase velocity*. Giddings[33] calls it the thermodynamic reflection of the distribution constant and points out that it can be related to fundamental values in all variants of chromatography; moreover, in ideal cases, $R = R_f$, the retention factor introduced for planar chromatography by Consden *et al.*[34].

The generalized IUPAC nomenclature recognizes R but the ASTM nomenclature does not: it only includes R_f and R_M. In our opinion, R should become part of all standard chromatography nomenclatures giving its relationship with the capacity factor:

$$R = \frac{1}{k + 1} \tag{7}$$

and

$$k = \frac{1 - R}{R} \tag{8}$$

As will be shown below when discussing planar chromatography, the symbol R_M introduced first by Bate-Smith and Westall[35] represents the following relationship:

$$R_M = \log\left(\frac{1 - R_f}{R_f}\right) \tag{9}$$

Since R_f and R are equivalent, $\log k$ would be equivalent to R_M. Based on a suggestion by Horváth[36], we feel that a new term representing $\log k$ should also be included in a

* In their basic paper on liquid–liquid partition chromatography[26], Martin and Synge also introduced an R term with a slightly different meaning. The use of the same symbol is simply due to the fact that LeRosen received the issue of the *Biochemical Journal* in which the Martin and Synge paper was published about one week after his own manuscript had been submitted.

revised liquid chromatography nomenclature and, on his suggestion, we propose the symbol κ for it:

$$\kappa = \log k = \log\left(\frac{1 - R}{R}\right) \tag{10}$$

Interstitial volume vs. column volume. There are two volumes related to a chromatographic column: the *volume of the column tube* and the *interstitial volume of the column*. The volume of the tube is the geometric volume, $d_c^2\pi L/4$, while the interstitial volume is the volume occupied by the mobile phase in the packed section of a column which, in ideal case, is equal to V_M; in actual systems, V_M represents the sum of the interstitial volume and the extra-column volumes.

IUPAC uses the symbol V_I for the interstitial volume and X for the column volume, while ASTM uses V_c for the interstitial volume. The latter is an unfortunate choice because the subscript c automatically is interpreted as "column" and, in fact, this is how it is used by both IUPAC and ASTM in a number of other symbols*. We also disagree with X for the column volume because it is not an indicative symbol. Our proposal is that in the future revisions V_I is used for the interstitial volume and V_c for the geometric volume of the column:

$$V_c = d_c^2\pi L/4 = A_c L \tag{11}$$

where L is the column length.

Dead volume. The IUPAC specification[3] of the dead volume (V_d) is incorrect because it confuses two different volumes. What it defines is not the "dead volume" but the *extra-column volume*, which may consist of two different components, the "dead" (*i.e.*, unswept) volume and the volume of the injector, connecting lines and detector, which are not "dead" (*i.e.*, unswept) volumes because mobile phase is flowing through them, but where, usually but not necessarily, owing to a reduction in its velocity, band broadening may occur. In modern systems there is really no "dead volume" and the extra-column volume (V_{ext}) consists of V_i, the volume between the effective injection port and the column inlet, and V_d, the volume between the column outlet and the effective detection point. Thus, in actual systems

$$V_M = V_I + V_{ext} = V_I + V_i + V_d \tag{12}$$

We propose that these modifications should be considered in any future revisions.

Nominal linear flow. This term is included in the generalized IUPAC nomenclature[3] and is highly misleading. The intent is clear: to distinguish between velocity in the empty part of the column and in the packed part. The problem is, however, that this term, the dimensions of which are length/time, is not "flow" but *velocity*, the name used at other places in the nomenclature. Therefore, if we want to keep this term, we have to change its name to "nominal linear velocity", with the possible

* For example, d_c = column tube inside diameter, A_c = column cross-sectional area.

symbol u_n. The difference between u_n and u (the linear velocity along the column) can be seen in the following two equations:

$$u_n = F_c/A_c \tag{13}$$

$$u = F_c/\varepsilon A_c = L/t_M \tag{14}$$

We see no reason to keep u_n in a general chromatography nomenclature.

Mobile phase. It should be stated that the definition of the mobile phase as given by IUPAC[3] is incorrect. In this definition the mobile phase is defined as *also including the fraction of the sample present in this phase.* This obviously would mean that if there is no sample in the system, we could not speak about the "mobile phase". It is interesting to note that the same nomenclature does not include this restriction in the definition of the stationary phase.

There is no reason to keep this statement in future revisions.

Open tubular vs. capillary column. In Part I[1], when discussing the nomenclature of gas chromatography, we emphasized the difference between "open tubular" and "capillary" columns. The generalized IUPAC nomenclature[3] gives a proper definition for the former, emphasizing at the same time that "capillary" *refers to a dimension and not a column type.*

Recently this distinction became very important in liquid chromatography. The trend indicates a greater emphasis in the future toward small-diameter ("capillary") columns, but one must be careful with the name because both open tubular and packed "capillary" columns have been described in the literature. Thus, the use of "capillary" in itself is highly misleading because it does not define the particular type. For this reason, any future revision of the nomenclatures must present clear definitions and terms for the columns prepared from small-bore tubing.

Theoretical vs. effective plates. Both nomenclatures are clear in using n for the number of theoretical and N for the number of effective plates and h and H for the corresponding plate height values. It is unfortunate that IUPAC[3] is using the terms "effective theoretical plate number" and "height equivalent to one effective theoretical plate", with the acronym HEETP for the latter. This is confusing: it is either "theoretical" or "effective", but it cannot be both! The proper term for N and H should be the *number of effective plates* (effective plate number) and the *height equivalent to one effective plate* (effective plate height, *HEEP*), respectively, *i.e.*, without "theoretical" in the name.

Peak widths. Peak width is conveniently measured at three places: at base, at half-height and at the inflection points, each peak width representing a multiple of the standard deviation of the peak. The peak width at base is the segment of baseline intercepted by the tangents drawn to the inflection points; in the case of a Gaussian peak, the inflection points are at 60.7% of the peak height at maximum.

IUPAC uses the term "peak width" automatically to refer to the peak width at base. This may give rise to a possibility of misunderstanding, and therefore in future revisions the full specification where it is measured should always be added.

There is another term, *peak base*, which should not be confused with the peak width *at* base. The "peak base" represents the baseline between the extremities of the peak. This is explained in Fig. 1.

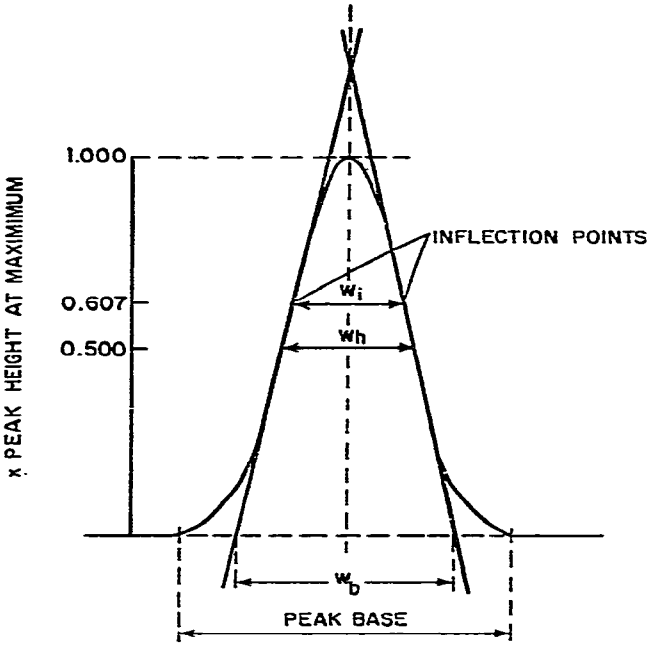

Fig. 1. Peak widths. w_b = peak width at base; w_h = peak width at half-height; w_i = peak width at inflection points.

Note that the symbol for the peak width should always be lower-case w: capital W is used for "weight".

6. GENERAL LIQUID CHROMATOGRAPHY TERMS IN OTHER NOMENCLATURES

As mentioned earlier, two specialized nomenclatures exist: the one developed by an IUPAC Committee for ion-exchange chromatography and the nomenclature developed by ASTM Committee D-20 for exclusion chromatography. Each of these includes symbols, terms and definitions which are also used in other liquid chromatography techniques and may refer to liquid chromatography in general.

A. General liquid chromatography terms in the ion-exchange chromatography nomenclature

As mentioned earlier, this nomenclature was basically compiled by the same persons as the generalized IUPAC nomenclature and thus, naturally, the same symbols were used for equivalent terms. It follows that comments on the symbols and terms used in liquid chromatography in general will also refer to the corresponding symbols and terms used in ion-exchange chromatography. Table 3 lists these symbols. We have already commented earlier on column volume, proposing the symbol V_c instead of X. The three distribution coefficients are identical with those discussed earlier in connection with Table 1, with definitions directly related to ion-exchange

TABLE 3

GENERALIZED LIQUID CHROMATOGRAPHY TERMS AND SYMBOLS INCLUDED IN THE IUPAC ION-EXCHANGE CHROMATOGRAPHY NOMENCLATURE[20]

Parameter	*Symbol*	*Note*
Column volume	X	
Concentration distribution ratio	D_c	
Diffusion coefficient	$\bar{D}$	Diffusion coefficient in the ion exchanger
Distribution coefficient	D_g	
Volume distribution coefficient	D_v	

chromatography. Thus, we propose that in future revisions the symbol K is used instead of D. In this way, K_c, K_g and K_v correspond to the respective symbols D_c, D_g and D_v, having the following definitions:

$$K_c = \frac{\text{amount of solute in the ion exchanger}}{\text{amount of solute in the external solution}} \cdot \frac{\text{volume of external solution}}{\text{volume of swollen ion exchanger}} \quad (15)$$

$$K_g = \frac{\text{amount of solute in the ion exchanger}}{\text{amount of solute in the external solution}} \cdot \frac{\text{volume of external solution}}{\text{weight of dry ion exchanger}} \quad (16)$$

$$K_v = \frac{\text{amount of solute in the ion exchanger}}{\text{amount of solute in the external solution}} \cdot \frac{\text{volume of external solution}}{\text{volume of exchanger bed}} \quad (17)$$

Finally, a brief comment may be made about the *diffusion coefficient*. The special symbol with the bar was undoubtly selected because of the use of D for the distribution constants (coefficients). If we change them to K as proposed above, then the symbol D (which is the proper symbol for the diffusion coefficient), with the proper subscript (in this case, D_s), can be utilized.

B. General liquid chromatography terms in the exclusion chromatography nomenclature

As mentioned earlier, ASTM has three standards related to liquid exclusion chromatography[23–25]. The terms and definitions included in these can be divided into two groups: those directly related to molecular weight and particle diameter distribution and those referring to general LC terms also used in exclusion chromatography. Here, we deal with the second group enumerated in Table 4, which compares them with the corresponding symbols used in the ASTM liquid chromatography nomenclature*.

If we examine Table 4 it is evident that there are major differences between the two nomenclatures: many of the symbols used in the general part of the exclusion chromatography nomenclature are exactly the opposite of those used in the LC nomenclature. It is difficult not to conclude that there was a lack of coordination between the two ASTM Committees and that the group which compiled the exclusion chromatography nomenclatures did not consult the general LC (and GC) literature and standards. The major discrepancies between the two nomenclatures are discussed below.

* For the sake of simplicity Table 4 lists only the symbols of the ASTM LC nomenclature; after all, these are practically identical with those recommended by IUPAC (*cf.*, Table 1).

TABLE 4

GENERALIZED LIQUID CHROMATOGRAPHY TERMS AND SYMBOLS INCLUDED IN THE ASTM EXCLUSION CHROMATOGRAPHY (EC) NOMENCLATURE[25] COMPARED WITH THE ASTM LIQUID CHROMATOGRAPHY (LC) NOMENCLATURE[10]

Parameter	*ASTM EC*	*ASTM LC*	*Notes**
Capacity factor of solute	k'	k	$k' = \frac{V_R - V_o}{V_o}$
Diffusion coefficient of solute	D_s		See Note 1
Distribution coefficient	K	K	See Note 2
Efficiency			
Number of effective plates	N_{eff}	N	
Number of theoretical plates	N	n	
Height equivalent to one theoretical plate	H	h	
Reduced plate height	h	h_r	$h = H/\bar{D}_w$
External volume	V_{ext}		See Note 3
Interstitial volume (void volume)	V_o		See Note 4
Mobile phase			
Flow-rate	F	F_c	At column temperature
Velocity	μ	u	See Note 5
Peak			
Area	A	A	
Width (at base)	W	w_b	
Width at half-height	$W_{\frac{1}{2}}$	w_h	
Pressure			
Inlet pressure to column	P	P_i	
Pressure drop	Δp	ΔP	
Resolution	$R_{1,2}$	R_s	$R_{1,2} = \frac{2(V_{R1} - V_{R2})}{W_1 + W_2}$ See Note 6
Retention volume	V_R	V_R	
Specific resolution	R_s		$R_s = R_{1,2}/\log(M_2/M_1)$ See Note 6
Stationary liquid volume	V_l		See Note 7
Total liquid volume	V_t		$V_t = V_l + V_o + V_{ext}$
General symbols			
Density	ϱ		
Temperature	T	T	Absolute (°K)
Time	t	t	
Weight	w	W	See Note 8

* *Notes:*

1. The nomenclature does not specify whether this represents the diffusion coefficient of the solute in the mobile phase or in the column packing. The ASTM symbol depends on this: if it represents diffusion in the mobile phase it is D_M, while if it represents diffusion in the stationary phase it is D_S, where the subscript S represents "stationary phase" and not "solute"!
2. There is some confusion in the definition of this term in the ASTM EC nomenclature: the equation describing it has V_t in the denominator while in all the textbooks V_l is used in the denominator, and this corresponds to the general chromatography theory. For details, see the discussion in the text.
3. The external volume represents the contributions of all system components external to the column to the retention volume (*cf.*, Table 1).
4. The volume of the mobile phase in the interstices between the gel or the solid particles.
5. It is defined as $\mu = F/A_c$, where A_c is the "internal cross-sectional area of the column". This A_c, however, is different than A_c of Table 1: there $A_c = d_c\pi/4$, while here $A_c = d_c\pi\varepsilon/4$.
6. As mentioned in the text, if $M_2 > M_1$, then $V_{R2} < V_{R1}$.
7. This is not the volume of the stationary phase but of the liquid (mobile phase) which is stationary in the pores of the gel or solid packing (*i.e.*, the intrastitial volume).
8. Weight is specified as W in the ASTM GC nomenclature[21].

Peak widths. The exclusion chromatography nomenclatures disregard the universal recommendation of the IUPAC Manual of Symbols[30] that capital W be used for weight and the universal usage of GC and LC nomenclatures using lowercase w for peak widths: W is used for peak widths and w for weight. Also, peak widths at different heights are not distinguished logically: W (without any subscript) is used for the peak width at base (w_b) while the peak width at half-height is characterized as $W_{\frac{1}{2}}$, a symbol long abandoned in both gas and liquid chromatography.

Column efficiency terms. The situation is even worse in the case of the terms related to column efficiency. While both IUPAC and ASTM GC and LC nomenclatures use n for the theoretical and N for the effective plate number, the original edition[22] of D 3016, the "GPC nomenclature", used N for the theoretical and n for the effective plate numbers. This was somewhat corrected in the revised edition[25]: while maintaining N for the theoretical plate number, it now uses N_{eff} for the effective plate number. Still, the use of a capital letter for the theoretical plate number creates confusion. The situation is similar with the various plate heights: while in the other nomenclatures h is used for the theoretical, H for the effective and h_r for the reduced plate heights, the ASTM exclusion chromatography nomenclature uses H for the theoretical and h for the reduced plate height!

Resolution. The exclusion chromatography nomenclature presents two terms: the regular resolution ($R_{1,2}$) and the so-called *specific resolution* (R_s):

$$R_{1,2} = \frac{2(V_{R1} - V_{R2})}{W_1 + W_2} \tag{18}$$

$$R_s = \frac{2(V_{R1} - V_{R2})}{W_1 + W_2} \cdot \frac{1}{\log(M_1/M_2)} \tag{19}$$

where V_R is the retention volume, W is the peak width at base and M is the molecular weight. The first expression is identical with peak resolution in Table I (symbol R_s), but we must recognize the difference in exclusion chromatography: here, the larger molecules elute first. In other words, if $M_2 > M_1$, then $V_{R2} < V_{R1}$.

The first confusion is in the symbol R_s, which is used by both IUPAC and ASTM GC and LC nomenclatures to express eqn. 18 and *not* eqn. 19. Unfortunately, there are also inconsistencies even within the standards developed by Committee D-20: while in D 3016, the general nomenclature for exclusion chromatography, the two resolution terms are specified as given in eqns. 18 and 19, in the two standards dealing with the determination of molecular weight averages and molecular weight distribution there is a mix-up, $R_{1,2}$ being defined as in eqn. 19 and not as in eqn. 18.

Internal cross-sectional area of the column. This term was included in the original text[22] and deleted from the revised text[25]; however, it is still included indirectly, in the definition of the mobile phase velocity.

We have seen earlier that in the general liquid chromatography nomenclatures, the cross-sectional area of the column refers to the geometric area, *i.e.*, $d_c^2\pi/4$. On the other hand, in the ASTM exclusion chromatography nomenclature "column cross-sectional area" does not mean this but the cross-sectional area available to the mobile phase flow; in other words, it is $\varepsilon d_c^2\pi/4$, where ε is the interparticle porosity (*cf.*, Table I).

V_o, V_i and V_t. One must be careful in properly interpreting the meaning of these terms. As listed in Table 4, V_0 is the interstitial volume of the column, *i.e.*, the volume of interstices between the solid particles. Since in general liquid chromatography (*cf.*, Table 1) we also have the "interstitial volume" of the column (V_I), it would seem to be obvious to think that the two are the same. This is, however, not entirely true, at least not in their interpretation.

In general liquid chromatography, disregarding the extra-column volume of the system, V_M, the mobile phase hold-up volume, and V_I, the interstitial volume, are the same. Furthermore, V_M represents the product of the mobile phase flow rate (F_c) and the mobile phase hold-up time (t_M):

$$V_M = t_M F_c \tag{20}$$

The mobile phase hold-up time represents the time it takes the mobile phase molecules to pass through the column. In practice, it is measured by taking a solute which is not retarded at all by the stationary phase during its passage through the column and thus the molecules of which are always in the mobile phase. Measuring the "retention time" of this solute (*i.e.*, the time period between introduction to and emergence from the column), we obtain t_M. In other words, t_M has two meanings: theoretically, it is the time the mobile phase molecules need to travel through the column, but in practice it also means the retention time of a non-retained solute. It is also obvious that t_M is smaller than the retention time of any other solute which has some interaction with the stationary phase.

In exclusion chromatography, we can also write the retention times corresponding to the three volumes:

$$V_o = t_o F_c \tag{21a}$$

$$V_i = t_i F_c \tag{21b}$$

$$V_t = t_t F_c \tag{21c}$$

Owing to the similarity between V_o in exclusion chromatography and V_I in general liquid chromatography, we would easily make the same connection between t_0 in exclusion chromatography and t_M in general liquid chromatography. This is, however, incorrect.

In exclusion chromatography a sample component the molecules of which are larger than the largest pores of the column packing will pass through the column faster than the molecules of the other sample components and will emerge first. On the other hand, the sample component the molecules of which are smaller than the smallest pores of the column packing will enter all these and thus will be the slowest, emerging last. If we have any substance present in the flowing system the molecules of which are smaller than the molecules of this last sample component, it will emerge from the column together with the last sample component. Obviously the mobile phase represents such a substance. In other words, while in general liquid chromatography both the retention time of an unretained solute and the mobile phase hold-up time (time of passage through the column) are the same, these are not the same in exclusion chromatography: here t_o represents the retention time of an unretained

compound but t_t represents the mobile phase hold-up time. Thus, while V_o is the retention volume of an unretained compound, it is not also the mobile phase hold-up volume: this is represented by V_t. In addition, V_t also represents the retention volume of all solutes the molecules of which are smaller than the smallest pores of the column packing.

This situation is best explained with help of Fig. 2. Here, peak A represents the sample component the molecules of which are larger than the largest pores while peak D represents the sample component the molecules of which are smaller than the smallest pores of the column packing. Later, when discussing the specialized nomenclatures (*cf.*, Table 7), MW_A will be denoted by M_H and MW_D by M_L.

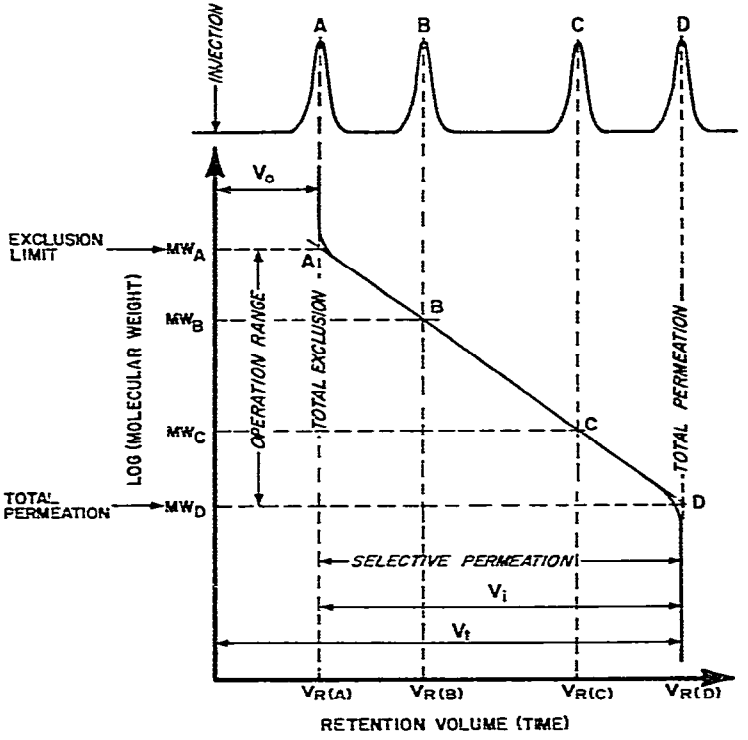

Fig. 2. Calibration curve for exclusion chromatography. A standard sample is analyzed (top); subsequently, the retention volumes (times) are plotted against the logarithm of the corresponding molecular weights. For the explanation of the symbols and the interpretation of the plot, see the text.

The third value, V_t, represents the volume *within* the pores of the column packing, *i.e.*, the *intrastitial volume*. As seen below (*cf.*, eqn. 27), this value may be interpreted as the volume of the "stationary phase", implying that in exclusion chromatography the volume of the pores has a function similar to the volume of the stationary phase in general liquid (and gas) chromatography, and the ASTM exclusion chromatography nomenclature indicates this synonymous interpretation by calling V_t the "stationary liquid volume".

To summarize, V_t represents the total volume of the mobile phase in the system and is composed of V_o, the interstitial ("between the particles") volume and V_i, the intrastitial ("within the particles") volumes:

$$V_t = V_o + V_i \tag{22}$$

In practice, the external volume, V_{ext}, may be added to the right-hand side of eqn. 22.

If we are using retention times instead of volumes, eqn. 22 becomes

$$t_t = t_o + t_i \tag{23}$$

and again, t_{ext} may be added to the right-hand side of the equation.

It should be noted here that the nomenclature of ASTM Committee D-20 uses the expression "liquid" for the mobile phase; thus, V_i and V_t are specified as the "stationary liquid volume" and the "total liquid volume", respectively. This is still a left-over of the former usage when "liquid" referred to the mobile phase. In future revisions, the term "mobile phase" should be substituted for "liquid".

Capacity factor and distribution constant. It is evident from the aforementioned discussion that the meaning of the *capacity factor* is also different in exclusion chromatography to that in general liquid (and gas) chromatography. Using, again, the corresponding retention times instead of volumes, the capacity factor, k', for exclusion chromatography is expressed as (*cf.*, Table 4)

$$k' = \frac{t_R - t_o}{t_o} \tag{24}$$

while in general gas and liquid chromatography, the capacity factor, k, is expressed as

$$k = \frac{t_R - t_M}{t_M} \tag{25}$$

We have mentioned the difference in the meaning of t_o and t_M; thus, strictly following the meaning of the capacity factor, t_t and not t_o should have been used in eqn. 24. This, however, would give negative values for the capacity factor, which obviously would be absurd. Thus, eqn. 24 should be considered as a special expression used in exclusion chromatography. Because of this difference, we feel that a difference in the symbols should be maintained: while k represents the capacity factor in general liquid and gas chromatography, the corresponding symbol in exclusion chromatography should be k' or preferably k_e.

Although the distribution between the two phases in exclusion chromatography is based on different principles than in the other variants of chromatography, a *distribution constant* (K_o) is also described in this method. Its meaning is derived in an analogous manner to the well known relationship in general liquid chromatography*:

$$V_R = V_M + KV_s \tag{26}$$

* Here V_R is the retention time, V_M and V_s represent the volumes of the mobile and stationary phases in the column, respectively, and K is the distribution constant (the K_c of eqn. 2). The same relationship is also valid in GC but here, due to the gas compressibility, V_G, the volume of the carrier gas in the column at atmospheric pressure, should be used.

In exclusion chromatography, V_o represents the retention volume of a non-retained compound (one of the two meanings of V_M) and V_i is the intrastitial volume in which the compounds are dissolved while within the pores; V_i may be considered as equivalent to (although not identical with) the "stationary phase" in general liquid chromatography. Thus, we can write for exclusion chromatography

$$V_R = V_o + K_o V_i \tag{27}$$

or

$$K_o = \frac{V_R - V_o}{V_i} \tag{28}$$

This value is used in textbooks dealing with exclusion chromatography: Snyder and Kirkland[5b] use the symbol K_o and call it the "distribution coefficient", while Determann[37] uses the symbol K_d and calls it simply the "K_d-value".

It is important to realize the meaning of the distribution constant in exclusion chromatography, which is different to that in the other variants. In all other chromatographic techniques the distribution constant corresponds to the ratio of the solute concentration in the stationary phase to that in the mobile phase*. However, as explained by Determann[37], the K_o (K_d) value expresses the fraction of the inner volume (*i.e.*, the volume of the pores) available to the molecules of the particular sample component for diffusion. Being a *fraction*, it is obvious that its value cannot be larger than unity and indeed, for the last peak representing total permeation**, $K_o = 1$, while for the first peak representing total exclusion, $K_o = 0$. Expressing it in a different way, K_o indicates the retention of a given sample component as a fraction relative to total permeation. Thus, it is similar to the R_f factor which also varies between zero and unity. In contrast, the "classical" distribution constants of gas and liquid chromatography vary between zero and infinity.

We believe that the K_o term as the "distribution constant" should definitely be included in any nomenclature dealing with exclusion chromatography.

It should be mentioned here that in the ASTM exclusion chromatography nomenclature[25] the equation for the distribution constant (called there the "distribution coefficient", K) is given as

$$K = \frac{V_R - V_o}{V_t} \tag{29}$$

which would give

$$V_R = V_o + KV_t \tag{30}$$

Comparing this with eqns. 26–27, it is obvious that eqns. 29–30 are incorrect because V_t has no connection with V_s in eqn. 26. The most likely explanation is that V_t in the

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* As expressed by eqns. 2–5 and 15–17, "concentration" may be expressed as g/volume, g/g, g/surface area, or a combination of these.

** In the case of the first peak, $V_R = V_o$, and thus $K_o = 0/V_i = 0$. In the case of the last peak, $V_R = V_t = V_o + V_i$, and thus $K_o = V_i/V_i = 1$.

denominator is a typing error instead of V_i. Unfortunately, however, the same error had already been made in the original edition of D 3016[22], first published in 1972. It seems to be that this typing error has never been discovered by anybody. Naturally, it should be corrected in future editions.

Retention volumes vs. retention times. The exclusion chromatography nomenclature[25] of ASTM Committee D-20 mentions only retention volumes and not retention times. With present, up-to-date instrumentation where proper mobile phase flow regulation is provided, this is no longer necessary and retention times could be used as well. Thus, the time equivalents of V_o, V_i and V_t (*i.e.*, t_o, t_i and t_t) should definitely be added to the nomenclature.

7. SPECIALIZED NOMENCLATURES

Naturally, owing to the differences in the various liquid chromatography techniques, each has some special symbols, terms and definitions which are not necessarily applicable to the other variants. In this section we shall deal with these.

A. Ion-exchange chromatography

The specialized symbols, terms and definitions of the IUPAC ion-exchange nomenclature are summarized in Tables 5 and 6. While no comments are necessary concerning the terms and definitions listed in Table 6, we have to comment on a few terms included in Table 5.

The first comment concerns the capacity terms; their definitions are as follows:

$$Q_o = \frac{\text{mequiv. of ionogenic group}}{\text{weight of dry ion exchanger}} \tag{31}$$

$$Q_v = \frac{\text{mequiv. of ionogenic group}}{\text{true volume of swollen ion exchanger}} \tag{32}$$

$$Q_A = \frac{\text{total amount of ions (expressed in mequiv. or mmol)}}{\text{weight of dry ion exchanger}} \tag{33}$$

$$Q_B = \frac{\text{total amount of ions (expressed in mequiv. or mmol)}}{\text{weight of dry ion exchanger or bed volume}} \tag{34}$$

$$\text{Bed volume capacity} = \frac{\text{mequiv. of ionogenic group}}{\text{bed volume}} \tag{35}$$

In Q_o, the weight of the exchanger should refer to the H form in a cation exchanger and the Cl form in an anion exchanger. In Q_v, the ionic form and the medium must be stated. Q_B, which is the practical capacity of an ion-exchanger bed in a dynamic system, is always determined experimentally under flow-through conditions and refers to the amount which has been taken up when the species is first detected in the effluent or when its concentration in the effluent reaches some arbitrarily defined volume. In *bed volume capacity*, and in Q_A, the conditions must be specified.

TABLE 5

SPECIALIZED TERMS AND SYMBOLS INCLUDED IN THE IUPAC ION-EXCHANGE CHROMATOGRAPHY NOMENCLATURE[20]

Parameter	*Symbol*	*Notes**
Capacity		See Note 1
Theoretical specific capacity	Q_0	
Volume capacity	Q_v	
Bed volume capacity		No symbol specified
Practical specific capacity	Q_A	
Breakthrough capacity of the ion-exchange bed	Q_B	
Selectivity coefficient	$k_{A/B}$	See Note 2
Corrected selectivity coefficient	$k^a_{A/B}$	See Note 2
Separation factor	$\alpha_{A/B}$	$\alpha_{A/B} = D_A/D_B$ (where D may be D_c, D_g or D_v)
Weight swelling in solvent	w_s	See Note 3

* *Notes:*

1. For the definition of the various capacity terms, see the text.
2. For example, for $Mg^{2+} - Ca^{2+}$ exchange:

$$k = \left(\frac{[Mg]}{[Ca]}\right)_S \Big/ \left(\frac{[Mg]}{[Ca]}\right)_M$$

The brackets refer to concentrations; subscript S indicates the concentrations in the ion exchanger ("stationary phase") and subscript M indicates the concentrations in the external solution ("mobile phase"). In the *corrected selectivity coefficient* the concentrations in the external solution are replaced by activities.

3. $w_s = \dfrac{\text{amount of solvent taken up}}{\text{amount of dry ion exchanger}}$

Note that the selectivity coefficient in the ion-exchange nomenclature has the same symbol as the capacity factor in general liquid (and gas) chromatography but its meaning is now different: it refers to the ratio of equilibrium concentrations. This might result in a misunderstanding and thus should probably be changed.

Finally, it should be mentioned that the symbol for the *weight swelling in the solvent* does not conform with the regulations set in the IUPAC Manual of Symbols[30]: it should be W and not w.

B. Exclusion chromatography

Table 7 lists the terms and symbols expressing particle and molecular parameters and their definitions according to the exclusion chromatography nomenclature of ASTM Committee D-20[25]. These are well defined and logical except the use of w and n in the subscripts: we have already mentioned that the universal symbol for weight is W and not w and thus it should have been used here also. This rule has been followed in the ASTM liquid chromatography nomenclature[10], which also contains some of these terms and uses M_N and M_W instead of M_n and M_w.

TABLE 6

SPECIALIZED ION-EXCHANGE CHROMATOGRAPHY TERMS (OTHER THAN THOSE IN TABLE 5) DEFINED BY IUPAC[20]

Term	*Notes**
Anion exchange	
Anion exchanger	
Base form	
Bed volume	See Note 1
Cation exchange	
Cation exchanger	
Acid form	
Co-ions	See Note 2
Counter ion	See Note 3
Fixed ions	See Note 3
Ion exchange	
Ion-exchange chromatography	
Ion-exchange isotherm	See Note 4
Ion-exchange membrane	
Ion exchanger	
Bifunctional	
Macroporous	
Monofunctional	
Polyfunctional	
Redox	
Salt form	
Ionogenic groups	See Note 5
Permselectivity	See Note 6
Redox polymers	
Resin matrix	
Sorption	See Note 4
Sorption isotherm	See Note 4
Volume swelling ratio	

* *Notes:*

1. Synonymous with column volume for a packed column.
2. Mobile ionic species in an ion exchanger with a charge of the same sign as the fixed ions.
3. *Counter ions* are the mobile exchangeable ions of the ion exchanger while the *fixed ions* are the non-exchangeable ions which have a charge opposite to that of the counter ions.
4. *Ion-exchange* and *sorption isotherms* refer to the concentration of a counter ion and a sorbed species, respectively, in the ion exchanger expressed as a function of their concentration in the external solution under specified conditions and a constant temperature. *Sorption* refers to the uptake of electrolytes and non-electrolytes by ion exchangers through mechanisms other than pure ion exchange.
5. In an ion exchanger, ionogenic groups refer to the fixed groupings which are either ionized or capable of dissociation into fixed ions and mobile counter ions.
6. Permselectivity refers to the permeation of certain ionic species in preference to other species through ion-exchange membranes.

C. Planar chromatography

Both the general IUPAC chromatography and ASTM liquid chromatography nomenclatures contain some terms, definitions and symbols for planar chromatography but do not go into detail. However, a very detailed and excellent listing of the

TABLE 7

TERMS AND SYMBOLS EXPRESSING PARTICLE AND MOLECULAR PARAMETERS SPECIFIED IN THE EXCLUSION CHROMATOGRAPHY NOMENCLATURE OF ASTM[25]

Parameter	*Symbol*	*Definition*
Particle parameters		
Number-average particle diameter	$\bar{D}_n$	First moment of the number distribution of particle diameters
Weight-average particle diameter	$\bar{D}_w$	First moment of the weight distribution of particle diameters
Weight-differential distribution of particle diameter	$f_w(D)$	Plot of weight population density as a function of D, the particle diameter
Molecular parameters		
Hydrodynamic volume	V_h	A polymer property proportional to $[\eta]M$
Intrinsic viscosity	$[\eta]$	It is equivalent to the reduced specific viscosity at infinite dilution
Molar volume	V_m	
Molecular weight (mol.wt.)	M	
Molecular weight distribution	MWD	
Weight-differential distribution of molecular weights	$f_w(M)$	Plot of weight population density as a function of M
Number-average molecular weight	$\bar{M}_n$	First moment of the number distribution of molecular weights
Weight-average molecular weight	$\bar{M}_w$	First moment of the weight distribution of molecular weights
Z-average molecular weight	$\bar{M}_Z$	First moment of the Z-distribution of molecular weights
$(Z+1)$-average molecular weight	$\bar{M}_{Z+1}$	First moment of the $Z+1$ distribution of molecular weights
Viscosity-average molecular weight	$\bar{M}_v$	A value related to the intrinsic viscosity (see above) of the polymer
Polydispersity factor (dispersity)	d	$d = \bar{M}_w/\bar{M}_n$
Instrument symmetrical spreading parameter	X_1	Used to correct for symmetric band broadening
Instrument skewing parameter	X_2	Used to correct for non-symmetric band broadening
Uncorrected number-average molecular weight	$\bar{M}_n(u)$	Values uncorrected for instrument spreading
Uncorrected weight-average molecular weight	$\bar{M}_w(u)$	
Corrected number-average molecular weight	$\bar{M}_n(c)$	Values corrected for instrument spreading
Corrected weight-average molecular weight	$\bar{M}_w(c)$	
Observable or "true" number-average molecular weight	$\bar{M}_n(t)$	Values obtained by classical methods such as osmometry and light scattering
Observable ot "true" weight-average molecular weight	$\bar{M}_w(t)$	
Lowest molecular weight	M_L	Lowest value of molecular weight in the mol.wt. distribution
Highest molecular weight	M_H	Highest value of molecular weight in the mol.wt. distribution
Exclusion limit	$V_{h,max}$	Maximum V_h that entered the pores
Weight-cumulative (or integral) distribution of molecular weights	$I_w(M)$	Sum of weight fractions as a function of molecular weight
Variance of molecular weight distribution	σ_j^2	Second moment about the mean of a specific type of mol.wt. distribution [$j = n, w, Z$ or $(Z+1)$]. It is a measure of the breadth of the distribution

TABLE 8

PLANAR (PAPER AND THIN-LAYER) CHROMATOGRAPHY TERMS AND SYMBOLS

Parameter	*ASTM*[10]	*IUPAC*[3]	*Notes**
Mobile phase distance			See Note 1
Number of theoretical plates	n	n	See Note 2
Retardation factor	R_f	R_f	See Note 3
R_M value	R_M	R_M	$R_M = \log\left(\frac{1 - R_f}{R_f}\right)$
R_s values	R_s	R_B	$R_s = R_{f(i)}/R_{f(s)}$
Solute distance			See Note 4
Spot diameter			See Note 5

* *Notes:*

1. The IUPAC nomenclature here retained the name *solvent*, calling it the *solvent migration distance*. This should be changed. No symbol is used in either nomenclature: it is equal to a in Fig. 3. Stahl calls it the "length of run", obviously as a translation of the German expression "Laufstrecke".
2. The number of theoretical plates is calculated using the parameters defined in Fig. 3 as $n = 16(b_i/c_i)^2$. If the spot is not circular, Note 5 should be followed.
3. It is calculated according to Fig. 3 as $R_f = b/a$. As shown, the distance b should be measured to the center of a spot while the distance a, the mobile phase migration distance, is measured to the mobile phase front.
4. No symbol is used in either nomenclature; it is equal to b in Fig. 3.
5. No symbol is used in either nomenclature: it is equal to c in Fig. 3. As pointed out by ASTM, if the spot is not circular, an imaginary circle is used whose diameter is the smallest diameter of the spot.

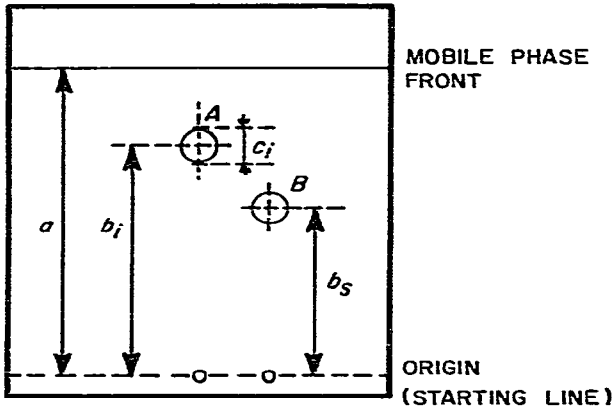

Fig. 3. Typical planar chromatogram. A = spot of the solute of interest (i); B = spot of the standard (reference) compound (s); a = mobile phase front; b = solute distance; c = spot diameter. $R_f = b_i/a$; $R_s = R_{f(i)}/R_{f(s)} = b_i/b_s$; $n_i = 16(b_i/c_i)^2$.

various terms and their definitions has been compiled by Stahl[17], which, in addition to English, also gives the appropriate terms in German and French. Here, we shall also consider this listing in addition to the two standards.

Table 8 lists the few symbols used in planar chromatography; Fig. 3 illustrates some of the parameters used to calculate these terms. It is interesting that no symbol

is used for the *solute distance* and the *mobile phase distance*. The obvious reason for this is that these are never used in themselves but always as a ratio, the R_f value.

We have dealt earlier with the evolution and importance of the R terms and its equivalent, the R_f term introduced first by Consden *et al.*[34]. It is a minor problem but should still be mentioned that there is no apparent agreement on the proper form of the subscript: while both IUPAC and ASTM use R_f, Stahl and most of the literature use R_F. Probably the latter should be followed in future revisions.

The value of R_f is always smaller than unity and, by convention, it is usually given to two decimal places. In order to simplify this, one often finds in the literature the so-called hR_f values, representing $100R_f$, *i.e.*, a value without decimal places. This is a useful term and should be included in future revisions.

The R_s value really represents relative retardation in planar chromatography: it is the ratio of two R_f values:

$$R_s = R_{f(i)}/R_{f(s)} \tag{36}$$

Since the mobile phase distance is common, we can express R_s directly as the ratio of the distance travelled by the spot of the solute of interest to the distance travelled by the spot of the standard (reference) compound; using the symbols of Fig. 3, we have

$$R_s = b_i/b_s \tag{37}$$

IUPAC uses the symbol R_B for R_s, indicating the solute of interest and the standard with the subscripts A and B, respectively. In our opinion, the ASTM symbol is more

TABLE 9

TERMS USED IN PLANAR (PAPER AND THIN-LAYER) CHROMATOGRAPHY DEFINED BY THE STANDARD NOMENCLATURES AND STAHL

Term	*ASTM*[10]	*IUPAC*[3]	*Stahl*[17]	*Notes**
Adsorption chromatography	+	+	+	
Apply (verb)			+	See Note 1
Ascending development	+			
Binder	+			
Chamber (developing chamber)	+	+	+	
Chamber saturation		+	+	See Note 2
Chromatogram	+	+	+	See Note 3
Consecutive development	+			See Note 4
Coupling of techniques			+	See Note 5
Densitometer	+			
Descending development	+			
Detection		+	+	See Note 6
Develop	+		+	
Development	+		+	See discussion in text
Elute		+		See discussion in text
Elution		+		
Equilibration		+	+	See Note 2
Front (mobile phase front, solvent front)	+	+	+	
Fronting			+	See Note 7
Gradient development (gradient elution)	+	+	+	
Gradient layer		+		See Note 8

TABLE 9 *(continued)*

Term	*ASTM*[10]	*IUPAC*[3]	*Stahl*[17]	*Notes**
Horizontal development	+			
Impregnation			+	See Note 8
Layer equilibration		+	+	See Note 2
Migration rate			+	See Note 9
Mobile phase	+	+	+	
Multiple development	+			See Note 4
Paper chromatography	+	+	+	
Radial development	+			
Reversed-phase chromatography		+		
Sandwich chamber	+			
Saturated development	+			
Saturation	+	+	+	See Note 2
Solute	+			Synonym for "sample"
Spot	+	+	+	
Spotting device		+		
Starting point (line)	+	+	+	
Support plate		+		
Tailing		+	+	See Note 7
Thin-layer chromatography	+	+	+	
Transfer			+	See Note 5
Two-dimensional chromatography (development)	+	+		See Note 4
Unsaturated development	+			
Visualization	+			See Note 6
Visualization chamber	+			

* *Notes:*

1. Recommended instead of "to spot".
2. Stahl distinguishes between *chamber saturation* and *equilibration*. "Chamber saturation" refers to the uniform distribution of the mobile phase vapor *in the chamber* until reaching equilibrium prior to elution (development). On the other hand, "equilibration" refers to the saturation of the *stationary phase* (layer) by the mobile phase vapor.
3. As already mentioned earlier, in planar chromatography, "chromatogram" refers to the paper or thin layer on which the separation took place.
5. In *coupling* the two techniques are directly connected and no mechanical transfer takes place. *Transfer* refers to the mechanical transfer of the sample from one analytical procedure to the other.
4. According to ASTM, in consecutive development different mobile phases are used, but only after the previous mobile phase is removed from the planar media. The technique is subdivided according to the direction of the developments: if the second development is accomplished in the same direction as the previous development, this is *multiple development*, while if it is at a right-angle to the first development, this is *two-dimensional development*.
6. In planar chromatography, *detection* also refers to the visualization of colorless, chromatographically separated substances using chemical, physical or biological procedures. Stahl proposes the use of this more general term instaed of "visualization".
7. In planar chromatography, *fronting* refers to a spot (zone) showing a diffuse region in front of the zone in the direction of the flow while *tailing* refers to the situation when the diffuse region is behind the zone. It is important to distinguish "fronting" from "front", which refers to the front line of the mobile phase.
8. *Impregnation* refers to the modification of the separation properties of the layer (or paper) by appropriate additives. If geographically there is a transition in the layer (or paper) from one property (*e.g.*, pH) to the other, then it is called a *gradient layer*.
9. Stahl proposes this term to express the distance travelled by the mobile phase in unit time; in other words, it is equivalent to the mobile phase velocity used in column chromatography.

appropriate, particularly because in the literature the "R_B value" often refers to the use of *p*-dimethylaminoazobenzene ("*B*utter yellow", hence *B*) as the reference standard when analyzing alcohols and phenols in the form of their 3,5-dinitrobenzoates[38].

Table 9 lists the terms (in addition to those already included in Table 8) for which clear definitions are given in the two standard nomenclatures or in Stahl's compilation. There are two terms for which no clear agreement exists: elution *vs.* development, and solvent *vs.* mobile phase.

As already mentioned, IUPAC particularly discourages the use of "development" as an obsolete term and proposes the use of "elution" instead of it, both in this form and in other words. It has already been stated that we feel that while this is acceptable for column chromatography, in planar chromatography, where the mobile phase usually does not leave the plate or paper, "development" is a more appropriate term than "elution" although, naturally, planar chromatography is still a variant of elution chromatography.

Concerning the term "solvent", we have already discussed its ambiguity. While ASTM and Stahl are clear in the elimination of this term and advocate the use of "mobile phase" instead, it is unfortunate that IUPAC is still using both terms. This should be eliminated in future revisions.

8. SUMMARY

The nomenclature of liquid chromatography in general as well as that of its variants is reviewed, with special emphasis on the existing differences. Proposals are made for the necessary modifications to create a uniform, general nomenclature for liquid chromatography and to adjust the individual, specialized nomenclatures to conform with such a generalized nomenclature.

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