



## Standard Practice for Gas Chromatography Terms and Relationships<sup>1</sup>

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*This standard has been approved for use by agencies of the U.S. Department of Defense.*

### 1. Scope

1.1 This practice covers primarily the terms and relationships used in gas elution chromatography. However, most of the terms should also apply to other kinds of gas chromatography and are also valid in the various liquid column chromatographic techniques, although at this time they are not standardized for the latter usage.

### 2. Names of Techniques

2.1 *Gas Chromatography*, abbreviated as GC, comprises all chromatographic methods in which the moving phase is gaseous. The stationary phase may be either a dry granular solid or a liquid supported by the granules or by the wall of the column, or both. Separation is achieved by differences in the distribution of the components of a sample between the mobile and stationary phases, causing them to move through the column at different rates and from it at different times. In this recommended practice gas elution chromatography is implied.

2.2 *Gas-Liquid Chromatography*, abbreviated as GLC, utilizes a liquid as the stationary phase, which acts as a solvent for the sample components.

2.3 *Gas-Solid Chromatography*, abbreviated as GSC, utilizes an active solid (adsorbent) as the stationary phase.

2.4 *Gas Elution Chromatography* utilizes a continuous inert gas flow as the carrier gas and the sample is introduced as a gas or a liquid with a finite volume into the carrier gas stream. If the sample is introduced as a liquid, it is vaporized in the system prior to or during passage through the separation column.

2.5 *Gas-Frontal Chromatography* is a technique in which a continuous stream of carrier gas mixed with sample vapor is instantaneously replaced by a continuous stream of carrier gas containing sample vapor at a different concentration. The concentration profile is therefore step-shaped at the column inlet.

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2.6 *Gas-Displacement Chromatography* employs a desorbent as the carrier gas or in the carrier gas to displace a less strongly held solute from the stationary phase which in turn displaces the next less strongly held one etc., causing the components to emerge in the normal order, that is, least-to-most strongly absorbed.

2.7 *Isothermal Gas Chromatography* is the version of the technique in which the column temperature is held constant during the passage of the sample components through the separation column.

2.8 *Programmed Temperature Gas Chromatography* (PTGC), is the version of the technique in which the column temperature is changed with time during the passage of the sample components through the separation column. In linear PTGC the program rate is constant during analysis. Isothermal intervals may be included in the temperature program.

2.9 *Programmed Flow, Pressure, or Velocity Gas Chromatography* is the version of the technique in which the carrier gas flow, pressure, or velocity is changed during analysis.

2.10 *Reaction Gas Chromatography* is the version of the technique in which the composition of the sample is changed between sample introduction and the detector. The reaction can take place upstream of the column when the chemical composition of the individual components passing through the column differs from that of the original sample, or between the column and the detector when the original sample components are separated in the column but their chemical composition is changed prior to entering the detection device.

2.11 *Pyrolysis Gas Chromatography* is the version of reaction gas chromatography in which the original sample is decomposed by heat to more volatile components prior to passage through the separation column.

### 3. Apparatus

3.1 *Sample Inlet Systems*, represent the means for introducing samples into the separation column, including the heated zones permitting the vaporization of the introduced liquid samples prior to their passage through the column. Sample introduction can be carried out by introduction of a liquid, solid, or gas into the carrier-gas stream. The sample may be vaporized before or after introduction into the column.

3.1.1 *Direct Inlets*, rapidly vaporize the sample prior to entering the column. All of the sample vapor enters the column.

3.1.2 *On-Column Inlets*, introduce a liquid sample into the column. The sample vaporizes as the column section containing the liquid heats up after injection.

3.1.3 *Split Inlets*, rapidly vaporize the sample prior to entering the column. A defined fraction of the sample vapor enters the column; the remainder leaves the inlet through a vent at a flow rate  $F_v$ . The ratio of the total inlet flow ( $F_v + F_c$ ) to the column flow ( $F_c$ ) is called the split ratio ( $s$ ):

$$s = \frac{F_v + F_c}{F_c} \quad (1)$$

3.1.4 *Splitless Injection*, utilizes a split inlet wherein the split vent flow is blocked during the injection period such that most of the sample vapor enters the column. The injection period is typically one minute. The split vent flow is reestablished afterward usually for the remainder of the run.

3.1.5 *Programmed-Temperature Vaporizers (PTV)*, accept a liquid sample that vaporizes as the inlet system heats up after injection. A PTV may operate in either a split, splitless, on-column, or direct mode.

3.1.6 A *Retention Gap*, is a section of tubing inserted between the inlet and the analytical column proper. The retention gap may have an inner diameter different than the analytical column. The retention gap has significantly lower retaining power than the analytical column; in practice the retention gap is deactivated but not coated.

3.2 *Columns*, consist of tubes that contain the stationary phase and through which the gaseous mobile phase flows.

3.2.1 *Packed Columns*, are filled with granular packing that is kept in place by gas-permeable plugs at both ends.

3.2.2 *Open-Tubular Columns*, have unobstructed central gasflow channels.

3.2.2.1 *Wall-Coated Open-Tubular Columns*, abbreviated WCOT columns, have the liquid phase coated directly on the inside, relatively smooth wall of the column tubing.

3.2.2.2 *Porous-Layer Open-Tubular Columns*, abbreviated PLOT columns, have a solid porous layer present on the tube wall but still maintain the unobstructed central gas-flow channel. This porous solid layer can either act as an adsorbent or a support which in turn is coated with a thin film of the liquid phase, or both. The solid layer can either be deposited on the inside tube wall or formed by chemical means from the wall.

3.2.2.3 *Support-Coated Open-Tubular Columns*, abbreviated SCOT columns, refer to those PLOT Columns where the solid layer consists of the particles of a solid support which were deposited on the inside tube wall.

3.3 *Detectors*, are devices that indicate the presence of eluted components in the carrier gas emerging from the column.

3.3.1 *Differential Concentration Detectors*, measure the instantaneous proportion of eluted sample components in the carrier gas passing through the detector.

3.3.2 *Differential Mass Detectors*, measure the instantaneous rate of arrival of sample components at the detector.

3.3.3 *Integral Detectors*, measure the accumulated quantity of sample component(s) reaching the detector.

3.3.4 *Spectrometric Detectors*, measure and record spectra of eluting components, such as the mass spectrum of the infrared spectrum.

3.4 *Traps*, are devices for recovering sample components from the mobile phase eluting from GC columns.

## 4. Reagents

4.1 *Carrier Gas* is the *Mobile Phase* used to sweep or elute the sample components through and from the column.

4.2 The *Stationary Phase* is composed of the active immobile materials within the column that selectively delay the passage of sample components by dissolving or adsorbing them, or both. Inert materials that merely provide physical support for the stationary phase or occupy space within the column are not part of the stationary phase.

4.2.1 *Liquid Stationary Phase* is one type of stationary phase which is dispersed on the solid support or the inner column wall and causes the separation of the sample components by differences in the partitioning of the sample components between the mobile and liquid phases.

4.2.2 An *Active Solid* is one that has ab- or adsorptive properties by means of which chromatographic separations may be achieved.

4.3 The *Solid Support* is the inert material that holds the stationary (liquid) phase in intimate contact with the carrier gas flowing through it. It may consist of porous or impenetrable particles or granules which hold the liquid phase and between which the carrier gas flows, or the interior wall of the column itself, or a combination of these.

4.4 The *Column Packing* consists of all the material used to fill packed columns, including the solid support and the liquid phase or the active solid.

4.4.1 The *Liquid-Phase Loading* describes the relative amount of liquid phase present in a packed column when the column packing consists only of the liquid phase plus the solid support. It is usually expressed as weight percent of liquid phase present in the column packing:

$$\begin{aligned} \text{Liquid - phase loading, wt\%} & \quad (2) \\ & = \frac{(\text{amount of liquid phase}) \times 100}{(\text{amount of liquid phase} + \text{amount of solid support})} \end{aligned}$$

4.5 *Solutes* are the introduced sample components that are delayed by the column as they are eluted through it by the carrier gas.

4.6 *Unretained Substances* are not delayed by the column packing.

## 5. Gas Chromatographic Data

5.1 A *Chromatogram* is a plot of detector response against time or effluent volume. Idealized chromatograms obtained with differential and integral detectors for an unretained substance and one other component are shown in Fig. 1.

5.2 The definitions in this paragraph apply to chromatograms obtained directly by means of differential detectors or by

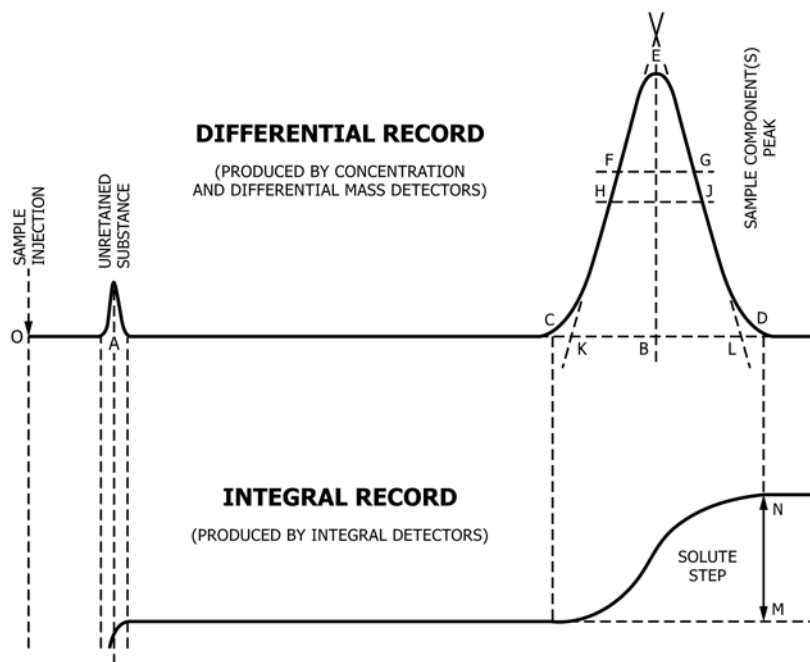


FIG. 1 Typical Chromatogram

differentiating the records obtained by means of integral detectors. The *Baseline* is the portion of the chromatogram recording the detector response in the absence of solute or solvent emerging from the column. A *Peak* is the portion of the chromatogram recording the detector response while a single component is eluted from the column. If two or more sample components emerge together, they appear as a single peak. The *Peak Base*, *CD* in Fig. 1, is an interpolation of the baseline between the extremities of the peak. The area enclosed between the peak and the peak base, *CHFEGJD* in Fig. 1, is the *Peak Area*. The dimension *BE* from the peak maximum to the peak base measured in the direction of detector response is the *Peak Height*. Retention dimensions parallel to the baseline are termed as the peak widths. The retention dimension of a line parallel to the peak base bisecting the peak height and terminating at the inflexion points *FG* of the tangents drawn to the inflexion points (= 60.7 % of peak height) is the *Peak Width at Inflexion Points*,  $w_i$ . The retention dimension of a line parallel to the peak base drawn to 50 % of the peak height and terminating at the sides *HJ* of the peak is the *Peak Width at Half Height*,  $w_h$ . The retention dimension of the segment of the peak base *KL* intercepted by the tangents drawn to the inflexion points on both sides of the peak is the *Peak Width at Base* or *Base Width*,  $w_b$ .

5.3 The following definitions apply to chromatograms obtained with integral detectors, or by integration of the records obtained by means of differential detectors. As sample components pass through the detector the baseline is displaced cumulatively. The change in baseline position as a single sample component is eluted is a *Step*. The difference between

straight line extensions of the baselines on both sides of the step, measured in the direction of detector response, is the *Step Height*, *NM*.

## 6. Retention Parameters

6.1 Retention parameters are listed in Table 1. The interrelations shown apply only to gas elution chromatography columns operated under constant conditions and for which the partition coefficients are independent of concentration. Fig. 1 can be used to illustrate some of these parameters:

Gas holdup time	= <i>OA</i>
Retention time	= <i>OB</i>
Adjusted retention time	= <i>AB</i>
Partition (capacity) ratio	= <i>AB/OA</i>
Peak width at half height	= <i>HJ</i>
Peak width at base	= <i>KL</i>
Number of theoretical plates	= $16 (OB/KL)^2 = v 5.54 (OB/HJ)^2$
Relative retention	= $(AB)_j / (AB)_i$ or $(AB)_i / (AB)_s$
Peak resolution	= $\frac{2[(OB)_j - (OB)_i]}{(KL)_i + (KL)_j} = \frac{(OB)_j - (OB)_i}{(KL)_j}$

Subscripts *i*, *j*, and *s* refer to any earlier peak, any later peak, and a reference peak, respectively.

## 7. Presentation of Isothermal Retention Data

7.1 Retention values should be reported in a form that can be applied for a specific stationary phase composition in different apparatus and for different conditions of column length, diameter, and inlet and outlet pressures, and for different carrier gases and flow rate. When the solid support is inert, its particle-size range and distribution, and (within limits)

the amount and mode of deposition of the liquid phase, may be varied also. While the solid support is commonly assumed to be inert, often this is not so. The physical disposition of the liquid phase may also affect retention values (1).<sup>2</sup> Consequently, all components of the column packing and the procedure for combining them must be fully specified to enable other workers to prepare identical compositions.

<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of this practice.

7.2 Retention in gas-liquid chromatography can be expressed on an absolute basis in terms of the partition coefficient or specific retention volume of a substance (tacitly assuming an inert solid support). Relative retentions are more conveniently determined, however, and they should be expressed relative to a substance which is easily available and emerges relatively close to the substance of interest.

7.3 Retention index is another retention parameter. It is defined relative to the retention of *n*-alkanes, and represents the number of carbon atoms, multiplied by 100, in a hypothetical *n*-alkane that would have an identical retention.

**TABLE 1 Summary of Parameters, Symbols, Units, and Useful Relationships in Gas Chromatography**

GC Parameter	Symbol	Unit	Definition or Relation to Other Parameters
Absolute temperature of carrier gas	<i>T</i>	K	°C + 273.15 at point where gas flow rate is measured
Absolute temperature of column	<i>T<sub>c</sub></i>	K	
Absolute ambient temperature	<i>T<sub>a</sub></i>	K	
Column inlet pressure	<i>P<sub>i</sub></i>	Pa	
Column outlet pressure	<i>P<sub>o</sub></i>	Pa	
Pressure drop along the column	$\Delta P$	Pa	$\Delta P = P_i - P_o$
Relative column pressure	<i>P</i>		$P = P_i/P_o$
Ambient (atmospheric) pressure	<i>P<sub>a</sub></i>	Pa	
Partial pressure of water at ambient temperature	<i>P<sub>w</sub></i>	Pa	a value used in correcting the flow rate to dry-gas conditions if measured with a soap-bubble flowmeter
Reference pressure	<i>P<sub>ref</sub></i>	Pa	pressure at which the reference column flow ( <i>F<sub>ref</sub></i> ) is expressed. An example of a reference pressure is 101.325 kPa (1.000 atm).
Reference temperature	<i>T<sub>ref</sub></i>	K	temperature at which the reference column flow ( <i>F<sub>ref</sub></i> ) is expressed. An example of a reference temperature is 293.15 K (20°C).
Detector pressure	<i>P<sub>d</sub></i>	Pa	pressure in the detector.
Detector temperature	<i>T<sub>d</sub></i>	K	temperature in the detector.
Mobile-phase compressibility correction factor	<i>j</i>		$j = \frac{3}{2} \left[ \frac{P^2 - 1}{P^3 - 1} \right]$
Factor relating pressure drop and column permeability	<i>j'</i>		$j' = \frac{3}{4} \left[ \frac{P^2 + 2P + 1}{P^2 + P + 1} \right]$ $\Delta P j' = \frac{L \bar{u} \eta}{B_o}$
Column length	<i>L</i>	cm	
Column inside diameter	<i>d<sub>c</sub></i>	cm	
Column inside radius	<i>r<sub>c</sub></i>	cm	
Average diameter of solid particles inside column	<i>d<sub>p</sub></i>	cm	
Average liquid film thickness in open-tubular columns	<i>d<sub>f</sub></i>	cm	
Interparticle porosity	$\epsilon$		fraction of column cross-section available for the mobile phase. For packed columns, $\epsilon < 1$ . For open-tubular columns, $\epsilon = 1.0$ .
Weight of stationary phase in column	<i>W<sub>S</sub></i>	g	equal to <i>W<sub>L</sub></i> in gas-liquid chromatography.
Density of stationary phase in column	$\rho_S$	g/cm <sup>3</sup>	equal to $\rho_L$ in gas-liquid chromatography.
Volume of stationary phase in column	<i>V<sub>S</sub></i>	cm <sup>3</sup>	at column temperature; equal to <i>V<sub>L</sub></i> in gas-liquid chromatography $V_S = W_S/\rho_S$
Gas holdup volume	<i>V<sub>M</sub></i>	cm <sup>3</sup>	$V_M = F_C t_M$
Corrected gas holdup volume	<i>V<sup>o</sup><sub>M</sub></i>	cm <sup>3</sup>	$V_M^o = F_C t_M j = j V_M$
Volume of mobile phase in the column (interstitial volume)	<i>V<sub>G</sub></i>	cm <sup>3</sup>	In ideal case, assuming no extracolumn volume in the system: $V_G = V_M^o = j V_M$ For open-tubular columns: $V_G = \pi L (r_c - d_f)^2$ In actual systems: $V_G = j [V_M - V_i P - V_D]$ where <i>P</i> is the relative pressure and <i>j</i> the pressure gradient correction factor as defined earlier; <i>V</i> is the volume between the effective injection point and the column inlet; <i>V<sub>D</sub></i> is the volume between the column outlet and the effective detection point; <i>V<sub>M</sub></i> and <i>V<sup>o</sup><sub>M</sub></i> are defined above.
Geometric column volume	<i>V<sub>c</sub></i>	cm <sup>3</sup>	$V_c = \frac{\pi d_c^2 L}{4}$
Specific permeability of column	<i>B<sub>o</sub></i>	cm <sup>3</sup>	For packed columns: $B_o = \frac{d_p^2 \epsilon^3}{180 (1 - \epsilon)^2}$ $B_o = 2 \eta \epsilon L \frac{P_o}{P_i^2 - P_o^2} u_o$ For open-tubular columns: $B_o = \frac{d_c^2}{32} = \frac{r_c^2}{8}$
Phase ratio of column	$\beta$		$\beta = V_G/V_L$

**TABLE 1** *Continued*

GC Parameter	Symbol	Unit	Definition or Relation to Other Parameters
			For open-tubular columns: $\beta = \frac{d_c}{4d_f}$
Gas flow rate from column	$F$	cm <sup>3</sup> /min	measured at ambient temperature and pressure (with a wet flowmeter).
Gas flow rate from column corrected to dry gas conditions	$F_a$	cm <sup>3</sup> /min	the value of $F$ corrected to dry gas conditions. $F_a = F \left( 1 - \frac{P_w}{P_a} \right)$
Gas flow rate from column corrected to column temperature	$F_c$	cm <sup>3</sup> /min	$F_c = F_a \left( \frac{T_c}{T_a} \right)$
Gas flow rate from column corrected to reference temperature and pressure	$F_{ref}$	cm <sup>3</sup> /min	$F_{ref} = F_a \frac{P_a}{P_{ref}} \frac{T_{ref}}{T_a}$ the values of $T_{ref}$ and $P_{ref}$ must be specified.
Gas flow rate from column corrected to detector temperature and pressure	$F_d$	cm <sup>3</sup> /min	$F_d = F_a \frac{P_a}{P_d} \frac{T_d}{T_a}$ the values of $T_d$ and $P_d$ must be specified.
Linear gas velocity at column outlet	$u_o$	cm/s	$u_o = \frac{4F_c}{\pi d_c^2 \pi 60}$
Average linear gas velocity	$\bar{u}$	cm/s	$\bar{u} = u_o j = \frac{L}{60t_M}$
Optimum average linear gas velocity in column	$u_{opt}$	cm/s	the value of $\bar{u}$ at the minimum of the HETP versus $\bar{u}$ plot
Viscosity of carrier gas	$\eta$	Pa·s	expressed at column temperature
Retention time (total retention time)	$t_R$	min	time from sample injection to maximum concentration (peak height) of eluted compound.
Gas holdup time	$t_M$	min	observed elution time of an unretained substance.
Adjusted retention time	$t'_R$	min	$t'_R = t_R - t_M$
Corrected retention time	$t''_R$	min	$t''_R = j t'_R$
Net retention time	$t_N$	min	$t_N = j t_R$
Retention volume (total retention volume)	$V_R$	cm <sup>3</sup>	$V_R = F_c t_R$
Adjusted retention volume	$V'_R$	cm <sup>3</sup>	$V'_R = F_c t'_R$
Corrected retention volume	$V''_R$	cm <sup>3</sup>	$V''_R = j F_c t'_R = j V'_R$
Net retention volume	$V_N$	cm <sup>3</sup>	$V_N = F_c t_N = j V'_R$
Specific retention volume	$V_g$	cm <sup>3</sup>	(net retention volume)/(g stationary phase), corrected to 0°C at effective column pressure: $V_g = \frac{V_N}{W_S} \cdot \frac{273.15}{T_c}$
Peak width at inflection points	$w_i$	min	retention dimension between the inflection points (representing 60.7 % of peak height) of any single-solute peak.
Peak width at half-height	$w_h$	min	retention dimension between the front and rear sides of any single-solute peak at 50 % of its maximum height.
Peak width at base	$w_b$	min	retention dimension between intersections of baseline with tangents to the points of inflection on the front and rear sides of any single-solute peak
Distribution constant (partition coefficient)	$K_c$		$K_c = \frac{\text{solute concentration in liquid phase, g/ml}}{\text{solute concentration in mobile phase, g/ml}}$ $K_c = \frac{W_{(S)}/V_S}{W_{(M)}/V_M}$ $V''_R = V_G + K_c V_S$
Retention factor (capacity or partition ratio capacity factor, mass distribution ratio)	$k$		$K = \beta k$ $k = \frac{t_R/t_M}{t_R/t_M} = \frac{\text{weight of compound in liquid phase}}{\text{weight of compound in mobile phase}}$ $= K\beta$
Plate number	$N$		$n = 16 (t_R/w_b)^2 = 5.54 (t_R/w_h)^2$
Effective plate number	$N_{eff}$		$N_{eff} = 16 (t'_R/w_b)^2 = 5.54 (t'_R/w_h)^2 = N \left( \frac{k}{k+1} \right)^2$
Plate height (height equivalent to one theoretical plate)	$H$	cm	$H = L/N$
Effective plate height (height equivalent to one effective plate)	$H_{eff}$	cm	$H_{eff} = L/N_{eff}$
Peak resolution	$R_s$		$R_s = \frac{2(t_{R2} - t_{R1})}{w_{b2} + w_{b1}} \cong \frac{t_{R2} - t_{R1}}{w_{b1}}$ where $t_{R2} > t_{R1}$
Relative retention	$r$		$r = t_R/t_{R(st)} = K_i/K_{(st)} = k/k_{(st)}$

**TABLE 1** *Continued*

GC Parameter	Symbol	Unit	Definition or Relation to Other Parameters
Separation factor	$\alpha$		$\alpha = t_{R2}/t_{R1} K_2/K_1 = k_2/k_1$ The symbol $r$ designates the retention of a peak relative to the peak of a standard while the symbol $\alpha$ designates the relative retention of two consecutive peaks. By agreement, $t_{R2} > t_{R1}$ and thus, $\alpha$ is always larger than unity while $r$ can be either larger or smaller than unity, depending on the relative position of the standard peak.
Number of theoretical plates required for a given resolution of peaks 1 and 2	$N_{req}$		$N_{req} = 16 R_s^2 \left( \frac{\alpha}{\alpha + 1} \right)^2 \left( \frac{k_2 + 1}{k_2} \right)^2$
Retention index (linear programmed temperature GC)	$I^T$		$I^T = 100 \left[ z + \frac{t_{Ri}^T - t_{Rz}^T}{t_{R(z+1)}^T - t_{Rz}^T} \right]$ where $t_{Ri}^T$ refers to the total retention times measured under temperature-programmed conditions. For definition of $z$ , see above
Designations of subscripts	a c eff f i o p st G L M N R S 1,2		Ambient Column Effective Film of liquid phase any solute outlet of column particle a standard or reference solute gas phase liquid phase mobile phase net retention stationary phase two solutes from which solute 2 elutes later than solute 1
Designation of superscripts	T ' °		temperature-programmed adjusted corrected

## REFERENCES

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- (2) “Recommendations on Nomenclature for Chromatography,” *Pure and Applied Chemistry*, Vol 37, No. 4, 1974, pp. 447–462.

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