GC Connections

A Compendium of GC Terms and Techniques

In this month's "GC Connections," John Hinshaw updates and expands his glossary of gas chromatography terms and techniques.

Gas chromatographers often use unique terms and acronyms that are well understood by those familiar with the field. For those not well versed in gas chromatography (GC), however, this lexicon can be confusing and misleading. This compendium lists chromatographic terms and symbols prevalent in today's usage, according to commonly accepted nomenclature. It is an updated version of a compendium that I put together 10 years ago (1). The terms and symbols conform to International Union of Pure and Applied Chemistry (IUPAC) recommendations where applicable (2). I have excluded trademarked names, except for cases in which the name is in common usage and designates more than one product or item.

A

α: Separation factor of two adjacent peaks; $\alpha = k_2/k_1$.

A_p: Peak area.

AFS: Amperes full scale.

Alumina: A gas–solid adsorbent stationary phase.

Average carrier gas linear velocity ($\bar{u}$): The average speed at which a molecule of carrier gas passes through a column.

B

β: Phase ratio. The ratio of mobile- to stationary-phase volumes. Thicker stationary-phase films yield longer retention times and higher peak capacities. For open-tubular columns, $\beta = V_G/V_L \approx d_c/4d_f$.

Backflush: Occurs when peaks at the end of a chromatogram are flushed from a column to vent or to another column by flow reversal.

Bakeout: The process of removing contaminants from a column by operation at elevated temperatures, which should not exceed a column's maximum operating temperature (MAOT).

Band broadening: Several processes that cause solute profiles to broaden as they migrate through a column.

Bleed: The loss of material from a column or septum caused by high-temperature operation. Bleed can result in ghost peaks and increased detector baseline offset and noise.

Bonded phase: A stationary phase that has been chemically bonded to the inner column wall. See also ***cross-linked phase.***

BTEX: Benzene, toluene, ethylbenzene, and xylene.

C

***CE*:** Coating efficiency. A metric for evaluating column quality. The minimum theoretical plate height divided by the observed plate height; $CE = H_{min}/H$.

Cold injection: An injection that occurs at temperatures lower than the final oven temperature, usually at or below the solvent boiling point.

Comprehensive GC (GC × GC): Two-dimensional technique in which all compounds experience the selectivity of two columns connected in series by a retention modulation device, thereby generating much higher resolution than that attainable with any single column.

Compressibility correction factor (j): This factor compensates for the expansion of a carrier gas as it moves along the column from the entrance, at the inlet pressure (p_i), to the column exit, at the outlet pressure (p_o).

Cross-linked phase: A stationary phase that includes cross-linked polymer chains. Usually, it also is bonded to the column inner wall. See also ***bonded phase.***

D

d_c: Average column inner diameter.

d_f: Average stationary-phase film thickness.

D_G: Gaseous diffusion coefficient; approximately 0.05 for hydrocarbons in helium carrier gas and 0.1 for hydrogen carrier gas.

D_L: Liquid–liquid diffusion coefficient; approximately 1×10^{-5} for hydrocarbons in silicones.

d_p: Average particle diameter.

Dead volume: Extra volume experienced by solutes as they pass through a chromato-

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graphic system. Excessive dead volume causes additional peak broadening.

DEGS: Diethylene glycol succinate; used as a stationary phase.

Direct injection: Occurs when sample enters an inlet and is swept into a column by carrier-gas flow. No sample splitting or venting occurs during or after the injection.

DMCS: Dimethylchlorosilane; used for silanizing glass GC parts.

E

Efficiency: The ability of a column to produce sharp, well-defined peaks. More-efficient columns have more theoretical plates (N) and smaller theoretical plate heights (H).

Electrolytic-conductivity detection (ELCD): In ELCD, the detector catalytically reacts halogen-containing solutes with hydrogen (reductive mode) to produce strong acid by-products that are dissolved in a working fluid. The acids dissociate, and the detector measures increased electrolytic conductivity. Other operating modes modify the chemistry for response to nitrogen- or sulfur-containing substances.

Electron-capture detection (ECD): In ECD, a detector ionizes solutes by collision with metastable carrier-gas molecules produced by β-emission from a radioactive source such as ^{63}Ni. The electron-capture detector is one of the most sensitive detectors, and it responds strongly to halogenated solutes and others with high electron-capture cross-sections.

F

***F*$_a$:** The column outlet flow rate corrected to room temperature and pressure; for example, the flow rate as measured by a flowmeter. F_a can be calculated from the average carrier-gas linear velocity and the column dimensions:

$$F_a = \frac{\bar{u}\,\pi\, d_c^2 T_o}{4jT_c}$$

***F*$_s$:** The split-vent flow rate, measured at room temperature and pressure.

FAME: Fatty-acid methyl ester.

FFAP: Free fatty-acid phase.

Flame ionization detection (FID): In FID, a detector ionizes hydrocarbon-containing solutes in a hydrogen–air flame. FID is a nearly universal detection technique that responds strongly to most classes of organic compounds.

Flame photometric detection (FPD): In FPD, the detector burns heteroatomic solutes in a hydrogen–air flame. The visible-range atomic emission spectrum is filtered through an interference filter and detected with a photomultiplier tube. Different interference filters can be selected for sulfur, tin, or phosphorus emission lines. The flame photometric detector is sensitive and selective.

FS: Fused silica.

FSOT: Fused-silica open-tubular column.

G

GALP: Good automated laboratory practice.

Gas–liquid chromatography (GLC): In this technique, solutes partition between a gaseous mobile phase and a liquid stationary phase. Selective interactions between the solutes and the liquid phase cause different retention times in the column.

Gas–liquid phase chromatography (GLPC): See ***gas–liquid chromatography.***

Gas–solid chromatography (GSC): In this technique, solutes partition between a gaseous mobile phase and a solid stationary phase. Selective interactions between the solutes and the solid phase cause different retention times in the column.

Ghost peaks: Peaks not present in the original sample. Ghost peaks can be caused by septum bleed, solute decomposition, or carrier-gas contamination.

GLP: Good laboratory practice.

H

***H*:** Height equivalent to one theoretical plate. The distance along the column occupied by one theoretical plate; $H = L/N$.

***H*$_{meas}$:** Height equivalent to one theoretical plate as measured from a chromatogram:

$$H_{meas} = \frac{L}{5.54\left(\frac{t_R}{w_h}\right)^2}$$

***H*$_{min}$:** Minimum theoretical plate height at the optimum linear velocity, ignoring stationary-phase contributions to band broadening. For open-tubular columns:

$$H_{min} = \left(\frac{d_c}{2}\right)\sqrt{\frac{1 + 6k + 11k^2}{3(1+k)^2}}$$

***h*$_p$:** Peak amplitude.

***H*$_{theor}$:** Theoretical plate height. For open-tubular columns (Golay equation):

$$H_{theor} = \left(\frac{2D_G}{\bar{u}}\right) + \bar{u}\left\{\left[\frac{\left(1 + 6k + 11k^2\right)}{96(1+k)^2}\right]\left(\frac{d_c^2}{D_G}\right) + \left[\frac{2k}{3(1+k)^2}\right]\left(\frac{d_f^2}{D_L}\right)\right\}$$

Headspace sampling: Gas-phase sampling technique in which solute is removed from an enclosed space above a solid or liquid sample.

Heartcut: Technique in which two or more partially resolved peaks that are eluted from one column are directed onto another column of different polarity or at a different temperature for improved resolution.

***HETP*:** Height equivalent to one theoretical plate; discontinued term for plate height (H).

I

Ion-trap detector: A mass spectrometric (MS) detector that uses an ion-trap device to generate mass spectra.

J

***j*:** Carrier-gas compressibility correction factor:

$$j = \frac{3\left(P^2 - 1\right)}{2\left(P^3 - 1\right)}$$

K

***k*:** Retention factor. A measurement of the retention of a peak; $k = (t_R - t_M)/t_M$.

***K*:** Partition coefficient. The relative concentration of solute in the mobile and stationary phases; $K = \beta k$.

L

***L*:** Column length.

Linear range (LR): Also called linear dynamic range. The range of solute concentration or amount beyond which detector response per solute amount is constant within a specified percentage.

Linear velocity (*u*): The speed at which the carrier gas moves through the column, usually expressed as the average carrier-gas linear velocity ($\bar{u}$).

Liquid phase: In GC, a stationary liquid layer coated on the inner column wall (WCOT column) or on a support (packed, SCOT column) that selectively interacts with different solutes to produce different retention times.

M

Mass spectrometric detection (MS, MSD): In GC–MS, the detector records mass spectra of solutes as they are eluted from the column.

Maximum allowable operating temperature (MAOT): Highest continuous column operating temperature that will not damage a column, if the carrier gas is free of oxygen and other contaminants. Slightly higher

temperatures are permissible for short periods of time during column bakeouts.

Method detection limit (MDL): The minimum amount of a solute that can be analyzed within specified statistical limits of precision and accuracy, including sample preparation.

Minimum detectable quantity (MDQ): The amount of solute that produces a signal twofold that of the noise level.

Molecular sieve: A stationary phase that retains solutes by molecular size interactions.

Multidimensional: Separations performed with two or more columns in which peaks are selectively directed onto or removed from at least one of the columns by a timed valve system. See ***backflush, heartcut,*** and ***precut.***

N

η: Viscosity. Carrier-gas viscosity increases with increasing temperature.

***N*:** Number of theoretical plates; $N = 5.54(t_R/w_h)^2 \approx 16(t_R/w_b)^2$.

***N*$_{eff}$:** The number of effective plates. This term is an alternate measurement of theoretical plate height that compensates for the nonpartitioning nature of an unretained peak; $N = 16(t'_R/w_b)^2$.

***N*$_{req}$:** The number of theoretical plates required to yield a particular resolution (R) at a specific peak separation (α) and retention factor (k):

$$N_{req} = 16R^2\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{k+1}{k}\right)^2$$

Nitrogen–phosphorus detection (NPD): The nitrogen–phosphorus detector catalytically ionizes nitrogen- or phosphorus-containing solutes on a heated rubidium or cesium surface in a reductive atmosphere. The nitrogen–phosphorus detector is highly selective and provides sensitivity that is somewhat better than that of a flame ionization detector.

O

On-column injection (OCI): In on-column injection, sample enters the column directly from the syringe and does not contact other surfaces. On-column injection usually signifies cold injection for capillary columns.

P

***P*:** Relative pressure across the column; $P = p_i/p_o$.

Δ*p*: Pressure drop across the column; $\Delta p = p_i - p_o$.

***p*$_i$:** Absolute inlet pressure.

***p*$_o$:** Absolute outlet pressure.

PAH: Polyaromatic hydrocarbon.

Peak capacity: The amount of solute that can be injected without a significant loss of column efficiency.

Peak overload: When too much of any one solute is injected, its peak can be distorted into a triangular shape.

PCB: Polychlorinated biphenyl.

PEG: Polyethylene glycol.

Photoionization detection (PID): The photoionization detector ionizes solute molecules with photons in the UV energy range. The photoionization detector is a selective detector that responds to aromatic compounds and olefins when operated in the 10.2 eV photon range, and it can respond to other materials with a more energetic light source.

PIONA: Paraffins, isoparaffins, olefins, napthenes, and aromatic compounds.

PONA: Paraffins, olefins, napthenes, and aromatic compounds.

Porous-layer open-tubular (PLOT) column: A capillary column with a modified inner wall that has been etched or otherwise treated to increase the inner surface area or to provide gas–solid chromatographic retention behavior.

Porous polymer: A stationary-phase material that retains solutes by selective adsorption or by molecular size interaction.

Precut: Peaks at the beginning of a chromatogram are removed to vent or directed onto another column of different polarity or at a different temperature for improved resolution.

Programmed-temperature GC (PTGC): The column temperature changes in a controlled manner as peaks are eluted.

Programmed-temperature injection (PTI): A cold injection technique in which the inlet temperature is specifically programmed from the gas chromatograph.

Programmed-temperature vaporizer: An inlet system designed to perform programmed-temperature injection.

Purge-and-trap sampling: A concentration technique for volatile solutes. Sample is purged with an inert gas that entrains volatile components onto an adsorptive trap. The trap then is heated to desorb trapped components into a GC column.

Pyrolysis GC: Sample is pyrolyzed (decomposed) in the inlet before GC analysis.

R

***r*:** Relative retention. For peak i relative to standard peak s; $r = k_i/k_s$.

Resolution (*R*): The quality of separation of two peaks. For two closely eluted peaks — $R = (t_{R,2} - t_{R,1})/w_{b,2}$ — where the subscripts 1 and 2 refer to the first and second peaks. From N, k_2, and α

$$R = \left(\frac{\sqrt{N}}{4}\right)\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_2}{k_2 + 1}\right)$$

where k_2 is the retention factor of the second peak. A resolution of 1.5 is said to be *baseline* resolution. R incorporates both efficiency and separation.

Retention gap: A short piece of deactivated but uncoated column placed between the inlet and the analytical column. A retention gap often helps relieve solvent flooding. It also contains nonvolatile sample contaminants from on-column injection.

Retention index: A uniform system of retention classification according to a solute's relative location between a pair of homologous reference compounds on a specific column under specific conditions.

RF: Response factor.

RSD: Relative standard deviation.

S

***s*:** Split ratio. The ratio of the sample amount that is vented to the sample amount that enters the column during split injection. Higher split ratios place less sample on the column. s usually is measured as the ratio of total inlet flow to column flow; $s = (F_s + F_c)/F_c$.

Sandwich technique: An injection technique in which a sample plug is placed between two solvent plugs in the syringe to wash the syringe needle with solvent and obtain better sample transfer into the inlet.

Selectivity: The fundamental ability of a stationary phase to retain substances selectively based upon their chemical characteristics, including vapor pressure and polarity.

Selectivity tuning: Several techniques for adjusting the selectivity of separations that involve more than one column or stationary-phase type. Serially coupled columns and mixed-phase columns can be selectivity-tuned.

Sensitivity: The degree of detector response to a specified solute amount per unit time or per unit volume.

Separation (α): The degree of separation of two peaks in time. See ***α*** and ***R.***

Septum: Silicone or other elastomeric material that isolates inlet carrier flow from the atmosphere and permits syringe penetration for injection.

Septum purge: Occurs when carrier gas is swept across the septum face to a separate vent so that material emitted from the septum does not enter the column.

Signal-to-noise ratio (S/N): The ratio of the peak height to the noise level.

Silica gel: A gas–solid adsorbent.

Simulated distillation (SIMDIS): A boiling-point separation technique that simulates physical distillation of petroleum products.

***SN*:** Separation number or Trennzahl (*TZ*). A measurement of the number of peaks that could be placed with baseline resolution between two sequential peaks — z and $z + 1$ — in a homologous series such as two hydrocarbons:

$$SN = \frac{t_{R(z+1)} - t_{R(z)}}{w_{h(z+1)} + w_{h(z)}} - 1$$

Solid-phase extraction (SPE): A sample cleanup technique.

Solid-phase microextraction (SPME): A sample cleanup technique that uses a removable sorptive microextraction device.

Solutes: Chemical substances that can be separated by chromatography.

Solvent effect: A solute-profile sharpening technique used with splitless and on-column injection. Condensed solvent in the column during and shortly after injection traps volatile solutes into a narrow band.

Solvent flooding: A source of peak-shape distortion caused by excessive solvent condensation inside the column during and after splitless or on-column injection.

Solvent flushing: A column rinsing technique that can remove nonvolatile sample residue and partially restore column performance.

Split injection: The sample size is adjusted to suit capillary column requirements by splitting off a major fraction of sample vapors in the inlet so that as little as 0.1% enters the column. The rest is vented.

Splitless injection: A derivative of split injection. During the first 0.5–4 min of sampling, the sample is not split and enters only the column. Splitting is restored afterward to purge the sample remaining in the inlet. As much as 99% of the sample enters the column.

Stationary phase: Liquid or solid materials coated inside a column that selectively retain solutes.

Sulfur chemiluminescence detection (SCD): A sulfur chemiluminescence detector responds to sulfur-containing compounds by generating and measuring the light from chemiluminescence.

Support-coated open-tubular (SCOT) column: A capillary column in which stationary phase is coated onto a support material that is distributed over the column inner wall. A SCOT column generally has a higher peak capacity than a WCOT column with the same average film thickness.

T

***T_C*:** Column temperature.

TCDD: Tetrachlorodibenzo-*p*-dioxin.

TCEP: Tris(cyanoethoxy)propane.

Theoretical plate: A hypothetical entity inside a column that exists by analogy to a multiple-plate distillation column. As solutes migrate through a column, they partition between the stationary phase and the carrier gas. Although this process is continuous, chromatographers often visualize a step-wise model. One step corresponds roughly to a theoretical plate.

Thermal-conductivity detection (TCD): A thermal-conductivity detector measures

the differential thermal conductivity of carrier- and reference-gas flows. Solutes emerging from a column change the carrier-gas thermal conductivity and produce a response. TCD is a universal detection technique with moderate sensitivity.

Thermionic-specific detection (TSD): See ***nitrogen–phosphorus detection.***

t_M: Unretained peak holdup time. The time required for one column volume (V_G) of carrier gas to pass through a column.

TMS: Trimethylsilyl, a chemical derivative.

T_o: Room temperature.

TPH: Total petroleum hydrocarbons.

t_R: Retention time. The time required for a peak to pass through a column.

t'_R: Adjusted retention time; $t'_R = t_R - t_M$.

Trennzahl (*TZ*): See ***separation number.***

U

$\bar{u}$: Average linear carrier-gas velocity; $\bar{u} = L/t_M$.

u_o: Carrier-gas velocity at the column outlet; $u_o = \bar{u}/j$.

u_{opt}: Optimum linear gas velocity. The carrier-gas velocity corresponding to the minimum theoretical plate height, ignoring stationary-phase contributions to band broadening:

$$u_{opt} = 8\left(\frac{D_G}{d_c}\right)\sqrt{\frac{3\left(1+k\right)^2}{1+6k+11k^2}}$$

UTE, UTE%: See ***coating efficiency (CE).***

V

V_G: The volume of carrier gas contained in a column. For open-tubular columns and ignoring the stationary-phase film thickness (d_f), $V_G \approx L(\pi d_c^2/4)$.

V_L: The volume of stationary phase contained in a column.

VOC: Volatile organic compounds.

VOCOL: Volatile organic compounds column.

W

w_b: The peak width at its base, measured in seconds. For a Gaussian peak, $w_b = 1.596(A_p/h_p)$.

w_h: The peak width at half height, measured in seconds. For a Gaussian peak, $w_h = 0.940(A_p/h_p)$.

Wall-coated open-tubular (WCOT) column: A capillary column in which the stationary phase is coated directly on the column wall.

Wide-bore open-tubular (WBOT) column: Open-tubular (capillary) column with a nominal inner diameter of 530 μm.

References

(1) J.V. Hinshaw, *LCGC* **10**(7), 516–522 (1992).
(2) IUPAC Nomenclature for Chromatography, *Pure Appl. Chem.* **65,** 819–872 (1993).

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